STUDIES ON CHEMICAL DEPOSITION OF THIN FILMS FOR SOLAR CELLS BY THIOUREAS AND THEIR TRANSITION METAL COMPLEXES

A THESIS SUBMITTED
IN PARTIAL FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By

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CONTENTS

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CERTIFICATE

This is to certify that the thesis entitled 'Studies on Chemical Deposition of Thin Films for Solar Cells by Thioureas and their Transition Metal Complexes' submitted by Shri R.P. Bhatnagar, ID No. 74S83002, for award of Ph.D. degree of the Birla Institute of Technology and Science, Pilani, embodies original work done by him under my supervision.

3/2/78

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Bhatnagar

(R.P. BHATNAGAR)

The world's hunger for energy is increasing day by day. As the supplies of economically recoverable oil, natural gas and uranium approach exhaustion in the 1990's, new sources of energy would be needed. India has considerable resources of coal to fall back on, but the mining and burning of coal impose a tremendous burden on the environment and present serious health hazards to the general population. The controversial nuclear breeder reactor will not have demonstrated its technical feasibility, economic viability and social acceptability for yet a decade or two and therefore, cannot now be relied upon with confidence. As the severity of the energy crisis is to be felt within next fifty years i.e. within this generation, the search for new sources gets immense importance.

Solar energy in this context beyond any doubt, offers tremendous possibilities[1]. It is available in plenty, in fact free of cost, and is not associated with serious pollution consequences. Historically solar energy was the earliest source of energy identified by man but ironically enough the least exploited source even to this day. Isolated attempts, in various countries have been made to trap it in one form or another since the later part of the last century. However, systematic efforts to utilize solar energy on a significant scale started all

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The solar energy utilization devices and process, in general, follow one of the three pathways namely:

(1) utilizing heat from the sun,

(2) using photosynthetic and biological conversion,

and (3) direct conversion into electricity.

Significant developments are taking place in all the three areas. Low grade thermal devices, solar water heaters, heating and cooling of buildings, solar dryers, solar cookers, solar distillations, solar pump, solar furnaces, etc. are the outcome of research and development in utilizing the heat from the sun. The second path essentially consists of the reduction of carbon dioxide from sugar and splitting of water to produce oxygen. Unfortunately this marvellous machine is something like a goose that lays the golden eggs but when we cut into it to see how the trick is done, we ruin the wonderful mechanism, and learn nothing. The path is still in its infancy.

Part of world wide activity in solar energy research is aimed at deriving electricity economically from sunlight and there is universal agreement that the economic generation of solar electricity would be an achievement of major importance. A wide variety of schemes have been proposed for this. Out of them, the following three are undergoing active development at the present time:

(1) conversion of sunlight to heat and heat to electricity e.g. a steam turbine,

(2) direct conversion of sunlight to electricity by the photovoltaic effect in semiconductors,

and (3) the hybrid system approach i.e. combining solar electricity with other functions such as heating and lighting.

The direct conversion among them is most attractive as the electrical energy is the most convenient form of energy to which all other forms of energy may be converted. The transportation of this form of energy requires only a capital expense with a minimal amount of maintenance cost. It is also easy to control and easy to transform into any form of work desired by the consumer (Fig. 1.1). Photovoltaic solar cells, which convert sunlight directly into electricity were initially fabricated for space applications only but are now being developed for terrestrial use also. They are already used in some portable electronic equipment and in remote locations not connected to national power grids in developed countries.

All solar cells[4,5,6,7] have several things in common. There is a semiconducting layer known as the base having an ohmic or injecting contact on one side and an electrostatic potential energy barrier on the other side formed by a p-n junction, a thin metal film Schottky barrier, or a heterojunction. A contact grid pattern is applied to provide a low series resistance and an anti-reflection coating is applied to reduce the optical loss. Encapsulation is usually added to protect the cell from the environment. There are several variants incorporating these basic features.

An illuminated solar cell connected to a load develops a photocurrent, and a photovoltage in the forward biased mode. The diode current normally present at this forward bias voltage opposes the photocurrent generated by the light, and the greatest power output from the cell is obtained when the product of the output voltage and net (photo minus dark) current is a maximum. The short circuit current Ise, the open circuit voltage Voc, the "squareness" of the I.V curve (fill factor) under illumination and efficiency are generally cited as the figure of merit of the solar cells.

Hovel[9] has classified solar cells into four types:

(1) Silicon Solar Cells,

(2) Concentrator Solar Cells,

(3) Cadmium Sulphide Solar Cells,

and (4) Thin Film Solar Cells.

Contemporary research on silicone solar cells is mainly focussed on two points:

(a) low-cost material effort, and

(b) device improvement effort.

As the metallurgical silicon is less expensive than semiconductor grade, efforts are being made to prepare a 'solar grade' silicon of sufficient purity and in sufficient amount from metallurgical grade without using the expensive preparation and purification process of $SiHCl_3$. Apparently Cr, Mn, Fe and vanadium have serious effect on cell performance whereas Ni and Cu do not. Most of them are removed by the following procedure. Metallurgical silicon could be freedfrom Fe, Al, Ni, Mn, Ti and Cu by a factor of 2 to 20[6,10] by blowing chlorine or oxygen through molten silicon and further purified by unidirectional freezing of silicon ingots using the Czochralski crystal growth method. Boron and phosphorus are difficult to remove by this method and hence high purity carbon could be used during the furnace reduction of silica. Solar cells of 2% efficiency were made by this material[6].

Silicon ribbons are being produced to provide low cost substrate for solar cells. Solar cells made by standard diffusion process and using dentritic web material show efficiency of 11% (AMO). Twin boundaries present in the center of the web show insignificant effect on cell behaviour. Edge defined film-fed Growth (EFG)[11] processed Si ribbon give 10% or more (AMO) efficient solar cells in particular case, though the average is about 5-6% only. Twins, slip bands and grain boundaries present in the ribbon cause wide variations in the cells from one ribbon section to another.[12] If Voc's and fill factor of EFG cells are good, efficiencies are low. Various factors are responsible for low efficiency of these cells. Some of them include poor lifetime and diffusion length in the ribbon when these defect boundaries are present. Moreover, molten silicon may react chemically with die to give structural defects. EFG crystals, 2.5 cm wide by 10 mils thick by 65 feet in length are grown at ~ 2 cm/minute rate.

High growth rate, an advantage of silicon ribbon technology has the disadvantage that the effective impurity segregation coefficient becomes unity and no further purification is obtained.[13] Purified metallurgical silicon as mentioned above, may be used as starting material in order to avoid the need of purification at ribbon growth.

Device improvement efforts follow two main paths:

(a) to obtain expensive but high efficiency cells, and

(b) to obtain less expensive cells though may be lesser efficient.

The former received a boosting with the advent of 'violet cells'[14]. These cells with their narrower junction depths and reduced surface concentration to eliminate dead layer at the surface of diffused region, enhance the photocurrent. Photocurrent is further enhanced by texturing the surface and using improved anti-reflection coating of Ta_2O_5 together with silica cover glasses and values of 46 mA/cm^2 (AMO) have been obtained.

The factor which most limits the efficiency of 'non-violet' Si cells now is the unexpectedly low Voc. The highest observed values have been ~~observed~~ 0.62-0.63 volts compared to 0.7 volts predicted for devices with 0.1 ohm-cm base material. The causes for discrepancy are the band gap shrinkages, sub-nanosecond lifetimes, tunneling and high doping effects in the diffused region. Textured surface or CNR (for Comsat Non Reflecting) cells made on 1-2 ohm-cm base material and with narrow junction depth have been 15% efficient (AMO), which is over 16% when corrected for the contact shading. These cells are 19% for terrestrial sunlight. 0.1 ohm-cm substrates, textured surfaces, narrow junctions and low diffusion concentration may bring the AMO efficiency to over 18% and terrestrial efficiency to over 22%.

Research efforts aimed to reduce the cost of silicon solar cells follow the following four pathways:

(1) Lower cost processing techniques,
(2) Heterojunction cells,
(3) Oxide-Silicone cells, and
(4) Schottky barrier devices.

Development of lower cost processing techniques involves:[15,16]

(a) screen printing of the contacts,
(b) spin on anti-reflection coatings,
(c) painted on diffusion sources, and
(d) sodium hydroxide etch to remove damaged area and texture the surface.

All these techniques are successful and painted on phosphorus diffusion have produced 10.3% efficient (AMO) cells.

Heterojunction cells are formed by depositing inexpensive and easy to apply wide band gap material such as SnO_2, In_2O_3, CdS or GaP upon an n-type or p-type silicon substrate. Wide band gap acts as window passing most of the light into the silicon. Shorter wavelengths are absorbed within the depletion region in the silicon enhancing the blue response of the cell, while longer wavelength response is good if the diffusion length in the Si is high.

Efficiencies of 9.9% AM1 for SnO_2-nSi cells and AM1.2 efficiencies of 11.7% (contact area corrected) have been reported using $(In_2O_3)_{0.9}(SnO_2)_{0.1}$ on p-Si. Later cells were probably aided by a thin SiO_2 layer at the interface between the silicon and the glass, without this oxide, In_2O_3-pSi cells would be less efficient than this due to unfavourable electron affinity match. This also restrict them to low voltage outputs.

Schottky barrier devices are yet another low cost method for obtaining terrestrial silicon cells. Very thin metal films (75-150A° thick and transparent enough to permit most of light to Si) of Au, Ag, Cr, Cu, Al and the like are deposited, usually by vacuum evaporation, upon a Si substrate. A thin, (10-20A° thick) oxide is incorporated between metal on Si to enhance the Voc (by lowering dark or leakage current) without affecting photocurrent[17,18]. Various theories[6,18,19,20] have been formulated to explain this oxide effect. Schottky cells of Al-oxide-p-Si type[21] show 8% (Am1) efficiency, 26 mA/cm^2 of photocurrent and 0.45 volt as Voc's, whereas Cr/Cu double layers on p-type Si have resulted in 9-10% efficient cells at Am1, with IS.C's of 22-25 mA/cm^2 and

Voc's of 0.55 volt. The Cr in this double layer produces a high barrier height, while the Cu provides a low sheet resistance[22,23].

Both conventional Si and unconventional solar cells have been used at higher intensities and temperature. Main advantages associated with the use of these cells are that if cheap concentrators are available, cost of cell becomes less important and hence expensive but high efficiency cells could be used. Secondly, hybrid system approach using both electrical and thermal output is possible. The disadvantages are:

(a) only direct sunlight could be used, incurring in optical loss even on the best of days,

(b) tracking of the sun is necessary, and

(c) series resistance becomes a major problem leading to increased design complexity.

With conventional Si cells at higher intensity, at constant temperature, Isc increases proportionally to the power input, while Voc increases logarithmically. Fill factor remains constant or in theory could even increase, provided series resistance is negligible. In practice, however, the series resistance quickly dominates the cell behaviour and increased numbers of narrow grid fingers are necessary to prevent this problem. Increase in operating temperature lowers the Voc and thus helps in decreasing the efficiency. To overcome this difficulty lower base resistivities (0.1-0.3 ohm cm rather than 9-10 ohm cm) can be used.

GaAs cells with series resistance problem intact have better efficiency at higher temperatures due to wide band gap. Their radiation tolerance is also more. GaAs solar cells with a covering of $Ga_{1-x}Al_xAs$ (to prevent the high surface recombination loss which would lower the efficiency) show 18% (AMO) efficiency[24] and more than 20% in terrestrial sunlight[25]. Similar efficiencies are predicted for graded GaAs though only 14-15% (AM1) have been obtained[26]. $Ga_{1-x}Al_xAs$-GaAs cells grown by liquid phase epitaxy[27] were found 23% efficient at 10 Suns (25°C) and 19% at 1700 Suns (60°C) at AM1.4. These devices also behaved well at high temperatures, with 14% (AM2) at 200°C for about 270 Suns input[28].

Low cost processing together with low cost material makes cadmium sulfide cells more attractive than silicon[29-31]. However, the low efficiency and steps necessary for stability are the main disadvantages. A very good account of history, development and fabrication of other cells is given by Shirland[29]. Basically a CdS cell consists of a plastic substrate, coated with electric contact of Zn, Indium-tin-oxide or cadmium stannate. A CdS layer then deposited onto the substrate and final structure is dipped into a Cu ion bath to obtain a 2000-4000A° thick Cu_2S layer. A 200-250°C heat treatment for several minutes is used to obtain the highest photosensitivity and best electrical properties.

Several advances have been made to understand and eliminate the stability problems of CdS solar cells[32]. Stoichiometry of the Cu_2S phase, necessary to obtain good diffusion lengths and high short circuit current, can be enhanced by deposition of a 100-150Å Cu film on the Cu_xS surface. This Cu film is then heat treated (180°C, 10-20 minutes) in air, forming a Cu_2O layer at the surface which reduces the surface recombination velocity. Proper stoichiometry can also reduce Cu ion migration effects, which would otherwise lower the cell output. Another problem has been the attack of Cu_xS by oxygen and H_2O vapours. This could be reduced by proper encapsulation. Tests under controlled temperature and atmospheric conditions predicted the lifetimes for these cells in excess of 20 years.

Highest reported efficiency for these comparatively less efficient cells is 8% (AM1) though 5-6% are obtained on production line devices. Isc and Voc's are found to be the order of 18-20 mA/cm^2 and 0.45-0.48 volt respectively. Most of the light in the cell is absorbed in Cu_2S layer. The factors limiting photocurrents thus are high surface recombination velocity, a short diffusion length in Cu_2S and recombination through interface states. The first one could be reduced by introducing Cu_2O layer as mentioned above, second by keeping Cu_2S layer to a diffusion length (0.2-0.3 µ) and the last by lowering the density of interface states, except that this density is more or less fixed by the lattice mismatch between Cu_2S and CdS. Low voltage outputs are caused by the excess tunneling leakage currents through interface states and a low electrostatic band bending due to a poor electron affinity match. One proposal for minimizing these problems is to replace CdS by a $Cd_{1-x}Zn_xS$ alloy[33]. This alloy has a better lattice match to Cu_2S, which reduces the number of interface states. In addition, the electron affinity discontinuity of 0.3 e.v. which limits the diffusion voltage in Cu_2S-CdS cells to about 0.8 e.v. can be reduced or even eliminated by the alloy, increasing the band bending to 1.1 e.v.[34] In this way it is hoped that Voc can be increased to 0.8 volt, the Isc to 25 mA/cm^2 and the fill factor to 0.75 which would result in a 15% efficiency rather than the present 6%. Experiments with Cu_xS-$Cd_{1-x}Zn_xS$ solar cells have indicated the expected improvements in voltage output but the photocurrent was low, possibly due to Zn in the Cu_xS.

Two other techniques used for improving efficiency of CdS are replacement of Cu_xS by InP and CdTe. In both cases electrostatic band bending (Vd1+Vd2) is about 1.1 e.v. leading to high expected voltage output. InP has a good lattice match with CdS, leading to low interface state densities, low dark currents and good photocurrents. Single crystal cells of InP grown by vapour transport onto

CdS substrate have resulted in Voc's of 0.72 volt, Isc's of 25 mA/cm^2 and efficiencies 14% (W light) and 12.5% (AM2)[34]. CdTe, on the other hand, does not have good lattice match to CdS[35] and will probably have higher dark currents than InP devices for that reason, but nevertheless good CdTe-CdS cells[36] have been made. CdS films evaporated on CdTe and contacted with Indium-tin-oxide layers have resulted in efficiency 7.9% (AM1), Voc's of 0.63-0.66 volt and Isc of 16 mA/cm^2. Both these cells have to show economic viability similar to CdS-Cu$_2$S to make a strong impact on conventional technology.

The most exploratory kind of solar cells is thin film solar cell. The advantages associated with these cells are that considerably less expensive semiconducting material is needed, cheaper substrate can be used and continuous, flow through processing of large sheets can be envisioned. The disadvantages of such cells are very low efficiency due to grain boundary effects and the poor quality semiconducting material resulted from growth upon foreign substrate. Glass, plastic, metal, graphite or metallurgical silicon are used as substrate and thin films of silicon, GaAs, InP, CdTe, CdS or organic material is deposited onto these substrate by vapour growth, evaporation, plating or the like, for such cells. It is observed that if semiconductor film thickness is larger than the inverse of the absorption coefficient, most of the light will be absorbed and if the diffusion length is larger than the film thickness, most of the generated carriers can be collected. Light penetrates deeply into Si and hence layers of 10μ or more are necessary to achieve 10% efficiency. For GaAs and InP, light is absorbed very near the surface and devices less than 1μ thick could be more than 12% efficient . Even poor quality GaAs and InP could theoretically result in 8-10% efficiency for 2μ thick film.

Grain boundaries introduce recombination losses which can lower the photocurrent and increase the dark current. Grain sizes of 30-40μ for Si cells, while 2-4μ for GaAs and InP cells could be tolerable.

An attractive alternative to p/n junction for use in thin film solar cells is Schottky barrier. For Au-oxide-GaAs cells Voc 0.45-0.62 volt and efficiency of 15% in terrestrial sunlight are obtained.[37] The experimental results obtained for various thin film solar cells are summarised in Table-1.1.

Polycrystalline films of Si about 30μ thick with 30μ grain size on graphite substrate have resulted in 1.5% (W light) efficiency.[38-40] By fast melting and recrystallization of Si, larger grain size (>100μ) with 3.6% efficiency are obtained. Thin films on metal substrate resulted in futile effort. Polycrystalline GaAs cells[41-43] have been made on Mo and Al substrate using Pt Schottky barrier and $Cu_{1.8}Se$ heterojunctions

TABLE-1.1

Experimental results for various thin film solar cells

Material	Substrate	Thickness	Grain size	Barrier	Efficiency
Si	Carbon	30μ	>100μ	p/n	3.6
GaAs	Mo	50μ	<1μ	Pt	5.0
GaAs	Al	15μ	<1μ	Cu_2Se	4.6
InP	Carbon	10μ	2-4μ	CdS	2.8
CdS	Glass	2μ	<10μ	Cu_2S	4.9
CdTe	Glass	10μ	<10μ	Cu_2Te	6.0
αSi	Glass	1.6μ	-	p/i/n	2.4
αSi	Glass	2.3μ	-	Au	4.0
Organic	Glass	500A°	-	Ga	0.1

with 4.6-5% (W light) efficiency. Single crystal thin film GaAs solar cells have been produced by a 'peeled film' technology, whereby the thin film cell is grown and later removed from a single crystal substrate. 20μ thick diffused p/n junction cells demonstrated 11% (AM2) and nGaAlAs-pGaAs heterojunction, 20μ thick, were 13% efficient.

Solar cells made by CdS (evaporation onto InP[44-45] layer) demonstrated 2.8% (AM1) efficiency. Although photo-current collection was good in these cells (20 mA/cm^2), Voc (0.4 volt) and fill factor (0.31) were very low, possibly due to a voltage barrier between the carbon and the InP. Better ohmic contacts to InP are expected to improve the efficiency considerably.

Extremely thin (2µ) CdS-Cu_2S solar cells have been made by spraying SnO_2, CdS and Cu_2S alternately on glass. SnO_2 contact to CdS is transparent and efficiency 4.9% (AM1) with photocurrent 20 mA/cm^2 and Voc's of 0.41 volt has been obtained. A 6% (W light) for polycrystalline and 7.5% for single crystal Mo or glass/CdS/CdTe/Cu_2Te solar cell configuration are obtained.[46-47]

Amorphous Si is another material[48] for thin film solar cells. It has a higher absorption coefficient than crystalline Si for wavelength greater than 7500A°, behaves like a high resistivity semiconductor with a (ill-defined) band gap of 1.4 e.v. and can easily be doped with B and P. 1-3µ thick layers by glow discharge in SiH_4 are grown onto Indium-tin-oxide coated glass. Solar cells with 1.6µ layer of intrinsic a-Si, sandwiched between B and P doped regions (a few hundred A°) have resulted in 2.4% (W light) efficiency with Isc = 10 mA/cm^2 and Voc's = 0.57 volt for 100 mw/cm^2 input. More recently Au-a - Si Schottky barrier cells with 4% efficiency are fabricated but they degrade with time. Pd and Pt Schottky barrier cells did not exhibit this degradation. Ultimate efficiency of 15% is predicted for these solar cells.

Finally, organic solar cells[9], have also been fabricated by growing thin organic semiconductor films on variety of substrates. A very low efficiency (.001-0.1%) primarily due to trapping effects is obtained for such cells. Organic cells degrade at high light intensities and thus their efficiencies are measured at 0.5-2 mW/cm^2 to prevent this effect. Cells made by evaporation or casting of 200-500A^o thick Squarylium dye films onto glass substrates have resulted in efficiency of 0.1% at 5 mW/cm^2 (AMO) and 0.02% at 135 mW/cm^2.

It is clear from the outgoing discussion that though single crystal solar cells are very well established and understood, the high manufacturing cost resulting due to low yield, wastage of precious semiconducting material in processing together with their sophisticated and thus expensive technological processibility, restrict their wider utilization. Hence, to bring the solar cells to domestic market, its cost must be reduced. An ambitious goal set by U.S. Government and private enterprises in this direction, is to reduce the cost from 15 ¢/cm^2 to about half cent per square centimeter (0.5 ¢/cm^2) or less which incidentally is about the price of a U.S. copper penny. For single crystal silicon cells, this requires a cost reduction by a factor of about thirty. Moreover, the efforts to minimize the cost of single crystal cells are more technological rather than scientific in nature.

Thin film solar cells in this context are attractive and challenging. They are in spite of their low efficiency (which incidentally is increasing steadily) are least expensive and most exploratory ones from the academic as well as scientific research point. They show a promise for both industry and domestics and would be of our interest in the present study.

Various techniques are used for the fabrication of thin film solar cells. As it is difficult to review all of them in detail, the various methods of growth and their relative merits in terms of simplicity, ease of deposition control, availability of starting material etc. are briefly presented in the next chapter.

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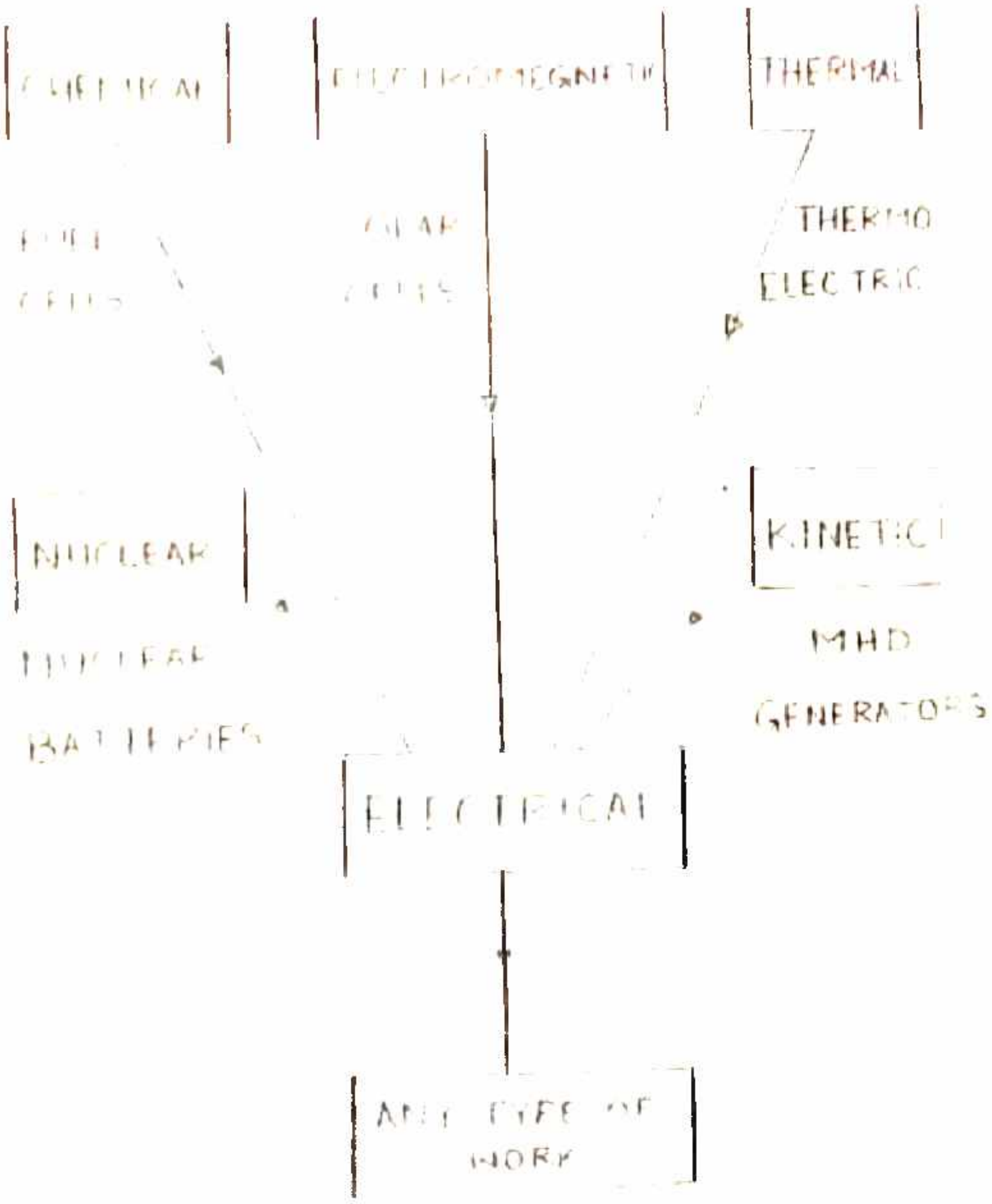
CHEMICAL
ELECTROMAGNETIC
THERMAL
FUEL CELLS
SOLAR CELLS
THERMO ELECTRIC
NUCLEAR
KINETIC
NUCLEAR BATTERIES
MHD GENERATORS
ELECTRICAL
ANY TYPE OF WORK

Fig. 11

REFERENCES

1. Energy and Man, Technical and Social Aspect of Energy, Ed. M. Granger Morgan, IEEE Press (1975).

2. Report of the NCST Expert Panel on Solar Energy, National Committee on Science and Technology - New Delhi 1974.

3. M.A. Duguay, American Scientist, 422 (1977).

4. H.J. Hovel, Solar Cells, Vol. 11 of Semiconductors and Semimetals, Beer and Willardson, eds., Academic Press, New York, 1976.

5. Solar Cells, C. Backus, editor, IEEE Press, New York, 1976.

6. Conference Record, 11th IEEE Photovoltaics Specialists Conference, Scottsdale, May 1975, IEEE Publication, Catalog No. 75CH0948-0ED. 54

7. Conference Record, 12th IEEE Photovoltaics Specialists Conference, Baton Roug~~h~~, LA No. (? 1976. e

8. Solar Cells, Proceedings of the International Colloquium (ECOSEC) - Toulouse, France, 1970.

9. Harold J. Hovel in Sharing the Sun Solar Energy in the Seventies, Winnipeg, Vol. 6, Photovoltaics and Materials, Ed. K.W. Boër, 1976.

10. L.P. Hunt, V.D. Dosaj, J.R. McCormic and L.D. Crossman, Extended Abstracts, Electrochemical Society, Spring Meeting, Washington, May 1976, Abstract No. 227.

11. K.V. Ravi and A.I. Mlavsky in ref. 9, p. 23.

12. H. Kressel, American Vacuum Society, New York Chapter, Polycrystalline Material Conference, April 1976. Also, R.V. D'Aiello, P.H. Robinson and H. Kressel, Tech. Digest, 1975 Intern. Elec. Dev. Mtg., Washington, Dec. 1975, page 335.

13. T.F. Ciszek, G.H. Schuttke, and K. Yang, Electronic Materials Conf., AIME, Salt Lake City, June 1976.

14. J. Lindmayer and J.F. Allison, Comsat Tech. Rev. 3, 1 (1972).

15. W.E. Taylor and F.M. Schwartz, NASA Report No. CR-134981, Contract NAS3-18566, October 1975.

16. F.T.C. Bartels, NASA Report No. CR-134743, Contract NAS3-17361, Sept. 1974.

17. D.R. Lillington and W.G. Townsend, Appl. Phys. Lett. 28, 97 (1976).

18. H.C. Card and E.H. Rhoderick, J. Phys. D 4, 1589 (1971).

19. H.C. Card and S. Yang, Appl. Phys. Lett. 29, 51 (1976).

20. R. Singh and J. Shewchun, Appl. Phys. Lett. 28, 512 (1976).

21. E.J. Charlson and J.C. Lien, J. Appl. Phys. 46, 3982 (1975).

22. W.A. Anderson, Quarterly Progress Report, NSF Grant AER73-03197, Report No. NSF/RANN/SE/AER73-03197/PR/76/1.

23. S.M. Vernon and W.A. Anderson, Appl. Phys. Lett. 26, 707 (1975).

24. G.A. Kamath, J. Ewan and R.C. Knechtli, Electronic Materials Conf., AIME, Salt Lake City, June 1976.

25. H.J. Hovel, J.M. Woodall and W.E. Howard, 1972 Symposium on GaAs, Boulder, Sept. 1972, p. 205.

26. M. Konagai and K. Takahashi, J. Appl. Phys., 46, 3542 (1975).

27. H.J. Hovel and J.M. Woodall, J. Electrochem. Soc. 120, 1246 (1973).

28. L.W. James and R.L. Moon, Appl. Phys. Lett., 26, 467 (1975) and ref. 6, page 437.

29. F.A. Shirland, Adv. Energy Conv., Vol. 6 (1966).

30. R.J. Mytton, Comparative Review of Si and thin film solar cells for space applications, Phys. Technol, 4(2), 92-112 (1973).

31. A.P. Kulshreshtha, J. Sci.and Indus. Res., 31, 7-9 (1973).

32. F.A. Shirland, International Workshop, CdS solar cells and other abrupt heterojunctions, University of Delaware, Newark, April 1975.

33. A. Rothwarf, Technical Report NSF/RANN/AER72-03478 A04/Tr 76/1, University of Delaware, March 1976.

34. S. Wagner, J.L. Shay, K.J. Bachmann and E. Buchler, Appl. Phys. Lett., 26, 229 (1975).

35. A.L. Fahrenbruch, V. Vesilchenko, F. Buch, K. Mitchell and R.H. Bube, Appl. Phys. Lett., 25, 605 (1974).

36. R.H. Bube, A. Fahrenbruch, E.H.Z. Tahen, J. Aranovich, F. Buch, M. Chu, K. Mitchell and Y. Ma, Report NSF/RANN/SE/AER-75-1679/76-1, March 1976.

37. R.J. Stirn and Y.C.M. Yeh, Appl. Phys. Lett., 27, 95 (1975).

38. P.H. Fang, L. Ephrath, W.B. Nowak, Appl. Phys. Lett., 25, 583 (1974). Also L.M. Ephrath, J. Electronic Meter, 4, 1207 (1975).

39. T.L. Chu, H.C. Mollenkopf and S.C. Chu, J. Electrochem Soc., 123, 106 (1976).

40. T.L. Chu, J.C. Lien, H.C. Mollenkopf, S.C. Chu, K.W. Heizer, F.W. Voltmer and G.F. Wakefield, Solar Energy, 17, 229 (1975).

41. P. Vohl, D.M. Perkins, S.G. Ellis, R.R. Addiss, W. Hui and G. Noel, IEEE Trans. Elect. Dev., ED-14, 26 (1967).

42. J.A. Amick, RCA Rev., 24, 555 (1963).

43. A.C. Thorsen, H.M. Manasevit, and R.H. Harada, Sol. St. Elects., 17, 855 (1974).

44. T. Saitob, S. Matsubara and S. Minagawa, J. Electrochem. Soc., 123, 403 (1976).

45. K.J. Bachmann, E. Buchler, J.L. Shay and S. Wagner, Appl. Phys. Lett., 29, 121 (1976).

46. D.A. Cusano, Solid St. Elects., 6, 217 (1963).

47. E.W. Justi, G. Schneider, and J. Seredynski, Energy Convers., 13, 53 (1973).

48. D.E. Carlson and C.R. Wronski, Appl. Phys. Lett., 28, 671 (1976).

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CHAPTER II

This Chapter reviews the definitions and mechanisms of growth of thin films. It also describes the various methods of fabrication of thin films. Chemical methods of deposition and spray techniques, which form part of the present studies have been emphasized.

The Chapter ends with a discussion of the basis of the present work.

The technology of thin films has already proving useful in such articles of daily use as artificial jewellery, anodised household appliances, Thermos flasks, magnetic tapes, goggles, coated optics of a camera or a microscope, xerox machines, miniaturised thin films resistors and capacitors, electroluminescent panel display devices, to name a few. It has been established to be preeminently suitable for cheaper solar cells. Thin film superconductors may carry electricity for hundred of kilometers without any transmission losses. The miniaturised integrated optical circuits using thin film devices akin to integrated electronic circuits, may soon bring about a revolution in communications technology. Indeed, the tremendous advances made by the science and technology of thin films in the last two decades have led to the creation of many new and full-fledged scientific disciplines.[82]

A material having one of its dimensions about one micron (10^{-4} cm or 10,000A°) or less is the geometrical description of a thin film. It is the growth process which is of fundamental importance to the science and technology of thin films since it largely determines the film's novel structural behaviour and properties. A thin film may, therefore, scientifically be defined as a thin two dimensional material - born of an atom by atom or molecule by molecule condensation process which generally is achieved by vapour phase of a material.

The condensation process involves the interaction of vapour atoms with the surface atoms of the substrate via van der Walls forces and their subsequent physical adsorption. The adsorbed atoms soon loose the velocity component normal to the substrate but retain the velocity component in the plane of the substrate. The motion they execute is a random walk. These adatoms encounter with others of same species and form a cluster by bonding with them. The volume cohesive forces due to bonding would increase with the increasing number of adatoms in the cluster, but, at the same time, the disruptive forces due to the presence of dangling or dissatisfied bonds at the free surface of the cluster would increase. Thus, there exists a critical size at and beyond which the cohesive forces are decisive in bringing about the chemical adsorption of the stable cluster. This process of nucleation yields three-dimensional random distributed islands which grow further by the addition of new atoms from the vapour phase as well as by surface diffusion. The growing islands coalesce into one another by surface and volume diffusion forming a network which fills gradually to form a continuous film. The solid state process of coalescence is very rapid in case of metals and appears liquid-like coalescence. The coalescence phenomena have a profound effect on the structure and properties of the resultant film since recrystallisation, grain growth orientation changes, incorporation and removal of defects etc. occur as a consequence of coalescence.

A film thus represents the ab initio birth of a material. The most significant aspect of the birth process is that it can be modified drastically by changing the conditions of deposition like the chemical nature and temperature of the substrate, rate and angle of deposition, energy and species of the vapour atoms, nature and degree of vacuum etc. These parameters affect the mobility of the adatoms and the size, distribution and coalescence characteristics of the islands.

Thus by controlling the temperature of deposition it is possible to nearly immobilise the adatoms on the substrate so that they have little chance to grow together in a harmonious and ordered manner. The result is an amorphous or glassy state. On the other hand, the adatoms can be given high mobility to form matter in granular form with regular arrangement of atoms or in polycrystalline state. If the surface happens to be a single crystal the periodic forces of the cohesion induce an oriented growth (called 'epitaxy' or 'arrangement on') in the film with a geometrical arrangement of atoms which is well defined and correlated with that of the substrate atoms. The single crystal films can be obtained at deposition temperature well below the melting points of the materials and also the normal temperatures required for the growth of bulk crystals. Thus, single crystal films of Au, Ag and Cu can be obtained at or below room temperature, in contrast to about a thousand degree required for the formation of bulk crystals of these metals.[83]

A large number of techniques are available for the fabrication of thin films. The technique of fabrication is particularly important since film properties are invariably observed to be a function of the manner in which they are fabricated and the choice of a method is governed by the combination of semiconductors and requirements of epitaxial growth such as crystalline order, degree of perfection.impurity concentration etc. Each of the technique is a field of an active research and it is difficult to go into the details of each of these. The following paragraphs, therefore, present the various methods of growth and their relative merits in terms of simplicity, availability of starting materials, ease of deposition control etc. only. Sharma and Purohit in their communications have presented the literature and the techniques, very well.

The thin film deposition methods can very broadly be classified in following two heads:

(a) Vacuum methods, and
(b) Non-vacuum methods.

Vacuum methods generally yield:

(a) good film thickness control,
(b) uniformity of films,
(c) compatibility with precise masking techniques,
and (d) capability of producing high purity material.[1]

As the name suggests vacuum methods involve the use of high vacuum for film deposition. This class can be further subdivided into two major sub-classes:

(i) Vacuum evaporation, and
(ii) Sputtering methods.

In case of vacuum evaporation the compound dissociates completely[2] and the dissociation step is rate limiting but is influenced by ~~C~~charge Transfer process at the solid surface and is thus sensitive to factors such as doping and illumination.[3] Material thus evaporates in approximate stochiometric proportions and the condensation and re-evaporation processes at the substrate determine the film composition. A high substrate temperature sufficient to prevent permanent condensation of unreacted material is desirable.[4] Both direct evaporation of semiconductors or coevaporation of constituent element of semiconductors and subsequent condensation on substrates in high vacuum are used to grow films by this method. The various techniques used for this method are:

(a) Single evaporation technique,

(b) Flash evaporation technique,

and (c) Coevaporation technique.

These techniques are particularly important where single crystallinity is not a prerequisite. Figures 2.1-2.3 give schematic representation of these.[5]

The simplest single evaporation technique (Fig. 2.1) consists of heating the material to be deposited with a resistively heated filament or boat, generally made of W or Mo, in a vacuum chamber or bell jar held at a pressure between 10^{-5}-10^{-6} torr. In case of indirect heating crucibles of quartz or graphite are used. An arrangement is provided inside the vacuum chamber to hold the substrate directly in line of material to be evaporated. A heater is also provided to raise the temperature of the substrate if necessary. The optimum deposition parameters such as deposition rates, thickness, uniformity etc. depend on a particular system, the substrate temperature and the evaporating material.

Using this technique the films of CdS[18,6], CdSe[18,7,8], CdTe[9], ZnS[10], ZnSe[11] and ZnTe[9] on Ge, Ge on Si[11] and GaAs[12,13]; CdS[14,15], CdSe[8], CdTe[16], ZnS[17] and ZnTe[16] on Si substrate have been deposited. Apart from these III-V compound semiconductors such as GaAs on Ge, InAs on GaAs, InSb on GaAs and InSb on ZnS have also been deposited. It has been observed that it is difficult to control the stoichiometric composition of the deposited films of these compounds by using this simple evaporation technique.

The main disadvantages of this method are these:

(a) the contamination from the evaporant container and its adjacent surfaces,

(b) the limitation on the maximum temperature of evaporation due to the melting temperature of heating element,

and (c) the difficulty in controlling the deposition rate due to fluctuations in the surface area of the molten evaporant.

These disadvantages have been overcome by using an electron-beam evaporation technique.

In this technique, the accelerated beam of electrons is focused, onto the surface of the evaporant. Upon impingement, the energy of the electrons is converted into heat. This is sufficient to melt the surface of the evaporant, if the other portions of the evaporants are maintained at lower temperatures. The technique has been recently utilized by Rawlins[19] to deposit epitaxial ZnS on Si and for ZnSe on Ge and Si.

Flash evaporation technique (Fig. 2.2) is used to grow precisely stoichiometric films of compounds whose constituents have widely different vapour pressures. The technique, in principal, involves instantaneous evaporation of the material with minimum possible contact with the evaporator. The finely powdered material is allowed to drop grain by grain onto a hot surface whose temperature is maintained well above the evaporation temperature of the least volatile constituent of the evaporant. Using such technique Muller[20] has deposited GaAs on Ge while Richards et al.[21] most of III-V compounds on Ge and GaAs and Berchtold[22] and Indo et al.[23] InSb on Si substrates. Moreover, CdSe-CdS and Cu_xTe-CdTe heterostructures have also been fabricated by this technique. Though this technique is superior to single evaporation, deposited layers of this technique contain many grain boundaries and packaging defects.

The coevaporation technique (Fig. 2.3) is used to deposit the films of compound semiconductors of precisely controlled composition. The components of the compound are evaporated at different temperatures and are allowed to jointly condense to form the compound on a common substrate maintained at an elevated temperature. The substrate temperature is critical in this case and is kept at a temperature above the condensation temperature of the most volatile component and below the melting point of the compound. The technique was first used by Guenther[24] for semiconducting compounds and is also known as 'three temperature' or a 'two source' technique. Using this, films of GaAs on Ge, InAs on Si, GaAs, InSb on CdS and AlAs on Si, CdS-CdTe, ZnS-CdS on heated glass substrate have been fabricated. The main advantage of the technique is that the condition of stoichiometric deposition are not critical and doping of impurity during deposition is also possible. However, the difficulty to control the nucleation and growth of the crystallites is the disadvantage with it.

Sputtering (Fig. 2.4) is yet another technique for deposition of films employing high vacuum. The material deposition in this technique results from the bombardment of the source by ions in a gaseous discharge. Cathodic sputtering is the principal technique widely used amongst the various sputtering techniques available to date. This consists of, in simplest terms, a cathode of the material to be sputtered, an anode and a substrate. A low pressure (10^{-2} to 10^{-3} torr) of an inert gas (frequently Ar) is used in chamber. High voltage (few kilovolts) is applied between the electrodes to create self-sustaining gaseous discharge. Positive ions from the plasma are accelerated into the surface of the cathode whereby momentum transfer from the ions the material is sputtered - which is then allowed to deposit on a heated substrate placed on or near the anode. The technique was used by Francombe and his coworkers[25] for deposition of GaAs films on Ge by Vlaslov and Semiletov[26] InAs films on Ge, Si and GaAs and by Rawlins and Woodward[27] for ZnS films on Si. The most important advantage of the technique is that it provides high purity and a good compositional control of sputtered films.

Non-vacuum methods are interesting because of their simplicity and could broadly be classified in the following heads:

(1) Alloying method,
(2) Solution growth method,
(3) Chemical vapour transport,
and (4) Chemical methods such as:
    (a) Precipitation,
    (b) Displacement,
    (c) Spraying, and
    (d) Sintering.

The simplest technique of alloying involves the complete melting of lower melting point semiconductor on top of a higher melting point single crystal substrate and then cooling in a temperature gradient such that the interface is the first to recrystallize. This technique is useful for growing low melting elemental semiconductors and low melting low-vapour pressure compound semiconductors. By this method Ge on Si and GaAs, Te on Ge, Si and CdS and

AlAs (in fact Al) on GaAs are grown.

The so-called diffusion is yet another form of alloying in which wafers of two semiconductors are kept at a temperature gradient so as to transport and then diffuse the vapours of one semiconductor into another one.

Apart from the simplicity of experimental set up and short process time these techniques suffer from many disadvantages, such as, impurity cross diffusion, graded nature of the junction, highly strained alloyed layers and difficulty in aligning crystal directions during alloying.

Solution growth methods are useful where thick epitaxial layer of relatively higher impurity concentrations are required. The method, as the name suggests utilizes the solution saturation-recrystallization process for growing epitaxial layers. The two approaches of the methods are:

(a) liquid epitaxial growth,

and (b) travelling solvent technique.

The former involves cooling of a solution in which desired constituents have been dissolved and hence the systems are transient, while in later the systems are in steady states i.e. the temperature of the system remains nearly constant and the material is transported by use of thermal gradient. Nelson[28], Donelly and Milnes[29], Laugier et al.[30], Sigmund[31], Feucht[32], Rosztoczy and Stein[33], Panish et al.[34], Mlavsky and Weinstein[35], Weinstein et al.[36], Nakano[37], Bauer etc.[38] have made several modifications to the method and have used them for growing different semiconducting layers.

By solution growth techniques large area heteroepitaxial layers, at temperatures much below the melting point of the growth materials, could be deposited. Because of lower growth temperatures the grown layers are free from chemical contamination and contain comparatively less crystalline defects. The main disadvantages of this technique are slower growth rate and high risk of cross diffusion, though slower growth rates help in maintaining dimensional control of the grown layers much more accurately than otherwise possible.

The method of chemical vapour transport is useful where monocrystallinity and electrical quality of the epitaxially grown materials are mandatory. The currently available methods could be classified into three categories:

(1) Closed tube vapour transport

(2) Open-tube vapour transport

(3) Close-spaced vapour transport.

The first one, basically, involves incorporating the source material, the transporting agent and the substrate into a close tube and heating the source material and substrate at different temperatures. The substrate temperature is kept lower than the source material. The source material reacts with the transporting agent to form volatile chemical intermediates which migrate along the thermal gradient to the substrate where decomposition and subsequent deposition on substrate take place according to the reversible disproportionation reaction. Marinace[39], Okade et al.[40], van Ruyven[41], Kasano and Iida[42], Oldham and Milnes[43], Alferov et al.[44], Moest and Shupp[45], Bertoti et al.[46] have used this technique to grow epitaxial layers of Ge, Si and III-V compounds on different substrates.

Although the closed-tube vapour transport is simplest among the chemical vapour transports, its uses are limited to research purpose only because of certain disadvantages namely, uneven and uncontrollable growth, difficulty in obtaining desired electrical properties of epitaxial layers, corrosive nature of transporting agents etc.

Open-tube vapour transport is more or less similar to that of closed tube except that in the former the pressure remains constant whereas in the later the volume of system remains constant. Moreover, open-tube is much more versatile and flexible in use and provides a better control of crystallinity and doping during growth. The technique is successfully used by Ing and Minden[47], Weinstein et al.[36], Davis et al.[48], Tietjen and Amick[49], Tietjen et al.[50], etc. The disadvantages of technique are continuous control of the flow of reactant vapours and their dependence on the geometry of the reactor tube, slower growth rates and lower yields whereas advantages are good quality and large area deposits.

Close-spaced vapour transport was first suggested by Nicoll.[51] They placed the source and substrate in close proximity and maintained a temperature gradient between them. Since the transport reactions, in the presence of a suitable transporting agent, take place in the closed space between the source and the substrate, they are not dependent on the geometry of the reaction tube. Hovel and Milnes[52] have deposited ZnSe on Ge and GaAs by this technique and placed source and substrates rigidly between oxidized silicon blocks separated by quartz spacers of 10-12 mils. The upper and lower silicon blocks were heated independently by infrared lamps. Using HCl as transporting agent and source and substrate temperature in the ranges of 620-760°C and 550-680°C good quality layers of ZnSe were obtained. The technique was used by Nicoll[51] for water vapours as transporting agent, Purohit and Flicker et al.[53] for depositing GaP on GaAs and Feucht et al.[54] for growing GaAs on Ge using HCl as transporting agent.

Because of the high efficiency, flexibility and economy in starting materials, this technique has an edge over other vapour-transport techniques. However, the experimental arrangement, being quite cumbersome, is the biggest obstacle in the mass production of epitaxial layers by this technique.

The chemical methods, as the name suggests, are chemical in nature and involve other species besides the group II and VI or group III and V elements. In some of these the films are built up on a molecular level, as in case of vacuum deposition. In others like sintered layer method films are formed from larger particles. A schematic representation of sintered layer technique for CdS is presented in Fig. 2.5. In this technique, as shown for CdS, a fine powder is produced that is made into a suspension with an appropriate liquid, $CdCl_2$ is used as a flux and an appropriate activator such as copper is added. The layer is applied to the substrate by silk screening or spraying or by printing. This layer is then fired at around 600°C to cause the grains to be sintered together and to drive off excess halide. This method is important in making photoconductive layers and is compatible with other thick film techniques. The biggest advantage of sintering is that it minimizes the problem of interparticle contacts which is common to many deposition techniques.

In solar cell fabrications sintering is generally used prior and after the deposition of thin films.[55]

The chemical deposition technique is certainly the easiest technique known for deposition of thin films and generally consists of depositing thin layers of semiconducting material, from a water solution of reacting chemicals at room temperature on a suitable substrate dipped into the solution. The layers grown by this procedure are normally polycrystalline in nature. Several semiconducting layers namely PbS on Ge[56,57], Si[58], GaAs[59], GaSb[60], CdS[61] and CdSe[62] and PbSe on Si[63] were grown using basically Kicinski[64] method. Davis and Norr[56] and recently Watanbe and Mita[61] have obtained nearly perfect single crystalline layers of PbS on Ge and on (002) surfaces of CdS single crystal substrates respectively by using lead nitrate instead of lead acetate. Kiewit[63] has grown PbSe on Si by selenourea process similar to Sigmund et al.[58]. Chocklingam et al.[65] have deposited Ag_2S and PbS layers on glass substrates. Kitaev et al.[66] have worked extensively for the deposition conditions of various semiconducting layers by this technique.

The chemical displacement techniques successfully used for growing Cu_2S layer on CdS in the fabrication of Cu_2S-CdS solar cells.[67,68] The two copper ions replace one cadmium ion and the entry and exit of copper and cadmium ions into and out of CdS crystal because concentration gradient takes place when the film or crystal of CdS is dipped into a saturated aqueous solution of copper ions containing few drops of HCl. The double displacement chemical reaction is represented as

$$2Cu^{+} + CdS = Cu_2S + Cd^{++}$$

The technique is further extended to grow Cu_2Se[69], Cu_2Te[70,71] and Cu_2Se[72] films. Hill et al.[73] and Singer and Faeth[74] have observed that for long periods the reaction is diffusion limited and rate of formation of Cu_2S is proportional to $t^{1/2}$ and for short period of immersion the rate of formation of Cu_2S is dependent on the surface reaction rate and is proportional to $t^{3/2}$.

The method of chemical spraying of reactants in liquid phase on a heated substrate was first fabricated and developed for growing this semiconducting layers by Chamberlein and Skarman.[75] They have suggested the method for industrial growth of thin films. The method was later used by other workers[1,76-78] to grow thin films for solar cells. The method, being of great potential in the field of thin film solar cell fabrication, is of current interest.

The outgoing discussion, clearly shows that though vacuum methods are good in terms of purity, well controlled growth, crystallinity and uniformity of thin films, they suffer from the biggest drawback of being applicable to grow thin films, only to a limited area. This drawback is further reflected in terms of the limitations of these methods to meet the present day challenge of cost reduction of solar cells all by themselves. Moreover, the experimental set-up is full of complexity and the technological barrier has yet to be overcome. Non-vacuum chemical methods on the other hand, in spite of their limitations of purity and lesser uniformity of deposited films have great potential for the mass production of thin films. The surmise is that the area does not seem to have any limit in these methods especially spray technique and the simplicity of the methods is the biggest boon. Moreover, the highest open circuit voltage (Voc = 1.04 volt) ever achieved for a $CdS-Cu_2S$ solar cell was obtained by employing spray technique only. These cells were found to be as high as 4% efficient.[79] It is also interesting to note that, unlike the general belief, Singer and Faeth[74] have reported, even in the case of very thick layer a single crystalline growth of Cu_2S on CdS. Chamberlein and Skarman[75] have reported such results too. However, it is surprising that in spite of considerable prospects very little attention has been paid to these methods. It is mainly because of these reasons that the simple chemical methods such as deposition, displacements and spray attracted our attention and form the crux of the present investigations.

Though the several semiconducting materials have been used for the fabrication of thin film solar cells, we have confined ourselves to the chalcogenides of transition metals such as Zn, Cd, Hg, Pb, Cu etc. only for the present study, because of the two reasons:

(i) they represent the most extensively used and promising class, and

(ii) the results obtained could be extended easily to selenide and tellurides of these metals which are also interesting class of compounds.

As the CdS-Cu_2S is the most challenging and well established combination and the expectation is that they would be the solar cells of tomorrow we have chosen this combination as a representative for thin film solar cells in the later part of present work.

Although a large number of chemical reactions are available[80,81] for the preparation of sulphides of above transition metals, it is the chemical reaction involving a water soluble cadmium salt and an organic sulfurizing agent such as thioacetamides or thioureas, which find the application for the growth of thin semiconducting films for solar cells. Surprisingly, no information is available in literature, about the kinetics, thermodynamics, nature of complex formed etc. of the chemical reactions involved.

The possible reasons may be the deterant to use H_2S as sulfidizing agent because of its unpleasant odour, toxic nature of H_2S and annoying physical characteristics of most sulfides precipitated. Moreover, the reaction is fast with H_2S and surmise is that it does not yield pure CdS as obtained by organic liquids.

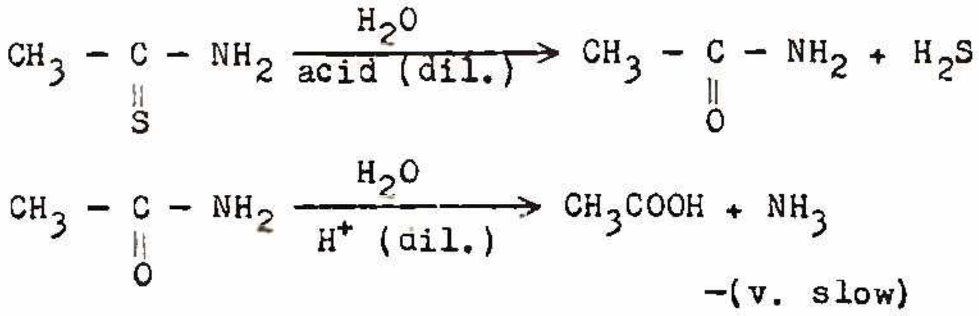
Unlike the general belief, thioacetamide did not give quantitative precipitate of certain halides under the similar conditions in which hydrogen sulfide did.[84] Swift and Butler have found that in some cases sulfides precipitate formed faster with thioacetamide than H_2S and in other it was slower. In some other cases, rate of precipitation was faster than seemed compatible with preliminary measurements of hydrolysis of thioacetamide.

Many workers have investigated the metal sulfide precipitation with thioacetamide both in acidic as well as in alkaline (ammonical) medium. In both these mediums two different mechanisms are involved for precipitation of metal sulfides with thioacetamide. They are:

I) (a) An individual metal ion may combine with the H_2S (generated by the hydrolysis of thioacetamide)
or (b) by some specific interaction between thioacetamide and another substance in solution.

II) Metal ion may undergo a direct pH dependent reaction with thioacetamide itself.

Although the two processes are competitive experimental conditions can be established such that one of these mechanism dominates. In fact, at lower pH (< 3) the precipitation proceeds through the hydrolysis of thioacetamide and rate of precipitation is same as the rate of hydrolysis i.e.



$$CH_3-\underset{\underset{S}{\|}}{C}-NH_2 \xrightarrow[\text{acid (dil.)}]{H_2O} CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + H_2S$$

$$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[H^+\text{ (dil.)}]{H_2O} CH_3COOH + NH_3 \quad -(\text{v. slow})$$

Reaction rate is first order with respect to both thioacetamide and H_2S, whereas at higher pH ($>$ 3.5-5.0) formation of sulfide is thousand times faster than rate of H_2S formation.

However, this chemical method of precipitating sulfide, is used only to deposit the PbS in preparing photo cells. For the deposition of cadmium sulfide it is the thiourea which is invariably used as the precipitating or sulfidizing agent. Unfortunately the literature regarding the detailed account of its application particularly regarding the conditions of reaction such as temperature, concentration and ratio of reactants, nature of reactions i.e. whether endothermic or exothermic, ground state properties of reactants etc. is either not available or is scanty and difficult to procure, in spite of the fact, that it has been adopted in all the three non-vacuum chemical techniques namely deposition, spray and sintering. Studies conducted in this field[66,75] show that the use of substituted thiourea may be useful in preventing the precipitation of unwanted materials, such as hydroxides, in the solution.

Our aim, therefore, in present study, is to study the feasibilities of improving the method of CdS film deposition both by precipitation and chemical spray and to explore the possibility of a new and better reagent than thiourea for these methods.

To achieve this goal, it has been felt necessary that both theoretical as well as experimental studies on both substituted thiourea and their transition metal complexes may be extensively investigated with reference to the nature of the complex formed, decomposition temperature and products of the reaction, the ground state properties such as ionization potential, electron affinity, charge density, heat of formation, energy of isomerization, delocalization energy, etc. of reactants. The following chapters represent the attempt in this direction.

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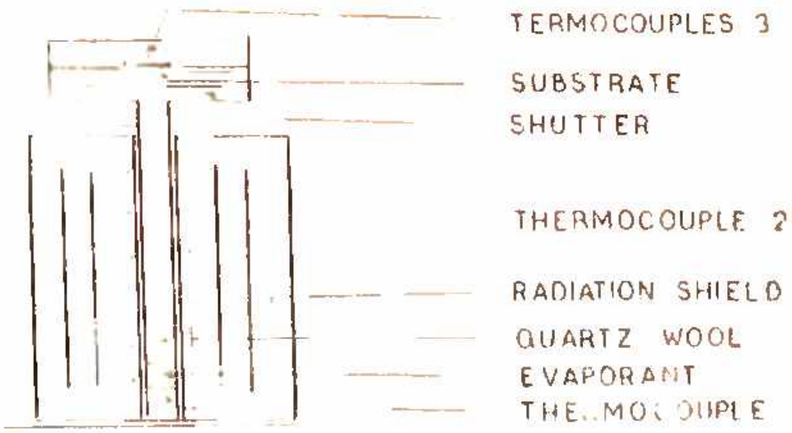

FIG 2.1 SINGLE EVAPORATION TECHNIQUE

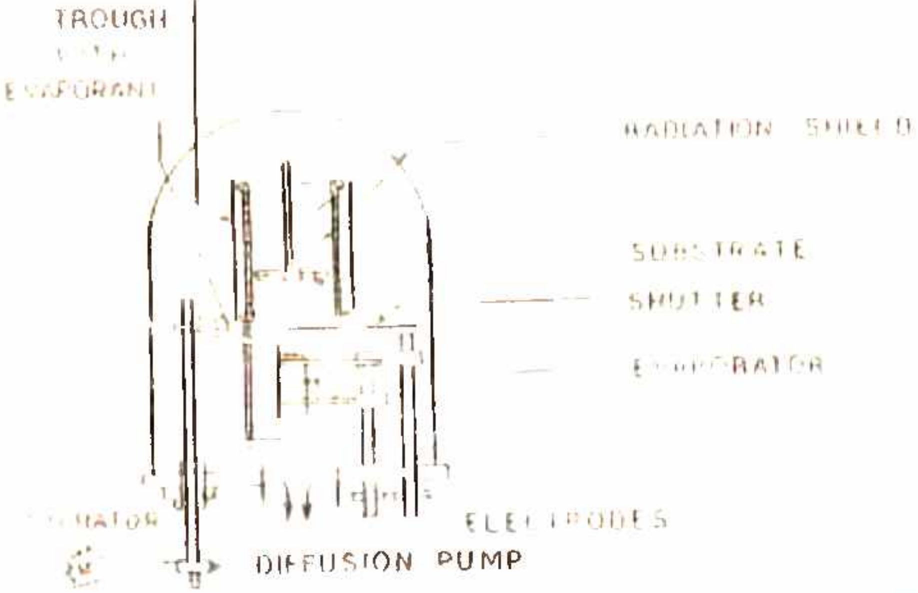

FIG 2.2 FLASH EVAPORATION TECHNIQUE

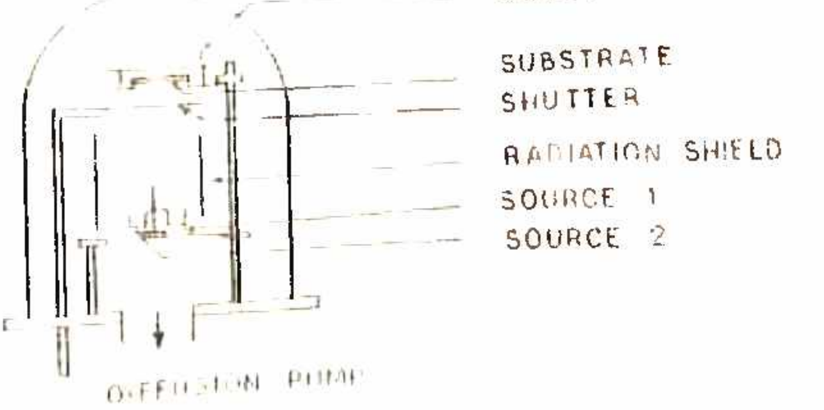

FIG. 2.3 COEVAPORATION TECHNIQUE

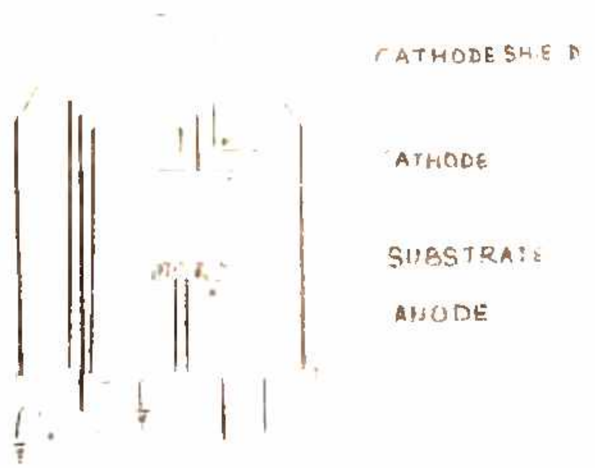

Fig. 2.4 CATHODE SPUTTERING TECHNIQUE

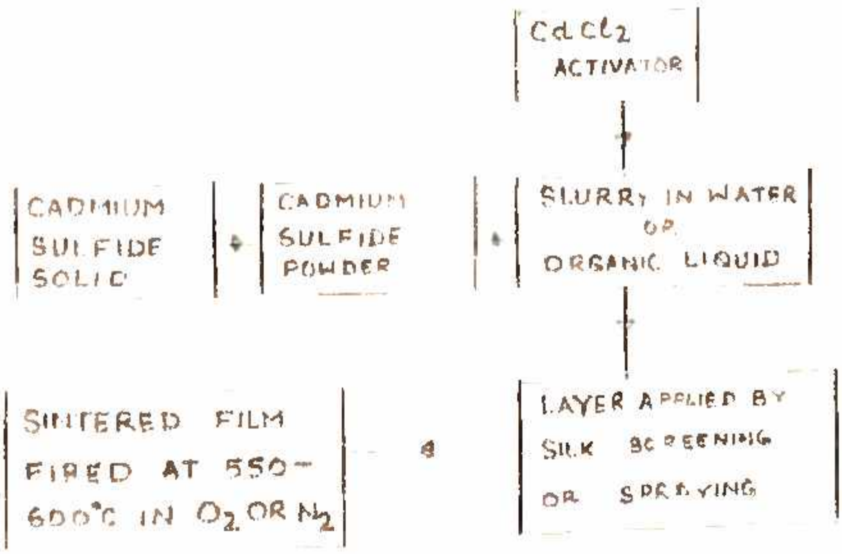

Fig. 2.5 SINTERED LAYER TECHNIQUE (For CdS)

REFERENCES

1. F.V. Shalleross, RCA Review, 28, 569 (1967).
2. Goldfinger et al., Trans. Faraday Soc., 59, 2851 (1963).
3. Somargai et al., J. Chem. Phys., 43, 1450 (1965) and 43, 1456 (1965).
4. Günther, 'Use of thin films in physical investigations', Academic Press, London, p. 213 (1966).
5. Sharma and Purohit, 'Semiconductor heterojunctions', Pergamon Press, Oxford (1974).
6. M.E. Chugnova, M.I. Elinson and A.G. Zhdan, Soviet Phys. Solid State, 11, 874 (1969).
7. M.J. Hampshire, T.I. Pritchard and R.D. Tomlinson, Solid State Electron, 13, 1073 (1970).
8. J. Nakai, A. Yashuka, T. Okumura and G. Kano, Jap. J. Appl. Phys., 4, 545 (1965).
9. M.V. Kot and V.A. Korotkov, Ukr. Fiz. Zh., 13, 1817 (1968).
10. P.J. Deasley, S.J.T. Owen and P.W. Webb, J. Mat. Sci., 5, 1054 (1970).
11. J.T. Calow, S.J.T. Owen and P.W. Webb, Phys. Stat. Sol., 28, 295 (1968).
12. J. Hale, Phys. Stat. Sol. (a) 1, 245 (1970).
13. I. Ryu and K. Takahashi, Jap. J. Appl. Phys., 4, 850 (1965).

14. H. Okimura and R. Kando, Jap. J. Appl. Phys., 9, 274 (1970).

15. S. Brojo, T.T. Riky and G.T. Wright, Brit. J. Appl. Phys., 16, 133 (1965).

16. M.V. Kot and L.M. Panasjuk, Soviet Phys. Semicond., 1, 155 (1967).

17. P.L. Jones, C.N.W. Litting, D.E. Mason and V.A. Williams, Brit. J. Appl. Phys., Ser. 2, 1, 283 (1968).

18. H. Okimura, Jap. J. Appl. Phys., 7, 1297 (1968).

19. T.G.R. Rawlins, J. Mat. Sci., 5, 881 (1970).

20. E.K. Muller, J. Appl. Phys., 35, 580 (1964).

21. J.L. Richards, P.B. Hart and L.M. Gallone, J. Appl. Phys., 34, 3418 (1963).

22. K. Berchtold, Proc. Int. Conf. on the Phys. and Chem. of Semicond. heterojunctions (Ed. in Chief G. Szigeti), Vol. II, Akademiai Kiado', Budapest, 221 (1971).

23. T. Ido, M. Hirose and T. Arizumi, ibid.

24. K.G. Gunther, The use of thin films in physical investigations, Ed. J.C. Anderson, Akademic Press Inc., New York (1966).

25. B. Molnar, J.J. Flood and M.H. Francombe, J. Appl. Phys., 33, 3554 (1964).

26. V.A. Vlasov and S.A. Semiletov, Soviet Phys. Cryst., 12, 645 (1968).

27. T.G.R. Rawlins and R.J. Woodward, J. Mat. Sci., 7, 257 (1972).

28. H. Nelson, RCA Rev., 24, 603 (1963).

29. J.P. Donnelly and A.G. Milnes, J. Electrochem. Soc., 113, 297 (1966).

30. A. Laugier, M. Gavand and G. Mesnard, Solid State Electron., 13, 741 (1970) and Thin Solid Films, 6, 217 (1970).

31. H. Sigmund, Proc. Int. Conf. on the Phys. Chem. of Semicond. heterojunctions (Ed. in Chief, G. Szigeti), Vol. II, Akademiai Kiado.

32. D.L. Feucht, ibid., Vol. I, p. 39.

33. F.E. Rosztoczy and W.W. Stein, ibid., p. 333.

34. M.B. Panish, I. Hayashi and S. Sumski, Appl. Phys. Letters, 16, 326 (1970).

35. A.I. Mlavsky and M. Weinstein, J. Appl. Phys., 34, 2885 (1963).

36. M. Weinstein, R.O. Bell and A.A. Menna, J. Electrochem. Soc., 111, 674 (1964).

37. T. Nakano, Jap. J. Appl. Phys., 6, 854 (1967).

38. G.E. Bauer, Z. Naturforsch, 22a, 284 (1967).

39. J.C. Marinace, IBM J. Res. Dev., 4, 248 (1960).

40. T. Okada, T. Kano and Y. Sasaki, J. Phys. Soc. Jap., 16, 2591 (1961).

41. L.J. Van Ruyven, Thesis, Tech. Hogeschool, Eindhoven, Netherlands, 1964.

42. H. Kasano and S. Iida, Jap. J. Appl. Phys., 6, 1038 (1967).

43. W.G. Oldham and A.G. Milnes, Solid State Electron, 6, 121 (1963).

44. Zh. I. Alferov et al., Soviet Phys. Solid State, 6, 1865 (1965).

45. R.R. Moest and B.R. Shupp, J. Electrochem. Soc., 109, 1061 (1961).

46. I. Bertoti, M. Farkas-Jahnke, E. Lendvay and T. Nemeth, J. Mat. Sci., 4, 699 (1969).

47. S.W. Ing, Jr. and H.T. Minden, J. Electrochem. Soc., 111, 674 (1964).

48. M.E. Davis, G. Zeidenbergs and R.L. Anderson, Phys. Stat. Sol., 34, 385 (1969).

49. J.J. Tietjen and J.A. Amick, J. Electrochem. Soc., 113. 724 (1966).

50. J.J. Tietjen, R.E. Enstrom and D. Richman, RCA Review, 31, 635 (1970).

51. F.H. Nicoll, J. Electrochem. Soc., 110, 1165 (1963).

52. H.J. Hovel and A.G. Milnes, J. Electrochem. Soc., 116, 843 (1969).

53. R.K. Purohit, J. Mat. Sci., 3, 330 (1968).

54. D.K. Jadus and D.L. Feucht, IEEE Trans. Electron Devices, ED-14, 102 (1969).

55. F.A. Shirland, W.J. Biter, E.W. Greeneich, A.J. Simon and T.P. Brody, Report NSF/RANN/SE/AER-74-14918 A01/FR/76.

56. J.L. Davis and M.K. Norr, J. Appl. Phys., 37, 1670 (1966).

57. G. Guizzetti, E. Reguzzoni and G. Samoggia, Alta Frequenza, 39, 554 (1970).

58. H. Sigmund and K. Berchtold, Phys. Stat. Sol., 20, 255 (1967).

59. B.L. Sharma and S.N. Mukerjee, Phys. Stat. Sol. (a) 2, K21 (1970).

60. B.L. Sharma and S.K. Suri, Phys. Stat. Sol. (a), 16, K47 (1973).

61. S. Watanbe and Y. Mita, J. Electrochem. Soc., 116, 989 (1969).

62. S.K. Suri and B.L. Sharma, Int. J. Electron. (1975).

63. D.A. Kiewit, Phys. Stat. Sol. (a) 1, 725 (1970).

64. F. Kicinski, J. Soc. Chem. Ind., 67, 54 (1948).

65. M.J. Chocklingam, K.N. Rao, N. Rangarajan and C.V. Suryanarayana, Ind. J. Pure and Appl. Phys., 7, 628 (1969).

66. G.A. Kitaev et al., Chemical Abstract: 66: 6045, 67 : 25520, 67: 120420, 68: 43731K, 70: 107572, 71 : 117014, 71: 34468, 72: P37036, 82: 30741 and 83 : 42712.

67. F.A. Shirland, Adv. Energy Conv., Vol. 6, 1966.

68. F.A. Shirland, T.P. Brody, N.S.F. Solar Energy Conversion Symposium, Tuscon, Arozona (1974).

69. V.N. Komashcenko, S. Kynev, A.I. Marchenko and G.A. Fedorus, Ukr. Fiz. Zh., 13, 2086 (1968).

70. D.A. Cusano, Phys. and Chem. of II-VI Compounds, Ed. M. Aven and J.S. Prener, North-Holland Publishing Co., p754, 1967.

71. A.P. Landsman and R.N. Tykvenko, Radio Engg. Electron. Phys., 12, 461 (1967).

72. M. Aven and D.A. Cusano, J. Appl. Phys., 35, 606 (1964).

73. E.R. Hill, B.G. Keramidas and D.J. Krus, IEEE Sixth Photovol. Specialists Conference, 1967.

74. J. Singer and P.A. Faeth, Appl. Phys. Lett., 71, 130 (1967).

75. R.R. Chamberlin and J.S. Skarman, J. Electrochem. Soc., 113, 84 (1966).

76. A.P. Lapin, B.A. Leonov, S.V. Syntkov and A.T. Gureev, Chemical Abstract, 82 : 179438 (1975).

77. S. Martinuzzi, F. Cabane Brouty, T. Cabot, A. Franco and J. Kalliontzis, Electricite Solaire, Colloque International Toulouse, 1-5 March, p293 (1976).

78. ibid., p303 (1976).

79. R.R. Chamberlin and J.S. Skarman, Proc. 4th Photovoltaic Specialists Conf., Vol. II, Thin film Solar Cells and Solar Cell testing, Cleveland (1964).

80. Jacobson, Encyclopaedia of Chemical Reactions.

81. J.W. Mellore, A comprehensive treatise on Inorganic and Theoretical Chemistry, Vol. IV, Longmans Green and Co., 1947.

82. K.L. Chopra, Thin Films, Science Today, page 13, July 1977.

83. K.L. Chopra, Thin Film Phenomena, McGraw Hill Book Co., New York (1969).

84. David F. Bowersox and E.H. Swift, Anal. Chem., 30, 1288 (1958) and E.H. Swift and E.A. Butler, Anal. Chem., 28, 146 (1956).

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CHAPTER III

This Chapter describes briefly HMO method and presents the theoretical calculations on various substituted thioureas. A critical discussion on comparison of thiourea with some substituted thiourea establishes the superiority of later to some former for the deposition of thin films. The pyridyl group substituted thioureas are found to be the best ligands for this purpose.

INTRODUCTION

It is apparent from a survey of the literature of the past decade that a growing number of scientists are employing theoretical chemistry to probe the chemical and biochemical events at the molecular level. Quantum chemistry provides us with two fundamental methods for the study of electronic structure of the molecules, the valence bond method whose simplified qualitative version frequently is referred to as the resonance theory and molecular orbital method. Both represent approximate procedure for obtaining approximate solution of the shrodinger equation relative to the molecule. The resolution of this equation provides the electronic level and the distribution of electronic cloud in the chemical species. However, the immense complexity of practically insoluble problem of calculating all the interactions among all the component particles of an atom compels us to rely upon these somewhat approximate procedures.

Both methods have met with outstanding success in the organic chemistry. However, the Valence Bond Theory is, in fact, far too complex and too difficult to handle, to be of any real use in the system of structure of biochemicals. On the other hand, the molecular orbital method exists in various stages of refinement. These are the so-called Huckel LCAO (linear combination of atomic orbitals) approximation, the SCF-LCAO molecular orbital approximation, the approximation of configuration mixing etc. Although based as the same general principle, these various procedures are widely different from each other in their mathematical development and precision. Consequently they also differ in the labour they require. Of all the approximations, the Huckel one is simple enough and a great number of fundamental biochemical structures and problems may be quite satisfactorily dealt with, at least to the first approximation by it. Refinements are, of course, always welcome and always useful but in many problems the essential results, the general idea of how things are and function at the electronic level, can be obtained with the use of this simple approximation.

HUCKEL APPROXIMATION

This method is described in detail in several texts.[1] In the orbital representation the individual molecular orbitals (represented by ψ_i) of a molecule are eigen functions of the corresponding one electron Hamiltonian operator H. Mathematically this is represented as:

$$H\psi_i = E_i\psi_i \qquad (3.1)$$

Equation (3.1) is known as Schrödinger equation. As it is difficult to get the exact analytical expressions for for polyelectronic system, ψ is factored into sets of

σ and π-bonds i.e.

$$\psi = \phi_\sigma \cdot \phi_\pi \tag{3.2}$$

ϕ_σ properties are assumed to be predictable from its components and hence only ϕ_π is taken into account. ϕ_π is further, approximated as a product of molecular orbitals each of which is taken as a linear combination of atomic orbitals i.e.

$$\psi_i = \sum_r C_{ir} \phi_r \tag{3.3}$$

Here, ψ_i represents a molecular orbital and ϕ an atomic orbital, while C_{ir} represents the coefficients of the atomic orbitals. The use of variation principle at this stage gives

$$\sum_j C_j (H_{ij} - ES_{ij}) = 0 \tag{3.4}$$

For non-trivial solution:

$$H_{ij} - ES_{ij} = 0 \tag{3.5}$$

where for many electron system

$$H = \sum_i \left(- \frac{h^2}{8\pi^2 m} \nabla_i^2\right) - \sum_i \sum_m \frac{z_m e^2}{r_{im}} \tag{3.6}$$

in which, the Laplacian operator, ∇_i^2, is defined as

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \tag{3.7}$$

and the integral H_{ij} and S_{ij} are defined as

$$H_{ij} = \int \phi_i \, H \, \phi_j \, dv \tag{3.8}$$

$$S_{ij} = \int \phi_i \, \phi_j \, dv \tag{3.9}$$

Instead of calculating the integrals H_{ij} we treat them as parameters. The diagonal element H_{ii} is called coulomb integral and written as α_i, and off diagonal element H_{ij} is called resonance integral and written as β_{ij}. These integrals are evaluated by the following two equations:

$$\alpha_i = \alpha_o + h \beta_o \tag{3.10}$$

$$\beta_{ij} = K \beta_o \tag{3.11}$$

where α_o and β_o are standard coulomb and resonance integrals for carbon atom and carbon-carbon bond respectively and h and k are semiempirical parameters under discussion. The values of the parameters h and k for different atoms and different pairs of atoms are listed in Table (3.1). For non-bonded pairs, the resonance integral β_{ij} is always taken as zero. If there are some hetero-atom adjacent to a carbon atom, the h parameter for that carbon atom is taken as calculated by:

$$hc = 0.1 \sum_{i}^{\text{adj.atom}} hi \tag{3.12}$$

where the summation extends over all the hetero-atoms bonded to the carbon atom, otherwise it is zero. This equation (3.12) takes into account the inductive effect produced on the carbon atom by the adjacent heteroatoms.

The overlap integral S_{ij} is assumed to be unity, if $i = j$, otherwise zero.

The ground state of a closed-shell molecule is supposed to be a situation where 2N electrons are placed in pairs in the N molecular orbitals of the lowest energy. The total binding energy E_T of the molecule is then equated, in this approximation, to the total orbital energy of the electrons i.e.,

$$E_T = 2 \sum_{i}^{\text{Occ.}} E_i \tag{3.13}$$

CALCULATION OF ELECTRONIC INDICES

A. Charge Density, Bond-order and Free Valency

The probability of finding any electron in a small volume element dv, is given by $|\Psi|^2$ dv. In the present case, the wave function ϕ_i, for each atomic orbital in any MO has been assumed to be the same and its contribution to a MO wave function, Ψ, is weighted by its coefficient, C_i. The probability of finding the electron in the region of space associated with atomic orbital ϕ_i is then C_i^2. The probability can be expressed in terms of a fractional charge or electron density, q at atom r based upon our charge cloud concept of electron distribution in its domain. Since there are two electrons in a filled MO, the electron density at atom r in the i^{th} MO is $q_r^i = 2\, C_r^2$. The total density at atom r is then a sum of the electron densities at atom r for all occupied MO's:

$$q_r = 2 \sum_i^{Occ.} Cir^2 \qquad (3.14)$$

The net charge density, Q_r, at atom r is then given by

$$Q_r = n_r - q_r \qquad (3.15)$$

where n_r is the number of π-electrons contributed by atom r.

The bond order is defined as

$$P_{tu} = 2 \sum_i^{Occ.} Cit\ Ciu \qquad (3.16)$$

The concept of Free Valency F, was proposed by Coulson[2] as being a residual bonding affinity of a π-electron on an atom. It is the difference between the maximum bond orders around an atom, N_{max}, and the calculated bond orders around that atom, N_r

$$F = N_{max} - N_r \qquad (3.17)$$

The maximum bond orders around C, N and O are taken to $\sqrt{3}$, $\sqrt{2}$ and 1 respectively[1].

B. Energies of HOMO, LUMO and Excitation Energy

Solving a secular determinant, equation (3.5) gives rise to a series of energy values corresponding to a particular molecular orbitals which are solutions of the wave equation. These energy values are of the form

$$E_i = \alpha + m_i \beta \qquad (3.18)$$

where i refers to an MO.

The positive m values correspond to occupied (bonding) orbitals and negative ones to unoccupied (anti-bonding) orbitals. The lowest positive m value gives the energy of HOMO and the lowest (in magnitude) negative one that of LUMO. It is customary to express the energy values only by m.

The excitation energy is taken as the difference between the energies of HOMO and LUMO.

C. Frontier Electron Theory and Reactivity

A different approach to reactivity using the isolated-molecule approximation was proposed by Fukui et al.[3] The theory presumes that the least tightly bound electron would react preferentially with an electrophillic reagent. The π-electrons in HOMO would thus be important in the reaction. The position in the molecule with the greatest density in these MO's would presumably be the most reactive. These orbitals are known as frontier orbitals and the electrons as frontier electrons.

Nucleophilic reactivity would be predicted to occur at a position in the molecule having the highest density of two ghost electrons in LUMO. The symbol $f_r^{(E)}$ and $f_r^{(N)}$ are used for the electron density, c_{fr}^{2}, at atoms r for the frontier orbital, f, for electrophilic or nucleophilic attack. The index permits only a comparison of relative reactivities within the same molecule.

The concept was extended to permit the comparison of reactivities of positions in different molecules[4]. The index called superdelocalizability, S_r, is defined as

$$S_r = 2 \sum_{i}^{occ/unocc} C_{ir}^{2}/m_i \qquad (3.19)$$

where the summation extends over all occupied orbitals for electrophilic substitution and over all unoccupied orbitals for nucleophilic substitution. For radical attack the superdelocalizability index is defined as

$$S_r^{(R)} = \sum_{i}^{occ.} C_{ir}^{2}/m_i + \sum_{j}^{unocc.} C_{jr}^{2}/m_j \qquad (3.20)$$

RESULTS AND DISCUSSION

Shporiko et al.[5] after comparing the X-ray fluorescence spectra of various thiocarbonyl compounds have reached to the conclusion that there is no substantial contribution of 3-d atomic orbitals of sulfur into the molecular orbitals of higher occupied levels. The surmise, therefore, is to neglect the $d\pi$-$p\pi$ interaction of sulfur and carbon atoms. The present study deals with a series of large number of similar compounds.

Shporiko et al. have further reported that the contribution of the 3s-atomic orbitals into the α-symmetry molecular orbital did not change significantly with nature of substituent, whereas studies of Kitaev et al.[6] clearly report the difference between the thiourea and allyl substituted thiourea.

Using the HMO method we have calculated the electronic indices such as charge density, total pi bond energy, energy of HOMO and LUMO etc., definitions and brief description of which are already presented in the earlier paragraphs. Tables (3.2-3.7) present the numerical values of these for the various substituted thioureas. Tables (3.2-3.4) contain the results on the keto form whereas Tables (3.5-3.7) deals with the corresponding enol forms. Table 3.2 shows the mono substituted thioureas and Table 3.3, N, N' symmetrically disubstituted thioureas whereas Table 3.4 contains results on the disubstituted unsymmetrical thioureas.

Ionization potential i.e. the energy of highest occupied molecular orbital, as mentioned earlier can be considered a criteria to determine the degree of ease by which a complex may be formed. It is observed that the lower is the Ionization potential for an electron donor the better it will co-ordinate with an electron acceptor to form a complex.[7] The columns showing the Ionization potential of Tables (3.2-3.7) of various substituted thioureas suggest that the substituted thioureas are better electron donors as compared to the thiourea itself. Methyl and ethyl substituted thioureas are found to be the worst electron donors among the compounds of present series. Table 3.2 shows that an aryl substituent reduces the ionization potential of thiourea more than an alkyl group, thereby, making it a better electron donor. Among the alkyl groups, the unsaturated group (allyl) is found to be better than the saturated alkyl groups in the sense that the later unlike the former, enhances the electron donor properties of thioureas. On the other hand, in the case of an aryl group substitution introduction of a heteroatom in substituent group (e.g. pyridyl) decreases or substituting it with an alkyl group (e.g. toludine) increases the electron donor power of the ligand.

Similarly a methylene group in between the substituent group and substituted nitrogen decreases the effect of aryl substituent group.

In case of symmetrically disubstituted thioureas similar trend is observed. Dimethyl and diethyl thioureas as expected are found to be lesser electron donors than thiourea and diallyl is better than thiourea, di-p-tolyl being the best among them. Whereas in case of unsymmetrical thioureas, especially N substituted, N'-2 (5-substituted-pyridyl) thioureas the chloro, bromo, nitro or 3-hydroxy groups either show no effect (N-phenyl) or increase (N-allyl) the electron donor properties of the ligand. Among all the thioureas listed in Tables (3.2-3.4) the 5-iodo pyridyl group gives the best electron donor ligands.

On the basis of ionization potential the trend towards better substituted thiourea can be written as: Saturated alkyl thioureas < thiourea < unsaturated alkyl thiourea < iodo pyridyl substituted thioureas.

The electrophilic superdelocalizability was first introduced by Fukui et al. to compare the chemical reactivity of compounds within a series. As the sulfur is the most reactive site in keto and nitrogen in enol form of the present molecules, the numerical values of this index are presented in Tables (3.2-3.7), only for these centers and are denoted by the symbols S_E^S and S_E^N

respectively. A similar trend as mentioned above is obtained on the basis of this electronic index. Thereby, further confirming the superiority of aryl group substituents and especially the iodo pyridyl group over the others.

The interaction of ligand molecules with metal could be explained by considering thiourea and its keto form as 'dipoles'.[8] The calculated charge densities show that though the thiourea and its keto forms are actually not charged a partial positive charge on nitrogen and a partial negative charge on sulphur in keto and just reverse in enol form exists. These dipoles, therefore, may interact with transition metals to form a complex.

As seen from Table (3.2) the charge density on nitrogen and sulphur of thiourea are 0.126 and -0.445 respectively for the keto form suggesting, thereby, that for an electrophilic reagent the sulphur of thiocarbonyl group is the only attacking site. Similarly from Table (3.5) it can be seen that for enol form the charge densities on nitrogens and sulphur are -0.419, 0.127 and 0.142 respectively. Charge density is negative, only on the nitrogen atom which is bonded by a π-bond with carbon of thiocarbonyl group and thus is the attacking site for an electrophile.

These observations indicate that for a tetrahedral complex of transition metal with thiourea, in which the two univalent anions remain attached to the metal in inner sphere, the complex must have a one to two (1:2) metal to ligand ratio. Similarly for an octahedral configuration the ratio must be 1:4.

The possibility of thiourea existing in its enol form may give rise to a mixture of two complexes, instead of a pure complex. This mixture will consist of (a) complex of enol form in which the co-ordination is through nitrogen and (b) complex of keto form in which co-ordination is through sulfur. Predominance of a particular form in the mixture would depend upon the experimental conditions for the preparations of these complexes. The experimental conditions such as the solvent system used, precipitating reagent employed or temperature of reactions etc. which greatly influence the tautomeric equilibrium of ligand, would be more important in this respect.

These observations are in fairly good agreement with the various experimental results.[9-18]

Further, substitution on one of the nitrogen atom of thiourea greatly influences the charge density on that atom, whereas a little effect is observed at the sulfur of the thiocarbonyl group and second nitrogen remains almost unaffected (Tables 3.2-3.7). N, N' disubstituted symmetrical thioureas have more or less the same charge density as the mono-substituted thioureas. However, a closer look on Table 3.2 and Table 3.3 shows that in former the charge density on sulfur becomes a little less negative than the corresponding monosubstituted thiourea. It can also be seen that substitution, in general, increases the charge density on substituted nitrogen. Replacing both the hydrogens of thiourea as in tetramethyl thiourea, the charge density increases further. Moreover, methyl, ethyl and allyl group increase it to lesser extent as compared to other aromatic groups.

These observations could be explained on the basis of electron donating properties of the substituent groups. In general, as the size of group increases the donating power increases. Moreover, a conjugated system and aryl group is better than alkyl group as the former helps in delocalization of the electronic cloud.[8]

Tables (3.2-3.4) show the increasing trend of electron donating groups, on the basis of charge densities alone, in the following order:

$$\mathrm{H} < \mathrm{CH_3} \sim \mathrm{CH_3CH_2} \sim \mathrm{CH_2 = CH - CH_2 -} < \text{benzyl} < \text{phenyl} \sim \text{o-tolyl} \sim \text{m-tolyl} \sim \text{p-tolyl} < \text{pyridyl}$$

This is in good agreement of the general trend.[19]

In case of pyridyl thiourea (Table 3.2) a second electrophilic center namely the nitrogen of pyridyl ring is also observed. The charge density at this atom (nitrogen) is found to be -0.204 which is about half than that at the sulfur. Hence, in this case, there exists a possibility of chelate formation in which the sulfur of thiourea and nitrogen of pyridyl group are co-ordinated to the same metal ion. This would give rise to a six membered chelate ring including metal which will impart an additional stability to the complex. We, therefore, have selected a series of pyridyl substituted thioureas for our study. In such cases the complex must have a 1:1 and 1:2 metal to ligand ratio for a tetrahedral and octahedral configuration respectively.

The ionization potential is not the sole factor relating to the ease of complex formation. The easiness of the molecular complex formation depends upon many factors such as delocalization energy, dispersion energy, exchange repulsion energy and electrostatic energy etc. Reactivity, therefore should be discussed taking all these factors into account.[20]

The individual bond energies were derived from the experimental data by using the method as described by Allen.[21] Selection of a proper value for bond energy for a particular bond is difficult as various values are quoted in literature. Considerable amount of this discrepancy seems to be due to the tendency to use outdated values for the heats of atomization of carbon and nitrogen. The current, more acceptable values, as suggested by Dewar and Gleicher[22], have been used for calculating the bond energies, in this presentation.

These are:

$C(\text{diamond}) \longrightarrow C(g)$ 170.9 Kcal/mole

$1/2\ H_2(g) \longrightarrow H(g)$ 52.1 Kcal/mole

$1/2\ N_2(g) \longrightarrow N(g)$ 113.0 Kcal/mole

$1/2\ O_2(g) \longrightarrow O(g)$ 59.5 Kcal/mole

$S(c) \longrightarrow S(g)$ 65.65 Kcal/mole

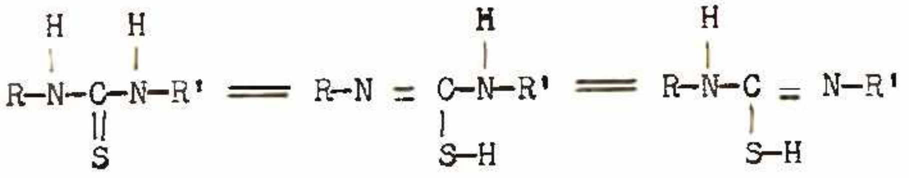
Bond energy both taken directly from literature and calculated are tabled in Table 3.8.

The heat of formation of present compounds is given by the following equation:

$$\Delta H_f = N_{CC}\ E_{CC} + N_{CN}\ E_{CN} + N_{CS}\ E_{CS} + N_{CH}\ E_{CH} + N_{NH}\ E_{NH} + N_{SH}\ E_{SH} + E_{\pi b}\cdot\beta$$

where N_{CC}, N_{CN}, N_{CS} N_{CH}, N_{NH} and N_{SH} are respectively the numbers of CC, CN, CS, CH, NH and SH bonds with sigma bond energies E_{CC}, E_{CN}, E_{CS}, E_{CH}, E_{NH} and E_{SH} respectively. $E_{\pi b}$ is the π-bond energy calculated by HMO method and β is an empirical constant.

The difference between the heats of formation of two isomeric forms is termed as the energy of isomerization and describes the relative stability of the two. Thioureas are known to exist in the following keto and enol forms:



(Keto) (Enol I) (Enol II)

The energy of isomerization, therefore, can be written as:

$$\Delta H_{f(\text{Keto})} - \Delta H_{f(\text{Enol})} = \Delta E_{\sigma} + \Delta E_{\pi b}\cdot\beta$$

Of the various definitions given for the resonance energy[24-26] one that is given by Dewar and De Llano is adopted here. The extra stabilization of the delocalized systems over and above the expected for their completely localized structures has been termed as the 'resonance energy' and is now commonly known as Dewar resonance energy.[27] The heat of formation of a localized system would be the additive sum of the bond energies of the various types of localized bonds. If this be represented by $-\Delta H_f'$, then the resonance energy of the corresponding delocalized system would be the difference between $-\Delta H_f$ and $-\Delta H_f'$. With the straightforward use of the bond energies of the localized bonds as listed in Table 3.8 the resonance energies for both the forms of thioureas are calculated and are listed in Tables 3.2-3.7.

The quantitative correctness of the theoretical predictions cannot be verified, as no measurements have been made on these properties of the thioureas. In order to calculate value of β, experimental value for the heat of formation of thiourea is taken from literature[28] and equated to ΔH_f^o i.e.

$$\Delta H_f^o = E_{\sigma} + E_{\pi b} . \beta$$

$$\text{or} \quad -0.96 = 23.25 + 10.28 \, . \, \beta$$

$$\therefore \beta = -2.36 \quad \text{e.v.}$$

This value of β was used throughout the series to calculate heat of formation, energy of isomerization and resonance energy. It can be seen that enol form of thiourea and substituted thiourea have higher heat of formation than corresponding keto form. This verifies the fact that enol form of substituted thioureas are more stable than keto form. The energy of isomerization gives the degree of stability. It can also be seen that, in case of monosubstituted thioureas the enol form is more stable as compared to the enol form of thiourea itself. In case of disubstituted thiourea the reverse is true, i.e. except diallyl and dibenzyl (where conjugation is hindered by the methylene group) thiourea all disubstituted thiourea have more stable keto form as compared to thiourea. This is because of the fact that second symmetrical substitution nullifies the effect of former. In case of N, N' unsymmetrically substituted thiourea two enol forms are possible depending upon the involvement of the particular substituted nitrogen. Taking into account the more stable form, one finds that the allyl-5-iodo pyridyl thiourea gives the most stable enol form whereas phenyl, pyridyl thiourea or phenyl-5-chloro pyridyl thiourea gives the most stable keto form. The case of allyl hydroxy pyridyl thiourea is exceptional in the sense that it has keto form more stable than the enol form. The reason for this may be the hydrogen bond between the oxygen of hydroxy group and hydrogen of substituted nitrogen. This is verified by the fact that the enol form involving pyridyl nitrogen is less stable than the enol form involving allyl nitrogen.

In addition to the above mentioned ground state properties of thioureas the bond orders were also calculated for various substituted thioureas. In Figs. 3.7-3.26 only a few selected bond orders have been shown, to keep the bulk of this presentation within limits. The calculation of pi bond shows that in each system each bond possesses some double bond character. After the isomerization has occurred, the system readjusts itself to attain a minimum energy state and consequently the bond alteration occurs. Though the tautomerization effect is observed for all the bonds it is more pronounced in -N-CS-N- skeletons, which is clear from the comparison of the bond orders of the two forms.

We now take up the application of the information obtained by the preceding work to the problem of thin film deposition by non-vacuum chemical methods. We find that in both these cases, as mentioned earlier in

Chapter I, the reactants are mixed in stoichiometric proportion in the solvent (say H_2O). The study of Chamberlin and Skarman reveals that at this stage some of the hydroxide of cadmium is also precipitated which greatly affects the semiconducting properties of the cadmium sulfide layer. The reaction taking place in spraying method can be written as:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$Cd^{+2} + 2OH^- \rightleftharpoons Cd(OH)_2$$

$$Cd^{+2} + \text{Ligand} \rightleftharpoons (Cd - \text{Ligand})^*$$

$$(Cd - \text{Ligand})^* + H_2O \overset{\Lambda}{\rightleftharpoons} CdS + NH_4Cl + CO_2$$

where $(Cd - \text{Ligand})^*$ denotes the complex formed in the solution.

Here we can see that a ligand with lower ionization potential, as mentioned earlier, will co-ordinate with metal more readily and thus would hinder the formation of cadmium hydroxide to great extent. Moreover, the stability of the complex also plays an important role here in the sense that a stable complex traps the Cd^{+2} better. In this respect thioureas containing pyridyl group are better ligands as they may give rise to the six membered chelate formation. Similarly an allyl group may also give rise to a second co-ordination site.[29]

However, as no concrete information is available in literature regarding the nature, stability decomposition temperature etc. for these complex an experimental attempt to synthesize, characterize and study the possibilities of making thin films for solar cells was made. The results obtained have been presented in the following chapters.

:::::::::::

TABLE 3.1

Values of h and k parameters**

Atom	h	Bonding	k
$\dot{N}$	0.5	$C = N$	1.0
$\ddot{N}$	1.5	$C - N$	0.8
N^+	2.0	$C = N^+$	1.0
		$N - O$	0.7
N(nitro)	1.0	$C - N$	1.0
O(nitro)	1.5	$N - O$	1.0
		$N^+ - O^-$	0.5
$\ddot{O}$	2.0	$C - O^-$	0.8
$\ddot{O}$(hydroxyl)	1.3	$O - H$	0.4
$\dot{O}$	1.0	$C = O$	1.0
F	3.0	$C - F$	0.7
Cl	2.0	$C - Cl$	0.4
Br	1.5	$C - Br$	0.3
I	0.4	$C - I$	0.53
$\ddot{S}$	0.8	$C - \ddot{S} -$	0.6
S	0.8	$C = S$	1.2
Hyperconjugation	$-C'-C''-H_3^*(H_2^*)$		
C', C''	-0.1	$C'-C''$	0.8
H_2^*, H_3^*	-0.5	$C-H_3^*$	3.0
		$C-H_2^*$	3.0

**These parameters were taken as given by:

1. A. Streitwieser (Jr.), 'Molecular orbital theory for organic chemists', John Wiley and Sons Inc., New York-London, 1961.
2. K. Fukui, K. Morokuma and C. Nagata, Bull. Chem. Soc., Japan, 33, 1214(1960); 34, 1224 (1961).
3. Matsen, F.A., J. Am. Chem. Soc., 72, 5243 (1950).
4. Pullman, B., Pullman, A., 'Quantum Biochemistry', Interscience, N.Y., 1963.
5. Peters, D., J. Chem. Soc., p. 1993, 1957.

TABLE 3.2

Name	$R-\overset{H}{N}-\underset{S}{\overset{\|}{C}}-\overset{H}{N}-R'$		Charge density			$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^S	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)
	R	R'	N(R)	S	N(R')						
1	2	3	4	5	6	7	8	9	10	11	12
Thiourea	H	H	0.126	-0.445	0.126	1.1366	-0.9591	1.0991	25.92	-0.96	26.88
Ethyl thiourea	Ethyl	H	0.150	-0.446	0.126	1.0993	-0.9570	1.1084	51.13	-2.26	53.39
Allyl thiourea	Allyl	H	0.150	-0.446	0.126	0.9263	-0.9557	1.1084	56.89	9.35	45.54
Phenyl thiourea	Phenyl	H	0.195	-0.441	0.126	0.7770	-0.8752	1.1196	75.81	22.96	52.85
o-tolyl thiourea	o-tolyl	H	0.196	-0.442	0.126	0.7650	-0.8740	1.1209	88.37	22.36	66.01
m-tolyl thiourea	m-tolyl	H	0.196	-0.441	0.126	0.7731	-0.8745	1.1195	88.37	22.36	66.01
p-tolyl thiourea	p-tolyl	H	0.196	-0.442	0.126	0.7548	-0.8720	1.1208	88.37	22.36	66.01

(contd.)

$I_{P(\beta)}$ - is ionization potential in terms of β. $E_{A(\beta)}$ - Electron affinity in terms of β.

S_E^S - Electrophilic super-delocalizability on sulphur. S_E^N - Electrophilic super-delocalizability on nitrogen.

N(R') - Nitrogen to which R' is attached. $\Delta H'$ - Heat of formation of localized system.

ΔH - Heat of formation of delocalized system. E_R - Resonance energy. E_I - energy of isomerization.

Table 3.2 (contd.)

1	2	3	4	5
Benzyl thiourea	Benzyl	H	0.149	-0.446
Pyridyl thiourea	2-pyridyl	H	0.203	-0.438
Tetramethyl thiourea	Dimethyl	Dimethyl	0.173	-0.448

* Charge density on Pyridyl Nitrogen

6	7	8	9	10	11	12
0.126	0.9223	-0.9556	1.1084	88.37	22.36	66.01
0.127 -0.204*	0.8229	-0.8013	1.1088	70.71	5.36	65.35
0.173	1.0220	-0.9508	1.1367	76.52	-4.08	80.60

TABLE 3.3

Name	$R-\overset{H}{\overset{\mid}{N}}-\underset{S}{\underset{\parallel}{C}}-\overset{H}{\overset{\mid}{H}}-R'$		Charge density		$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^S	ΔH' (e.v)	ΔH (e.v)	E_R (e.v)
	R	R'	N	S						
Dimethyl thiourea	Methyl	Methyl	0.569	0.549	1.3250	1.0778	0.1944	41.22	2.51	38.71
Diethyl thiourea	Ethyl	Ethyl	0.567	0.542	1.3173	1.0760	0.1987	76.34	1.55	74.79
Diallyl thiourea	Allyl	Allyl	0.149	-0.447	0.9242	-0.9526	1.1176	87.86	19.73	68.13
Diphenyl thiourea	Phenyl	Phenyl	0.196	-0.438	0.7745	-0.8281	1.1402	125.70	46.87	78.83
Di-o-tolyl thiourea	o-tolyl	o-tolyl	0.196	-0.439	0.7613	-0.8267	1.1427	138.26	45.74	92.52
Di-m-tolyl thiourea	m-tolyl	m-tolyl	0.196	-0.438	0.7703	-0.8275	1.1401	138.26	45.74	92.52
Di-p-tolyl thiourea	p-tolyl	p-tolyl	0.196	-0.438	0.7503	-0.8249	1.1426	138.26	45.74	92.52
Di-benzyl thiourea	Benzyl	Benzyl	0.149	-0.447	0.9446	-0.9535	1.1176	138.26	46.19	92.07
Di-pyridyl thiourea	2-pyridyl	2-pyridyl	0.204	-0.432	0.8209	-0.7604	1.1191	105.50	31.73	73.77

TABLE 3.4

Name	$\mathrm{R{-}\overset{H}{N}{-}\underset{\overset{\|}{S}}{C}{-}\overset{H}{N}{-}R'}$		Charge density			$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^S S_E^N	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)
	R	R'	N(R)	S	N(R')						
Methyl pyridyl thiourea	Methyl	2-pyridyl	0.151	-0.439	-0.204	0.8229	-0.8009	1.1181 0.8713	83.36	14.56	68.80
Ethyl pyridyl thiourea	Ethyl	2-pyridyl	0.105	-0.439	-0.204	0.8229	-0.8009	1.1182 0.8713	95.92	12.44	83.48
Allyl pyridyl thiourea	Allyl	2-pyridyl	0.150	-0.439	-0.204	0.8229	-0.8009	1.1182 0.8713	101.68	24.75	76.93
Phenyl pyridyl thiourea	Phenyl	2-pyridyl	0.196	-0.435	-0.204	0.7769	-0.7827	1.1297 0.8715	120.68	39.32	81.30
o-tolyl pyridyl thiourea	o-tolyl	2-pyridyl	0.197	-0.435	-0.204	0.7648	-0.7824	1.1310 0.8715	133.24	43.18	90.06
Benzyl pyridyl thiourea	Benzyl	2-pyridyl	0.160	-0.439	-0.204	0.8229	-0.8009	1.1181 0.8713	133.24	39.0	94.24
Allyl 5-chloro pyridyl thiourea	Allyl	5-chloro 2-pyridyl	0.151	-0.439	-0.205	0.8356	-0.7880	1.1159 0.8690	100.66	14.67	85.99
Allyl 5-bromo pyridyl thiourea	-do-	5-bromo 2-pyridyl	0.150	-0.439	-0.205	0.8263	-0.7912	1.1165 0.8695	100.33	16.88	83.45

(contd.)

Table 3.4 (contd.)

Name	$\overset{H}{R-N}-\underset{\overset{\parallel}{S}}{C}-\overset{H}{N}-R'$		Charge density			$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^S S_E^N	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)
	R	R'	N(R)	S	N(R')						
Allyl 5-iodo pyridyl thiourea	Allyl	5-iodo 2-pyridyl	0.150	-0.441	-0.202	0.3118	-0.8131	1.1384 0.8744	99.64	21.32	78.32
Allyl 3-hydroxy pyridyl thiourea	Allyl	3-hydroxy 2-pyridyl	0.150	-0.439	-0.205	0.7889	-0.8004	1.1184 0.8709	109.86	34.30	75.48
Phenyl 5-chloro pyridyl thiourea	Phenyl	5-chloro 2-pyridyl	0.196	-0.434	-0.205	0.7769	-0.7709	1.1276 0.8692	119.60	28.23	85.28
Phenyl 5-bromo pyridyl thiourea	Phenyl	5-bromo 2-pyridyl	0.197	-0.435	-0.205	0.7769	-0.7738	1.1281 0.8697	119.33	30.76	88.57
Phenyl 5-iodo pyridyl thiourea	Phenyl	5-iodo 2-pyridyl	0.196	-0.437	-0.202	0.3117	-0.7949	1.1500 0.8746	118.64	34.88	83.76

(contd.)

Table 3.4 (contd.)

Name	$R-\overset{H}{N}-\underset{\|\|}{\overset{}{C}}-\overset{H}{N}-R'$ with $C{=}S$		Charge density			$I_{P(8)}$	$E_{A(8)}$	S_E^S S_E^N	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)
	R	R'	N(R)	S	N(R')						
Phenyl 5-fluoro pyridyl thiourea	Phenyl	5-fluoro 2-pyridyl	0.196	-0.434	-0.205	0.7769	-0.7682	1.1273 0.8688	121.80	25.33	96.47
Phenyl 5-nitro pyridyl thiourea	Phenyl	5-nitro 2-pyridyl	0.197	-0.429	-0.200	0.7769	-0.1346	1.1151 0.8505	132.13	29.37	102.76

TABLE 3.5

Name	$\text{R-}\overset{\text{H}}{\text{N}}\text{-}\underset{\text{SH}}{\text{C}}\text{=NR'}$		Charge Density			$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^N	ΔH' (e.v)	ΔH (e.v)	E_R (e.v)	E_I (e.v)
	R	R'	N(R)	S	N(R')							
Thiourea	H	H	0.127	0.142	-0.419	0.7028	-0.9073	1.5592	26.04	4.24	21.80	5.20
Ethyl thiourea	Ethyl	H	0.151	0.142	-0.580	0.7011	-0.9054	1.5717	51.25	3.38	47.87	5.64
Allyl thiourea	Allyl	H	0.151	0.142	-0.420	0.7009	-0.9051	1.5716	56.91	15.00	41.91	5.65
Phenyl thiourea	Phenyl	H	0.198	0.143	-0.414	0.6811	-0.8400	1.5840	75.93	28.57	47.36	5.61
o-tolyl thiourea	o-tolyl	H	0.198	0.142	-0.414	0.6780	-0.8390	1.5857	88.49	28.02	60.47	5.66
m-tolyl thiourea	m-tolyl	H	0.198	0.143	-0.414	0.6805	-0.8396	1.5839	88.49	28.02	60.47	5.66
P-tolyl thiourea	p-tolyl	H	0.198	0.142	-0.414	0.6757	-0.8378	1.5857	88.49	28.02	60.47	5.66
Benzyl thiourea	Benzyl	H	0.150	0.142	-0.420	0.7008	-0.9051	1.5716	88.49	28.02	60.47	5.66
Pyridyl thiourea	2-pyridyl	H	0.215	0.143	-0.411	0.6908	-0.7853	1.5682	70.83	10.98	59.85	5.62

TABLE 3.6

Name	$\mathrm{R{-}\overset{H}{N}{-}\underset{SH}{C}{=}N{-}R'}$		Charge density		$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^N	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)	E_I (e.v)
	R	R'	N(R')	S							
Dimethyl thiourea	Methyl	Methyl	-0.401	1.192	1.0476	0.6447	0.3612	76.46	5.63	68.73	3.13
Diethyl thiourea	Ethyl	Ethyl	1.088	0.399	1.0454	0.6440	0.3618	87.98	4.75	83.23	3.20
Di-allyl thiourea	Allyl	Allyl	0.612	0.141	0.6386	-0.8905	1.5841	125.82	24.96	100.86	5.23
Diphenyl thiourea	Phenyl	Phenyl	0.657	0.158	0.4679	-0.6710	1.5203	138.38	51.13	84.86	5.39
Di-o-tolyl thiourea	o-tolyl	o-tolyl	-0.342	0.157	0.4797	-0.6700	1.5263	138.38	51.13	84.86	5.39
Di-m-tolyl thiourea	m-tolyl	m-tolyl	-0.343	0.158	0.4872	-0.6708	1.5203	138.38	51.13	84.86	5.39
Di-p-tolyl thiourea	p-tolyl	p-tolyl	-0.342	0.157	0.4775	-0.6693	1.5264	138.38	51.13	84.86	5.39
Di-benzyl thiourea	Benzyl	Benzyl	-0.388	0.141	0.6404	-0.8912	0.5571	138.38	51.81	84.18	5.62
Di-pyridyl thiourea	2-pyridyl	2-pyridyl	-0.341	0.167	0.5364	-0.6116	1.4420	105.62	37.11	61.70	5.38

<u>TABLE 3.7</u>

Name	R-N(H)-C(SH)=NR'		Charge density			$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^N	S_E^N	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)	E_I (e.v)
	R	R'	N(R')	S	N								
Methyl, pyridyl thiourea	Methyl	2-pyridyl	-0.348	0.165	-0.227	0.5431	-0.6469	1.4484	0.9928	83.48	17.51	65.97	2.95
	2-pyridyl	Methyl	-0.378	0.152	-0.205	0.6336	-0.7808	1.5779	0.8785	83.48	20.11	63.37	5.55
Ethyl, pyridyl thiourea	Ethyl	2-pyridyl	-0.378	0.142	-0.205	0.6329	-0.7808	1.5780	0.8785	96.04	19.65	76.39	7.21
	2-pyridyl	Ethyl	-0.348	0.164	-0.227	0.5431	-0.6469	1.4484	0.9928	96.04	19.38	76.66	6.94
Allyl, pyridyl thiourea	Allyl	2-pyridyl	-0.348	0.165	-0.227	0.5429	-0.6469	1.4484	0.9928	101.80	30.01	71.79	5.26
	2-pyridyl	Allyl	-0.378	0.142	-0.205	0.6281	-0.7806	1.5781	0.8785	101.80	30.28	71.52	5.53
Phenyl, pyridyl thiourea	Phenyl	2-pyridyl	-0.340	0.158	-0.205	0.4932	-0.6554	1.5032	0.8808	120.80	44.61	76.19	5.29
	2-pyridyl	Phenyl	-0.344	0.166	-0.227	0.5308	-0.6238	1.4567	0.9949	120.80	44.59	76.21	5.27
o-tolyl, pyridyl thiourea	o-tolyl	2-pyridyl	-0.339	0.158	-0.205	0.4860	-0.6548	1.5071	0.8812	133.36	48.45	84.91	5.27
	2-pyridyl	o-tolyl	-0.339	0.166	-0.226	0.3312	-0.4391	1.5009	1.0059	133.36	50.66	82.70	7.48

(Contd.)

Table 3.7 (contd.)

Name	$R-\overset{H}{N}-\underset{SH}{C}=NR'$		Charge density			$I_{P}(\beta)$	$E_{A}(\beta)$	S_{E}^{N}	S_{E}^{N}	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)	E_I (e.v)
	R	R'	N(R')	S	N								
Benzyl, pyridyl thiourea	Benzyl	2-pyridyl	-0.348	0.166	-0.227	0.5430	-0.6469	1.4484	0.9928	133.36	44.22	89.14	5.22
	2-pyridyl	Benzyl	-0.365	0.739	-0.137	0.6297	-0.7807	1.5641	0.7952	133.36	44.47	88.89	5.47
Allyl, 5-chloro pyridyl thiourea	Allyl	5-chloro 2-pyridyl	-0.348	0.168	-0.229	0.5537	-0.6327	1.4349	0.9873	100.78	21.19	79.59	6.52
	5-chloro 2-pyridyl	Allyl	-0.378	0.142	-0.206	0.6298	-0.7683	1.5745	0.9873	100.78	21.49	79.29	6.82
Allyl, 5-bromo pyridyl thiourea	Allyl	5-bromo, 2-pyridyl	-0.348	0.167	-0.228	0.5496	-0.6360	1.4382	0.9885	100.45	22.16	78.29	5.28
	5-bromo, 2-pyridyl	Allyl	-0.378	0.142	-0.206	0.6291	-0.7713	1.5755	0.8766	100.45	22.40	78.05	5.52
Allyl, 5-iodo pyridyl thiourea	Allyl	5-iodo, 2-pyridyl	-0.345	0.167	-0.223	0.149	-0.6784	2.8647	1.2809	99.76	20.18	71.58	6.86
	5-iodo, 2-pyridyl	Allyl	-0.389	0.140	-0.276	0.0066	-0.3104	6.0556	2.2625	99.76	29.36	70.40	8.04

(contd.)

Table 3.7 (contd.)

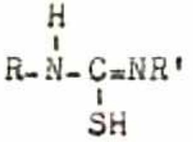
Name	 $R-\overset{H}{N}-\underset{SH}{C}=NR'$		Charge density			$I_{P(\beta)}$	$E_{A(\beta)}$	S_E^N	S_E^N	$\Delta H'$ (e.v)	ΔH (e.v)	E_R (e.v)	E_1 (e.v)
	R	R'	N(R')	S	N								
Allyl, 3-hydroxy pyridyl thiourea	Allyl	3-hydroxy 2-pyridyl	-0.344	0.166	-0.216	0.5373	-0.6331	1.4486	0.9748	109.98	32.36	77.62	-2.02
	3-hydroxy 2-pyridyl	Allyl	-0.373	0.142	-0.206	0.6257	-0.7806	1.5784	0.8782	109.98	32.86	77.12	-1.52
Phenyl 5-chloro pyridyl thiourea	Phenyl	5-chloro 2-pyridyl	-0.343	0.169	-0.228	0.5413	-0.6107	144.32	0.9894	119.78	33.49	86.29	5.26
	5-chloro 2-pyridyl	Phenyl	-0.339	0.160	-0.206	0.4944	-0.6500	1.4996	0.8784	119.78	33.53	86.25	5.30
Phenyl 5-bromo pyridyl thiourea	Phenyl	5-bromo 2-pyridyl	-0.343	0.168	-0.228	0.5374	-0.6138	1.4465	0.9907	119.45	35.66	83.79	4.90
	5-bromo 2-pyridyl	Phenyl	-0.149	0.126	-0.209	0.3737	-0.6924	1.0067	0.8984	119.45	37.05	82.40	6.29
Phenyl 5-fluoro pyridyl thiourea	Phenyl	5-fluoro 2-pyridyl	-0.343	0.168	-0.228	0.5425	-0.6625	1.5322	0.8843	120.92	30.59	86.32	5.26
	5-fluoro 2-pyridyl	Phenyl	-0.338	0.169	-0.206	0.3681	-0.6082	1.4414	0.9885	120.92	33.02	83.89	7.69
Phenyl 5-nitro pyridyl thiourea	Phenyl	5-nitro 2-pyridyl	-0.319	0.189	-0.218	0.5974	-0.1417	1.3295	0.9408	132.25	34.55	97.70	5.18
	5-nitro 2-pyridyl	Phenyl	-0.331	0.169	-0.200	0.5000	-0.1343	1.4720	0.8577	132.25	34.84	97.41	5.47

TABLE 3.8

Bond	Energy in (e.v.)	References
C − H	4.43	a
C − N	2.90	a
C − S	3.29	a
C − Cl	3.41	a
C − Br	3.08	b
C − I	2.39	b
C − O	7.70	a
C − C	3.70	a
S − H	3.34	c
N − H	3.54	c
C = S	5.96	
C = C	5.76	d
C = N	5.89	d
C = O	7.23	d
O − H	4.91	b

a) Ind. J. Chem., 15A, 238 (1977); Ferguson, L.M. The Modern Structural Theory of Organic Chemistry 1969, p. 48.

b) R.T. Sanderson, Chemical Bonds and Bond Energies, Academic Press, pp. 185, 1976.

c) Janz, George J., Thermodynamic Properties of Organic Compounds, Academic Press (Revised Edn.), 1967.

d) M.J.S. Dewar and Gleicher, G.J., J. Chem. Phys., 44, 759 (1966).

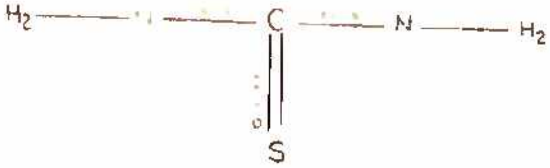


Fig 3.1 THIOUREA

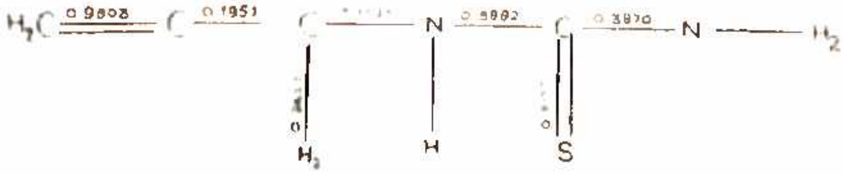


Fig 3.2 ALLYL THIOUREA

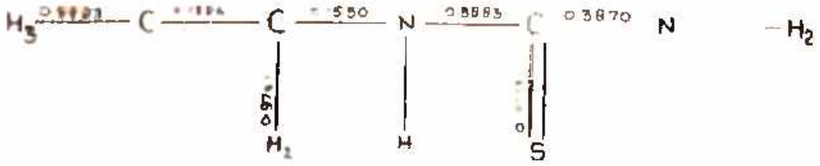


Fig 3.3 ETHYL THIOUREA

Fig 3.4 PHENYL THIOUREA

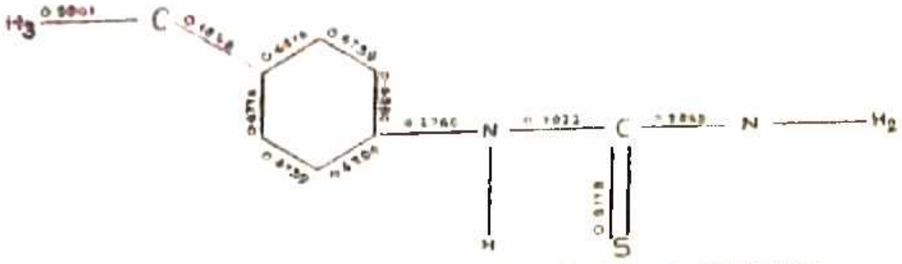


Fig 3.5 O-TOLYL THIOUREA

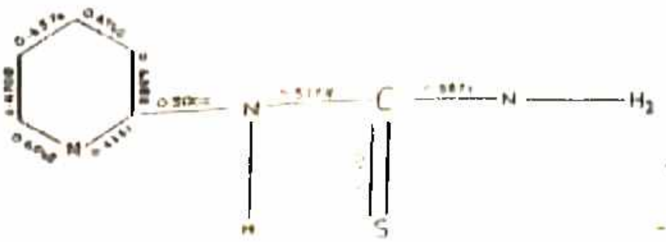


Fig 3.6 PYRIDYL THIOUREA

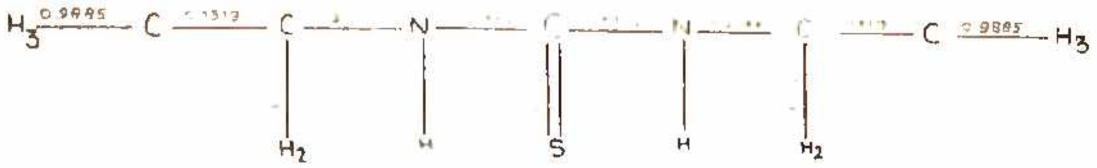


Fig 3 7 DIETHYL THIOUREA

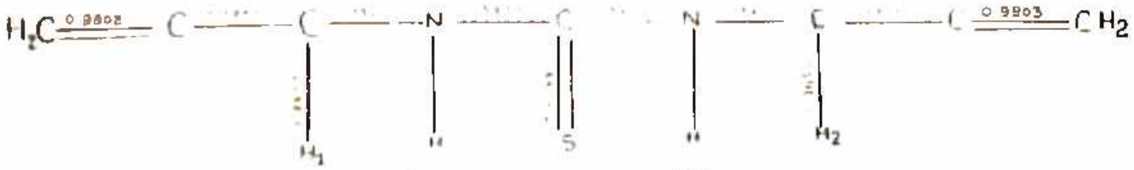


Fig 3 8 DIALLYL THIOUREA

Fig 3 9 ALLYL 5 IODO PYRIDYL THIOUREA

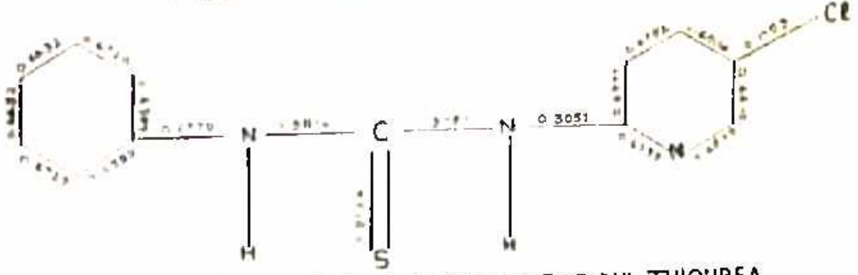


Fig 3 10 PHENYL 5-CHLORO PYRIDYL THIOUREA

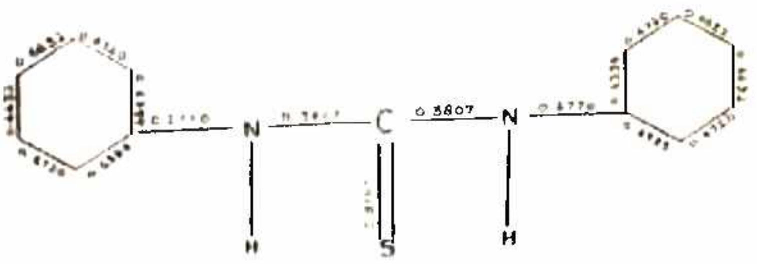


Fig 3 11 DIPHENYL THIOUREA

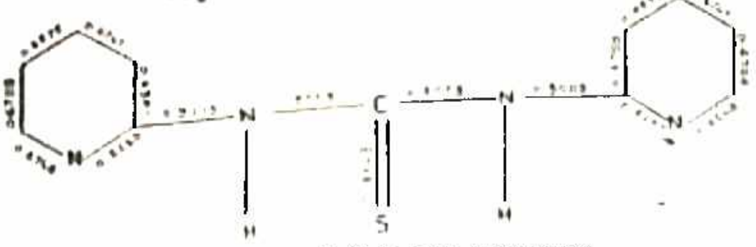


Fig 3 12 DIPYRIDYL THIOUREA

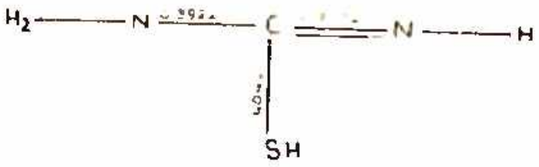


Fig 3 13 THIOUREA ENOL

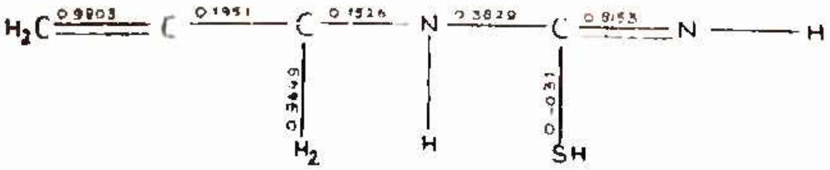
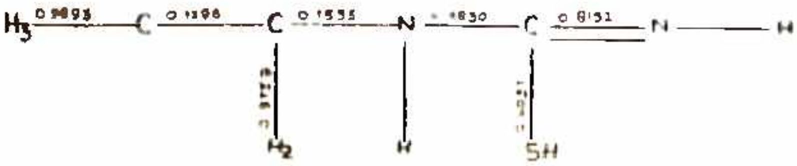


Fig 3-14 ALLYL THIOUREA ENOL



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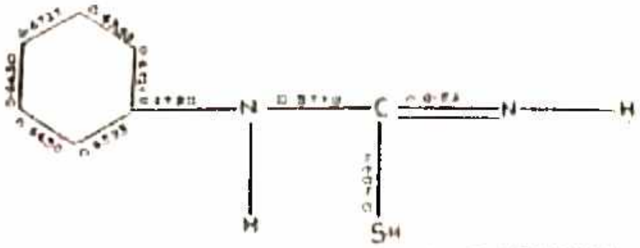


Fig 3 16 PHENYL THIOUREA ENOL

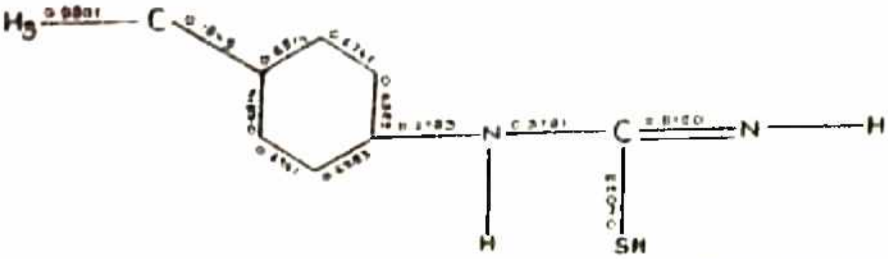


Fig 3 17 O-TOLYL THIOUREA ENOL

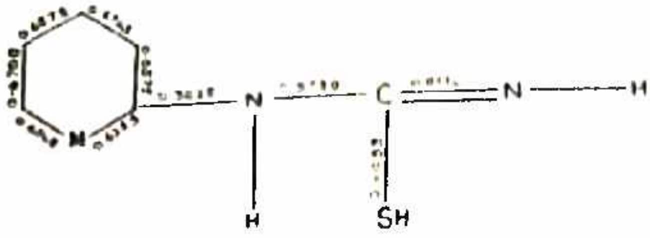


Fig 3 18 PYRIDYL THIOUREA ENOL

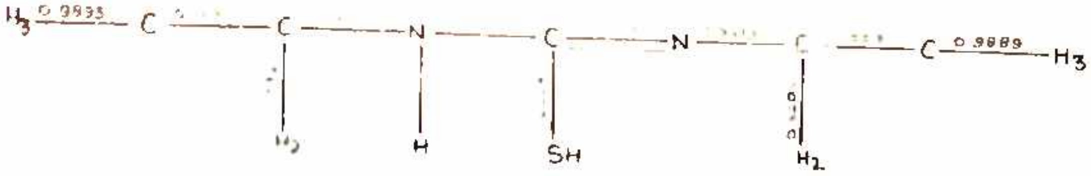


Fig 3.19 DIETHYL THIOUREA ENOL

Fig 3.20 DIALLYL THIOUREA ENOL

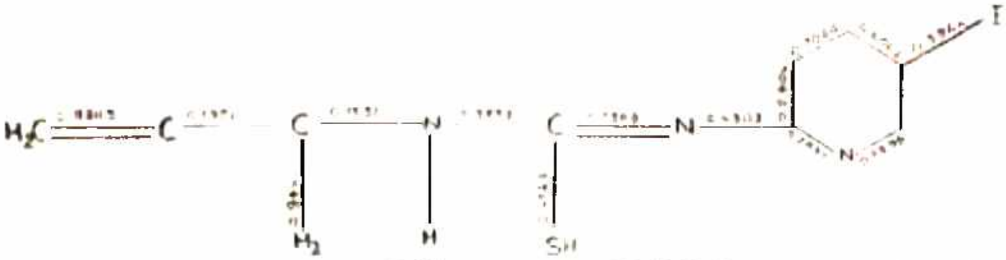


Fig 3.21 ALLYL 5-IODO PYRIDYL THIOUREA ENOL I

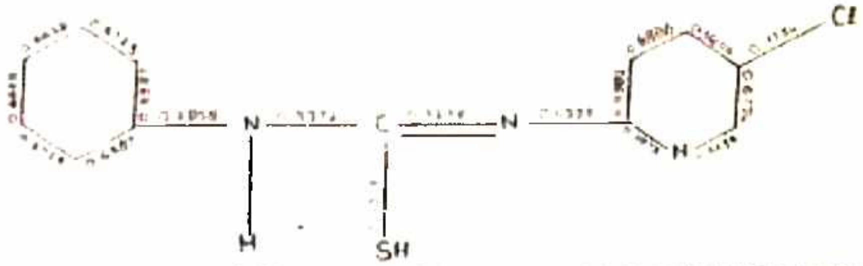


Fig 3.22 PHENYL 5-CHLORO PYRIDYL THIOUREA ENOL 1

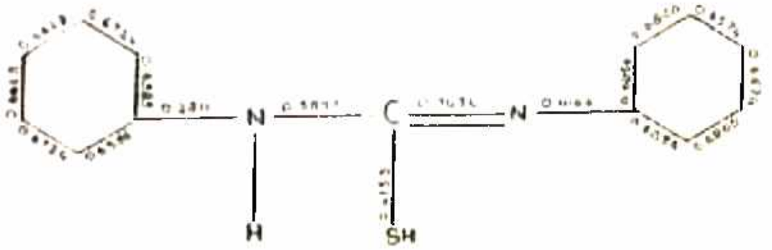


Fig 3.23 DIPHENYL THIOUREA ENOL

Fig. 3.24 DIPYRIDYL THIOUREA ENOL

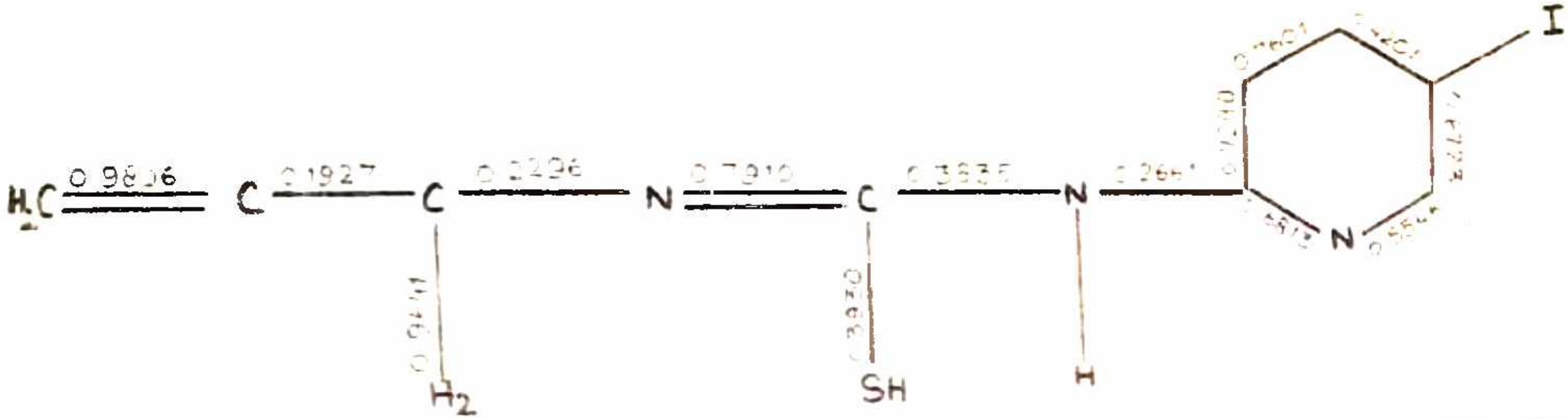


Fig 3.25 ALLYL 5-IODO PYRIDYL THIOUREA ENOL II

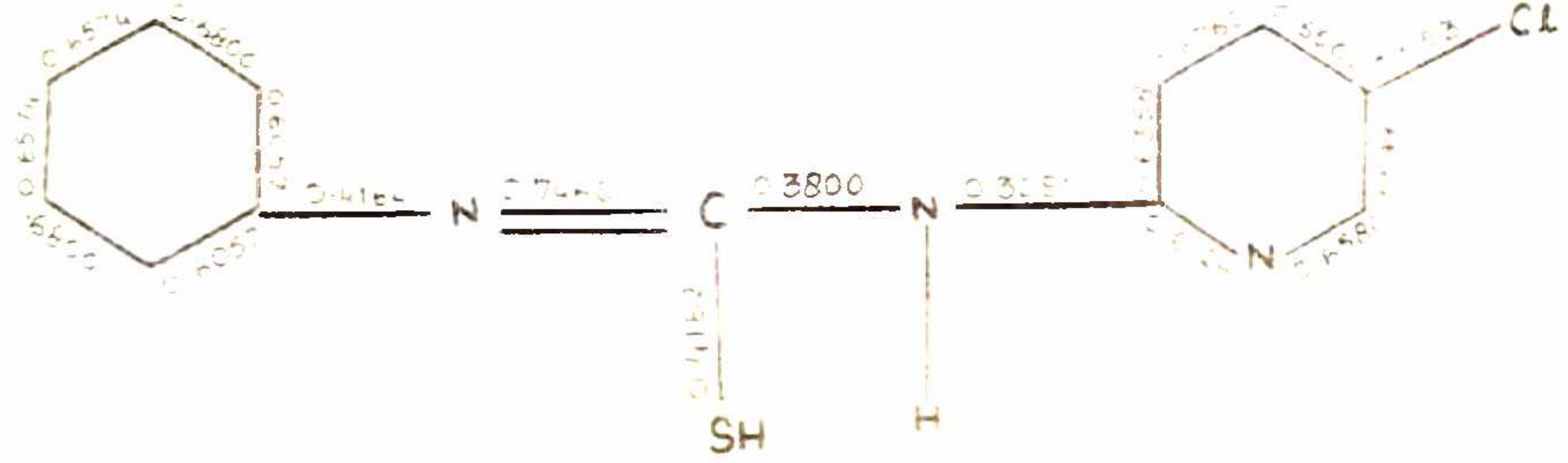


Fig 3.26 PHENYL 5-CHLORO PYRIDYL THIOUREA ENOL II

REFERENCES

1. For example see, B. Pullman and A. Pullman, 'Quantum Biochemistry', Interscience Publishers, N.Y. (1963); A. Streitwieser (Jr.), 'Molecular Orbital Theory for Organic Chemists', John Wiley and Sons, Inc., N.Y. (1961).

2. C.A. Coulson, Discuss. Farad. Soc., 2, 9 (1947).

3. K. Fukui, T. Yonezawa and H. Singu, J. Chem. Phys., 20, 722 (1952).

4. C.C.J. Roothan, Revs. Modern Phys., 23, 69 (1951).

5. A.I. Shporiko, L.N. Mazalov, A.P. Sadovski, S.V. Lavidnov and G.K. Parigina, Chemical Abstracts, 83: 210875d.

6. Kitaev et al., Chemical Abstracts, 66: 6045, 68: 43731, 70: 107572, 71: 105443, 82: 30741 and 83: 42712.

7. J. Weiss, J. Chem. Soc., 245 (1942) and 462 (1943).

8. Edwin S. Gould, 'Mechanism and Structure in Organic Chemistry', Holt, Reinhold and Winston Inc., N.Y. (1959).

9. M. Narvelli, L. Cavalca and A. Brainbanti, Gazetta, 86, 867, 1037 (1956).

10. O. Foss and S. Hauge, Acta Chem. Scand., 13, 1252 (1959).

11. M. Narvelli, Gazetta, 89, 619 (1959).

12. O. Foss and S. Hauge, Acta Chem. Scand., 15, 1616 (1961).

13. V.B. Evodokmov et al., Doklady Akad. Nauk. SSSR, 143, 1282 (1962).

14. A. Lopez-Castro and M.R. Truter, J. Chem. Soc., 1309 (1963).

15. L.F. Lindoy, S.G. Livingstone and T.M. Lockyer, Austral. J. Chem., 18, 1549 (1965).

16. M. Nardelli, A. Braibanti and G. Fava, Gazetta, 87, 1209 (1957).

17. P. Pantani and P.G. Desideri, Talanta, 5, 69 (1960).

18. R. Rivest, Can. J. Chem., 40, 2234 (1962).

19. R.T. Morrison and R.N. Boyd, 'Organic Chemistry', 2nd Edn., Prentice Hall of India Private Ltd., New Delhi (1973).

20. Kenichi Fukui et al., Bull. Chem. Soc., Japan, 34, 1076 (1961).

21. J.A. Allen, 'Energy Changes in Chemistry', Blackie and Son Ltd., 90-5 (1965).

22. M.J.S. Dewar and G.J. Gleicher, J. Chem. Phys., 44, 759 (1966).

23. Weast (Ed.), 'Handbook of Physics and Chemistry', 52nd edition, Chemical Rubber Co., F182 (1971-72).

24. E. Huckel, Z. Phys., 70, 204 (1931).

25. R.S. Mulliken and R.G. Parr, J. Chem. Phys., 19, 1271 (1951).

26. M.J.S. Dewar and C. De Llano, J. Am. Chem. Soc., 91, 189 (1969).

27. S.P. Gupta and P. Singh, Ind. J. Chem., 13, 668 (1975).

28. J.D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds', Academic Press, London (1970).

29. A. Dutta Ahmed and P.K. Mandal, J. Inorg. Nucl. Chem., 29, 2347 (1967).

* * *

CHAPTER IV

In this Chapter, after a brief review of metal complexes of substituted thiourea the results obtained on the preparation and characterization of substituted thiourea and their transition metal complexes are detailed out.

Complex compounds are defined as the combinations of two or more atoms, ions or molecules which arise as a result of the formation of a bond by the sharing of a pair of electrons originally associated with only one of the components (ligands), and which possesses some identifiable physical or chemical characteristics of a distinct species. Ligands, depending upon number of donor groups are classified as monodentate, bidentate, tridentate etc. A combination of metal with bidentate or polydentate ligands with the formation of one or more rings is termed as metal chelate. Chelation is favoured by the formation of a ring with low strain, usually a five or six membered ring.

The origin of the chemistry of co-ordination compounds is found in Werner's theory of complexes which is based on the concept of secondary valencies.[1] The electronic interpretation of the co-ordination theory was made by Sidgwick[2] and Lawary[3]. The valence bond theory of Pauling[4] introduced the concept of hybridized bonds to explain the stereochemistry and magnetic properties of complexes. This theory is limited to a qualitative treatment and cannot predict even the relative energies of different structures. It cannot interpret or predict the spectra. It also in many instances fails to explain their magnetic properties. The crystal field theory of Bethe[5] is an electrostatic theory, which

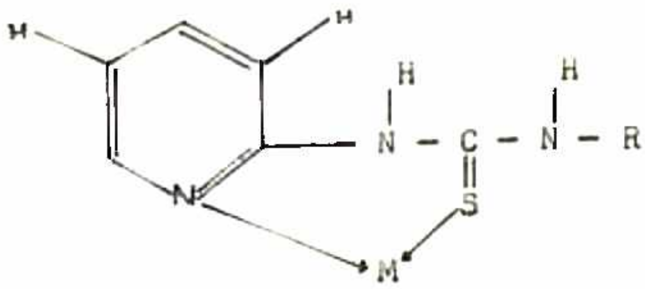
Van Vleck, Schlapp and Penny[7,8] have applied to metal complexes. This theory assumes the ligands as point charges or point dipoles, and considers the effects of the electrostatic field generated by such an array of ligands on the orbitals of the metal ion, especially the d-orbitals. Depending upon the pattern in which the metal ion is surrounded by the ligands, the degeneracy of the metal ions is lifted. The concept of splitting up of orbitals leads to various well-known consequences, admirably explained elsewhere[9-11]. Since the metal-ligand interactions are not point charges or point dipoles, therefore the theory can be regarded as only a first approximation. The molecular orbital theory due to Van Vleck[6] is based on symmetry considerations. The ligand field theory developed mostly due to Orgel[9], Griffith[12] and Ballhausen[10] is a more recent approach. The theory which is a combination of crystal field and molecular orbital theories may at present be regarded as one of the best available approach to the understanding of bonding in complex compounds.

METAL COMPLEXES OF THIOUREA AND SUBSTITUTED THIOUREAS

Thiourea is a tridentate ligand and the two nitrogens as well as sulfur atom can act as donors. In the case of Ti(IV) complex of thiourea, Rivest[13] has reported co-ordination through nitrogen on the basis of ir spectral studies, whereas similar studies by Yamagauchi et al.[14] on thiourea complexes of Hg(II), Cu(I), Ag(I) and Au(I) revealed that the ligands co-ordinate through sulfur. Co-ordination through sulfur has also been observed in thiourea complex of Sn(IV), Pb(II) and Tl(II) by Bystrov et al.[15], Nardelli et al.[16] and Foss et al.[17] Nardelli[18] determined the crystal structure of Ni $(tu)_4Cl_2$, $Cd(tu)_2Cl_2$ and $Pb(tu)_2Cl_2$ (tu = thiourea). $Cd(tu)_2Cl_2$ was found to be tetrahedral and $Pb(tu)_2Cl_2$ was found to be a polymeric species with chlorine bridges. Similar studies in the case of thiourea complexes of Te(IV) and Mo(III) were carried out by Foss and Hauge[19] and Evodokomov et al.[20] X-ray crystal structure of high and low spin Ni(II) complexes of thiourea was done by Lopez-Castro and Truter[21]. The magnetic measurements of thiol bridged complexes of Mo(III) were made by Lindoy et al.[22] Nardelli et al.[23] studied the mixed ligand complexes of Ni(II) with thiourea and thiocyanate. A polarographic study on Rh(IV) complex of thiourea was made by Pantani and Desideri[24].

Metal complexes of substituted thioureas have also received considerable attention of the chemists. Carlin and Holt[25] reported that Co(II) forms octahedral complexes with ethylene thiourea in which sulfur acts as donor atom. Ni(II) complex of ethylene and naphthyl thiourea were also investigated by these workers.[26] X-ray crystallographic studies of the ethylene thiourea complexes with Fe(II), Co(II) and Ni(II) were made by Nardelli and coworkers[27], whereas Cu(I), Ag(I) and Au(I) complexes of ethylene thiourea were investigated by Morgan and Burstall[28]. Harris and Livingstone[29] isolated the complex Ni(ethylene thiourea)$_4$I$_2$ which was shown to be rare example of tetragonal diamagnetic Ni(II). N, N' diethyl thiourea, N, N' diphenyl thiourea and N, N diphenyl thiourea were found to be bidentate chelates co-ordinating through N and sulfur.[13] Banerji and co-workers[30,31] studied the metal complexes of Cu(I) with N-acetyl thiourea, S-acetyl thiourea, N-phenyl thiourea and di-N-phenyl thiourea. Hirsch[32] synthesized N,N'-diaryl-N-hydroxy thioureas and their metal complexes with Co(II), Ni(II), and Cu(II). In all the cases, co-ordination was found to occur through sulfur and oxygen. Foss and Johannessen[33] have studied the complexes of Te(II) and Te(IV) with a large number of substituted thioureas. Malik and Farooq[34] have studied the substitution reaction of square planar tetrakis Pd(II) chloride with amino acids. The first order reaction was showed to follow a displacement mechanism. Kharitonov et al.[35] have studied the ir spectra of thiourea complexes of bivalent metals such as Mn, Ni, Cd, Fe, Cu, Pd and Pt. Marcotiango et al.[36] have studied the halogen bridged complexes of Pd(II) with thiourea and their splitting reactions. Pt(II) complexes were also studied by them.

More recently substituted thioureas having a heterocyclic group as a substituent have been studied by various workers[37-40]. In these compounds nitrogen in heterocyclic ring and sulfur are found to be donor atoms. A six membered ring (I) can be formed in the case of metal chelates of these compounds making the chelate quite stable.



(I)

Banerjea and Singh[38] carried out ir spectral studies on the complexes of Cu(I), Hg(II), Pd(II) and Rh(III) with N,N'-bis (α pyridyl)-2 thiourea. Dutta Ahmed and Mandal[37] have calculated the ligand field parameters, 10 Dq for various metal complexes of 1-allyl-3-(2-pyridyl)-2-thiourea (APTU) and have made suggestions regarding the ligand's place in spectrochemical series. Metal complexes of 1-phenyl-3-(2-pyridyl) were also synthesized by Krishnaswamy and Bhargava[39]. Metal complexes of 1 substituted-3-(2 pyridyl)-2 thioureas and N aryl, N'-2-(5 halo-pyridyl) thioureas were also studied by Prasad and Kashyap[41-42].

The donor site for chelate formation in such thioureas has become controversial. Though the sulfur, in all such cases is found to be one donor site, it is the second e.g. pyridyl nitrogen or thiourea nitrogen on the allylic site which is difficult to assign. The work of Datta Ahmed and Mandal[37] shows the probability of both pyridyl nitrogen and allylic group as second donor site whereas work of Banerjea and Singh[38] and Kashyap et al.[42] shows pyridyl nitrogen as the second donor site.

Contrary to this Prasad et al.[41] have predicted the nitrogen of thiourea as the second donor site. Sharma et al.[43] have used N-phenyl N'(α pyridyl) thiourea for the spectrophotometric determination of Bi(III), Co(II), Ni(II), Cu(I), Zn(II), Cd(II), Pd(II), Pt(II), and Rh(III) complexes for the same ligand were reported by Mondal.[44] Hg(II) complexes of N-methyl, N-phenyl, N,N' diethyl, N-allyl, diphenyl, o-tolyl and p-tolyl thioureas were reported by Rath Mohapatra[45]. Ag(I) complexes of substituted thioureas were studied by Dash et al.[46] whereas spectrophotometric determination of Os(VIII) by thioureas was carried out by Bhowal[47]. Petrukin[48] made X-ray electron study on extractable complexes of the Pt metals with diphenyl thiourea. Marcotrigiano et al.[49] have studied the preparation, ir, Raman and nmr of N,N' diethyl thiourea complexes with Zn(II), Cd(II) and Hg(II) halides. Mandal[50] has also reported Ni(II) complexes of phenyl allyl thiourea and naphthyl allyl thioureas.

EXPERIMENTAL

(A) Chemicals and Instruments

All the reagents used were of BDH, AnalaR, E. Merck GR, or Reidel extra pure quality. Solvents used were purified by distillation after drying[51]. Dioxane was purified by the method of Kraus and Vingee[52]. All the solutions were made up immediately before use. The ir spectra were recorded on a Perkin Elmer Infrared Grating

Spectrophotometer (Model 237B) using KBr pellet technique. Conductance measurements were made on conductivity meter, type LBR of Wiessenschaflich Technique, Warkstatten, Germany using dip type cell. Magnetic measurements were made on a Guoy's balance using $HgCo(CNS)_4$ as the calibrant.

Allyl isothiocyanate of B.D.H. and 5 nitro 2 amino pyridine and 3 hydroxy 2 amino pyridine of Aldrich Co. were used for the preparation of substituted thiourea. 3 hydroxy-2 amino pyridine was recrystalized in ethanol before use. The other two were used as such as they were found to be sufficiently pure.

In the present work the following thioureas were chosen for a systematic and detailed investigation:

1. N Allyl, N'-2-(5 chloro pyridyl) thiourea
2. N Allyl, N'-2-(5 Bromo pyridyl) thiourea
3. N Allyl, N'-2-(5 Iodo pyridyl) thiourea
4. N Allyl, N'-2-(5 nitro pyridyl) thiourea
5. N Allyl, N'-2-(3 hydroxy pyridyl) thiourea
6. N Phenyl, N'-2-(5 nitro pyridyl) thiourea
7. N Phenyl, N'-2-(3 hydroxy pyridyl) thiourea
8. N-o-tolyl, N'-2-(5 nitro pyridyl) thiourea
9. N-o-tolyl, N'-2-(3 hydroxy pyridyl) thiourea

Metal ions chosen for this purpose were Cu(II), Zn(II), Cd(II), Hg(II) and Ni(II) and Co(II). In all the cases corresponding metal chlorides were taken. The structure of the complexes have been proposed on the basis of their elemental analysis, ir spectroscopy, molar conductance and magnetic measurements.

(B) General Methods of Synthesis of the Substituted Thioureas

Synthesis of 5-halo, 2 amino pyridines: The 5-chloro, 5-bromo and 5-iodo, 2 amino pyridines were synthesized by the methods described below:

(i) 5-chloro-2 amino pyridine

The compound was prepared by the method described by Shozo Shibata et al.[53] The chlorination was done by passing chlorine through the solution of 2-amino pyridine in 20% sulfuric acid at about 25°C. Highly chlorinated derivatives were removed by shaking the precipitate with carbon tetrachloride. The residue was reprecipitated, after dissolving the former in dilute hydrochloric acid. The other coloring materials were removed by the usual method of treatment with charcoal.

(ii) 5-bromo, 2-amino pyridine

The bromination was done by adding bromine (40g) to an ice cold solution of 2-amino pyridine (18.8g) in ethanol (200 ml). The addition of bromine was done drop by drop and with constant stirring. The precipitate was washed with ethanol and dissolved in water. The precipitation was done by adding sodium hydroxide. The precipitate was extracted thrice with petroleum ether to remove the dibromo derivative. The product was finally crystallized from benzene.

The above method was described by Leese and Raydon.[54]

(iii) 5-iodo, 2 amino pyridine

The method followed was that of Caldwell.[55] 2 amino pyridine (100g) was dissolved in water (150 ml). To this iodine (100g) was added in small portions with constant stirring. To this 60% aqueous KOH (100 ml) was added and the product was acidified with concentrated hydrochloric acid. The above procedure was repeated twice, first with 80g of iodine and 60 ml of 60% KOH, and then with 40g of iodine and just enough KOH. The solution was saturated with NaCl and then subjected to steam distillation. The distillate was cooled and acidified with HCl. The solution was decolourized by charcoal after concentrating it at reduced pressure. The precipitation was done with KOH. The product was recrystallized from benzene.

(C) Synthesis of phenyl and o-tolyl isothionates

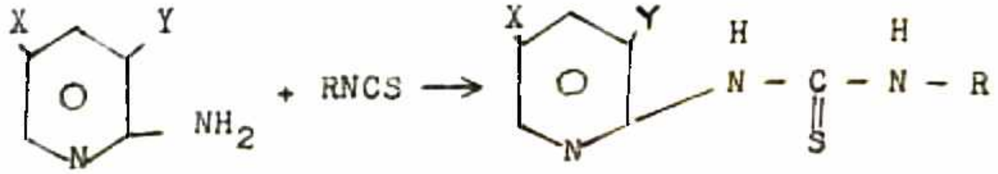
Phenyl isothiocyanate was synthesized by the method described by Vogel.[56] O-tolyl isothiocyanate was also synthesized by the similar method except that, in this case the amine used was o-toludine in place of aniline. The reactionstaking place in the preparation of the mustard oils are given below:

$$R - NH_2 + CS_2 \xrightarrow{NH_3} RNH - \overset{\overset{S}{\|}}{C} - SNH_4$$

$$\begin{aligned} R - NH\ CS\ SNH_4 + Pb(NO_3)_2 &\longrightarrow RNCS + NH_4NO_3 \\ \text{or } FeCl_3 \quad & + HNO_3 + PbS \text{ or } Fe_2S_3 \end{aligned}$$

(D) Synthesis of N-substituted, N'-2-(substituted-pyridyl) thioureas

Equimolar amounts of the 5-halo, 2 amino pyridine and the mustard oil were taken in ethanol. The mixture was refluxed for about four hours. The product i.e. the substituted thiourea started separating out even in the boiling ethanol because of its low solubility in ethanol. The precipitate was filtered and washed with ethanol. It was then subjected to charcoal treatment in benzene to remove the colouring material. The compounds were finally recrystallized from benzene and dried in air oven. The formation of the substituted thioureas can be represented by the following equation:



where $X = -Cl, -Br, -I, -NO_2$ and $Y = H$

or $X = H$ and $Y = OH$

and $R = -C_6H_5$ or $O-CH_3-C_6H_4$ or $CH_2 = CH-CH_2-$

The purity of compounds was checked with thin layer chromatography. They were found to have sharp and high melting points. The ir spectra and elemental analysis of these compounds revealed the above structure of substituted thioureas.

THIN LAYER CHROMATOGRAPHY OF SUBSTITUTED THIOUREAS

Several reagents have been used for chromatographical detection and separation of thioureas[57,58] and isothiocyanates.[59,60] Recently Devani et al.[61] have reported separation of isothiocyanates from thioureas in their natural form.

Ag(I) salts are found to give an immediate black precipitate (Ag_2S) when a dilute solution of Ag(I) salt is added to the dilute solution of N-N' aryl substituted thioureas or isothiocyanates. This property is, therefore, used in the detection of such compounds.

Experimental

Glass plates (20×20 cm) coated with an aqueous slurry of silica gel (E Merck - TLC Grade) and activated at 120°C for 2-3 hours were used in all experiments.

Standard Solutions for Samples: 0.1M solution in ethanol was used for substituted thioureas and aromatic amines and a 5% W/V solution, in chloroform was used for mustard oils. Spots 2-3 mm in diameter were employed. 1-10 µg was found sufficient amount for detection of all compounds.

Development and Detection

Dried spotted plates were run in various solvent systems. However, only two solvent systems viz. pure chloroform and chloroform : Et Ac (10:1 V/V) were found to give best results. Spotted plates were therefore run for 20-30 minutes in a saturated chamber of these two solvent systems. After evaporation of solvent the plates were sprayed with $AgNO_3$ solution (0.1M in H_2O).[62] In case of 5-nitro-2 amino pyridine a yellow spot and for all mustard oils and substituted thioureas a black spot developed immediately. However, for rest of the amino pyridines the black spots could not be observed. Therefore, plates sprayed with $AgNO_3$ were either heated at 120°C for an hour or left at room temperature in air for 24 hours so that the whole plate turns black leaving behind white spots for the detection of amines. The R_f values obtained are given in Table 4.1.

Next, volumes of 5 µml of mustard oils and amino pyridines and thioureas and aminopyridines were co-spotted in a few samples and the above procedure was repeated. The R_f values thus obtained are tabulated in Tables 4.2 and 4.3 respectively.

RESULTS AND DISCUSSION

From Tables 4.1, 4.2 and 4.3 it is clear that both substituted thioureas and mustard oils can be easily separated from amino pyridines. The distinction could also be made according to their behaviour with silver nitrate solution as is clearly evident from experimental procedure.

The strange behaviour of aromatic amines towards $AgNO_3$ could be explained by considering the formation of Ag complexes of these amines which like other silver compounds are white in colour except for 5 nitro 2-amino-pyridines.

Therefore, excess of mustard oil and other two constituents of the mixture viz. thioureas and amines could be easily separated chromatographically by using any of the two solvents and spraying reagents described in the preceding paragraphs.

Preparation of Complexes

.01 mole of $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $HgCl_2$, $ZnCl_2$ or $CdCl_2$ in n-butanol or ethanol was added slowly to a hot 0.025 mole solution of the ligand in the same solvent. The solution containing cobalt or nickel chloride was concentrated by boiling and the precipitate appeared after keeping the solution for some time. The precipitate in the case of copper, zinc, cadmium and mercury appeared in the mixture just after the addition. The precipitate so obtained was filtered and washed with n-butanol, ethanol and ether and dried in vacuum.

Analysis of the Complexes

The compositions of the complexes were determined by the estimation of the elements[56] metals, S and chlorine.

Sulfur was oxidized to sulfate by potassium permaganate and was estimated as barium sulfate.

For the estimation of chlorine the complexes were decomposed with nitric acid. The residue was extracted with dilute nitric acid. To the extract barium nitrate was added in order to remove sulfur. Chlorine was then estimated as silver chloride from the filterate.

In all the cases complexes were decomposed with nitric acid for the estimation of metals. Copper, Cadmium, Zinc and Cobalt were estimated by pyridine method as $[M(C_5H_5N)_4]\cdot(CNS)_2$, where M denotes the metal being estimated. Mercury was estimated as $Hg[Zn(CNS)_4]$ and the nickel as the dimethyl glyoxime complex.

Results and Discussion

The results of the elemental analysis and molar conductance and magnetic measurement data are recorded in Tables 4.4-4.9. The ir spectra of complexes form Figs. 4.4-4.19. The relevant ir peaks are recorded in Tables 4.10-4.16.

General Properties

The Zn(II), Cd(II) and Hg(II) complexes are white, the Co(II) complexes are blue and the Ni(II) complexes are green in color. The ligands on reaction with Cu(II) chloride reduce it to Cu(I) and then the complex of Cu(I) gets formed. The reduction of Cu(II) to Cu(I) by thiourea and substituted thioureas have also been observed by many workers. The melting points of complexes are very high (> 200°C) and decomposition takes place near melting points.

Co(II) complexes are soluble in acetone, benzene, pyridine, nitrobenzene, dimethylformamide and acetonitrite; Ni(II) complexes are soluble in pyridine chloroform and dimethylformamide; Cu(I) complexes in nitrobenzene, pyridine, chloroform, dimethylformamide and dioxane; Zn(II) complexes in acetone, pyridine ethanol and dimethylformamide and Hg(II) complexes in pyridine and dioxane.

The ir spectra of the metal complexes (Figs. 4.4-4.19) have been compared with those of the ligands (Figs. 4.1-4.3) to decide the donor sites of the ligands. The possible donor sites in the present case are:

(a) the nitrogens of thiourea unit
(b) nitrogen of pyridine ring
(c) sulfur of the thiocarbonyl group
and (d) the allylic group linkage

It is clear from Figs. 4.1-4.19 and Tables 4.10-4.16 that ir spectra of ligand and their metal complexes are quite complicated and therefore, the effect of substitutions could not be undertaken with a degree of certainty. Some of the major ir peaks could however be assigned and they are as follows:

The bands appearing around 3100-3400 cm^{-1} have been assigned to γ_s(NH) and γ_{as}(NH) , the later being the lower frequency band. In case of hydroxy pyridyl substituent a band at higher frequency ∽ 3500 cm^{-1} appears which may be assigned to γ(OH). A shift, both bathochromic as well as hypsochromic in nature, ranging from 10-20 cm^{-1} (as in case of Cu(I) and Hg(II)) and 100-150 cm^{-1} (as in case of Ni(II), Co(II), Cd(II) and Zn(II)) has been observed in case of metal complexes.

A very weak band appearing ∽ 3000 cm^{-1} has been assigned to 2 amino-pyridine vibrations.

Bands appearing ∽ 1640 cm^{-1} and ∽ 1600 cm^{-1} have been assigned to γ(C=C) of allylic group and γ(C=C+C=N) of aryl group respectively. In some of the cases these two mix up so well that it is difficult to isolate them individually. In case of metal complexes there is little change in these bands.

The band appearing ∽ 1100 cm^{-1} has been assigned to γ(N-C-N+C=S) mode in case of ligands. This band is either reduced in its intensity or shifted to lower frequencies in most of the spectra of metal complexes. The mode γ(C=S), occurring at ∽ 700-740 cm^{-1} is also found to be reduced in its intensity or shifted to lower frequencies in case of metal complexes.

Although, of lesser significance for deciding the donor sites of the ligands, the following bands, in addition to above have also been assigned: band ∽ 1550 cm^{-1} to

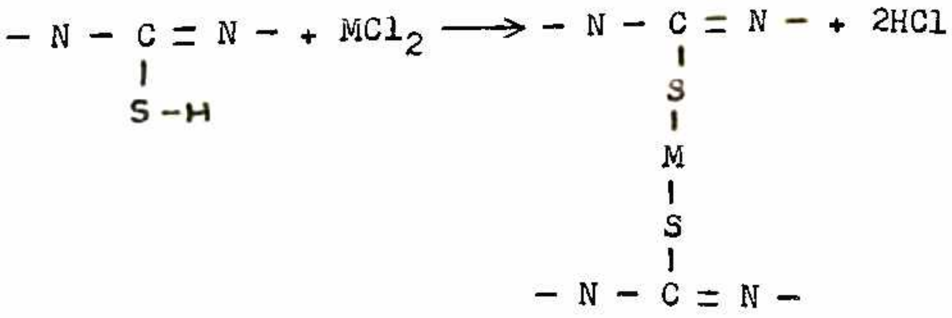
δ_{as}(NH), ~ 1350 cm^{-1} to δ_s(NH) and ~ 810 cm^{-1} to 2-amino pyridyl mode.

On complexation, the ligand stretching frequencies, in general, are shifted to lower region. This can be due to a decrease in the bond order and consequently the force constant. But in some cases, i.e. in nitrile complexes, the C≡N stretching frequencies[63] and in biuret-metal complexes the NH stretching frequencies[64] are found to be increased. If the shift of γ(NH) mode to higher regions is taken to be due to the sulfur-metal bond formation, in the present case, the complexes should not take any chlorine atoms from the metal chloride as shown below:

In case of 1:1 metal complex

$$-N-\underset{SH}{\underset{|}{C}}=N- + MCl \longrightarrow -N-\underset{S-M}{\underset{|}{C}}=N- + HCl \qquad (1)$$

and in the case of 1:2 complexe



$$-N-\underset{S-H}{\underset{|}{C}}=N- + MCl_2 \longrightarrow \begin{array}{c} -N-C=N- \\ | \\ S \\ | \\ M \\ | \\ S \\ | \\ -N-C=N- \end{array} + 2HCl \qquad (2)$$

It has been found by elemental analysis that both the chlorine atoms appear to be present in the metal complexes. Moreover, in the sodium derivatives of substituted thioureas[42] where a bond is proposed as being formed (as in equations 1 and 2), there is not much increase in the frequencies of γ(NH) mode. On the basis of these observations, it is reasonable to assume that the metal ions and the ligands do not combine as shown by eqns. 1 and 2.

The behaviour of the band assigned for γ(C=C+C=N) is of considerable importance in deciding whether or not the heterocyclic nitrogen is involved in the co-ordination with the metal ion. In the case of the complexes reported in the present work this band is shifted to higher or lower frequencies in an irregular fashion which precludes any unambiguous assertion of metal ligand bonding through the pyridyl nitrogen.

The shifting of the bands, assigned for γ(H-C-N+C=S) and γ(C=S) modes to lower frequencies or reduction in their intensities, in the case of metal complexes may be due to the sulfur metal co-ordination bond formation. These observations agree with the findings of Banerjea and Singh.[38] in the case of metal complexes of N,N'-bis-(α pyridyl) thiourea. Yamagauchi et al.[14] were of the opnion that the band assigned for γ(N-C-N+C=S) was more important in the diagnosis of metal-sulfur bond in thiourea and substituted thioureas but Swaminathan and Irving[65] gave more importance to the γ(C=S) mode. However, the later band appears in a region, where other bands also appear and thus its detection is usually associated with quite some uncertainty.

One more possible site, where the co-ordination between metal and ligand may occur, is one of the nitrogens in the thiourea unit. If this nitrogen along with sulfur act as donors, a four membered chelate ring would be formed, which would be considerably less stable than a six membered ring formed by the donation of electrons from the nitrogen in the pyridine ring and the thiocarbonyl sulfur. Thus, the nitrogen in the thiourea unit as a donor is not favoured by the lesser stability of the four membered ring than that of the six membered ring. Similarly, the possibility of allylic group co-ordination giving rise to a seven membered ring may be ruled out.

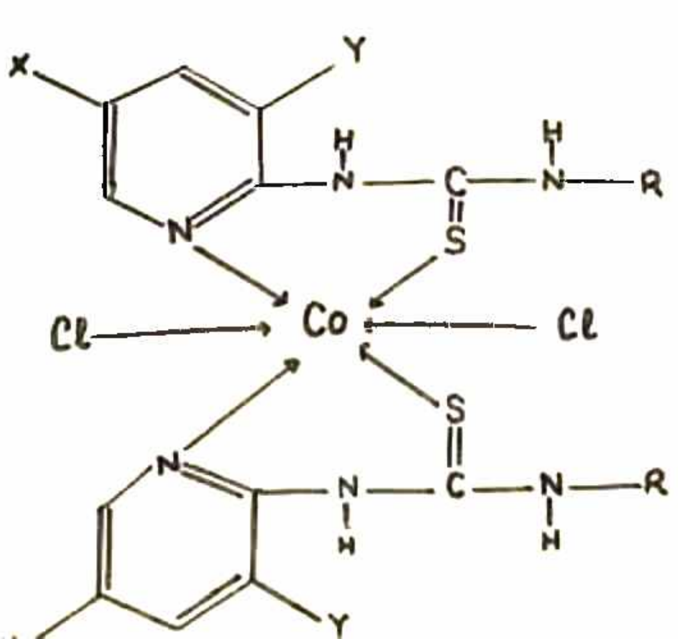
From these observations one may infer that there is a co-ordination bond formed between sulfur and the metal. The nitrogen of the pyridine ring may be considered as the most probable site to which the metal can attach itself giving rise to a metal chelate with a stable, six membered ring.

Cobalt (II) Chloride Complexes

The elemental analysis shows the composition of metal complexes to be $CoCl_2L_2$ where L is the ligand. The molar conductances of these complexes in dimethylformamide are found to be quite low (7-18 mhos). 1:1 electrolytes generally have conductances in the range 70-110 mhos.[66] It shows that the complexes are non-electrolytes and the chlorine is not present as an ion but is co-ordinated to the metal. The magnetic moments of the complexes lie in the range 4.6-4.8 BM at 25°C. The spin only value for Co(II) ion in an octahedral environment is 3.87 BM which is increased to around 5.00 BM when orbital contribution is also taken into account. The values obtained in the present cases are indicative of the octahedral geometry of the cobalt complexes.

Analysis of these compounds together with molar conductances and magnetic moments are reported in Table 4.4.

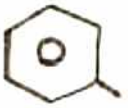
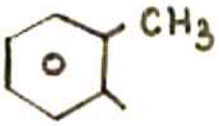
From the ir spectra (Figs. 4.18-4.19, Table 4.16) as described earlier, it may be concluded that Co(II) complexes have six membered rings with sulfur and pyridyl nitrogen acting as donors. Thus on the basis of these observations, the structure of the cobalt complexes may be tentatively represented as shown below:



where

$Y = H$, $X = Cl, Br, I, NO_2$

$Y = OH$, $X = H$

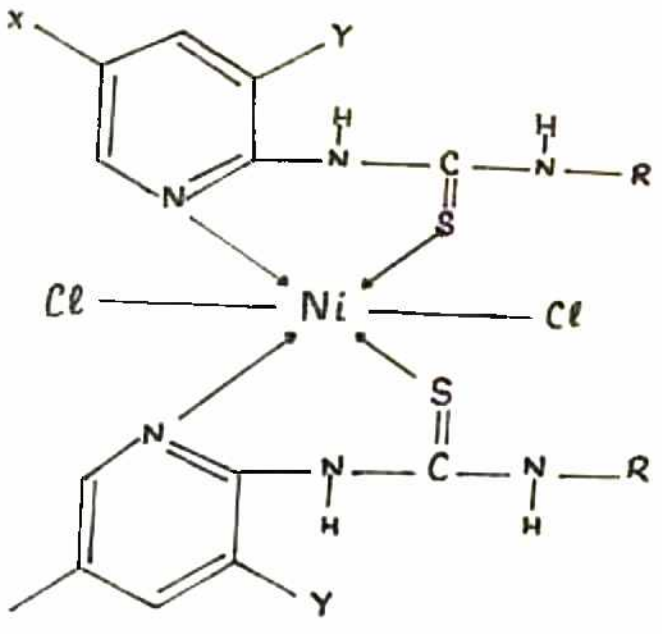
$R = CH_2 = CH\text{-}CH_2\text{-}$,  , 

Nickel (II) Chloride Complexes

The analytical data, molar conductance, elemental analysis and magnetic moments of these compounds are reported in Table 4.5. Analysis of these complexes reveal the general formula to be $NiCl_2L_2$, where L is the ligand.

Molar conductance of these complexes lie in the range 4-9 mhos indicative of the non-electrolytic nature, with chlorine atoms attached to the metal. The magnetic moments of these complexes (3.1-3.4 BM) are quite close to the value for the Ni(II) ion in the octehedral environment. The spin only values for the Ni(II) ion is 2.83 BM.

The band assigned to γ(N-C-N+C=S) mode is shifted to lower frequencies which is indicative of metal to ligand co-ordination. Slight shifts to lower or higher frequencies in the case of γ(C=C+C=N) band, are also observed. Thus the sulfur and pyridyl nitrogens may be considered as the donor sites in the probable chelate represented as:

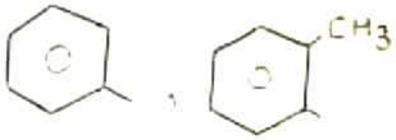


where

$X = Cl, Br, I, NO_2$ $\quad$ $Y = H$

$Y = OH,$ $\quad$ $X = H$

$R = CH_2 = CH\text{-}CH_2,$

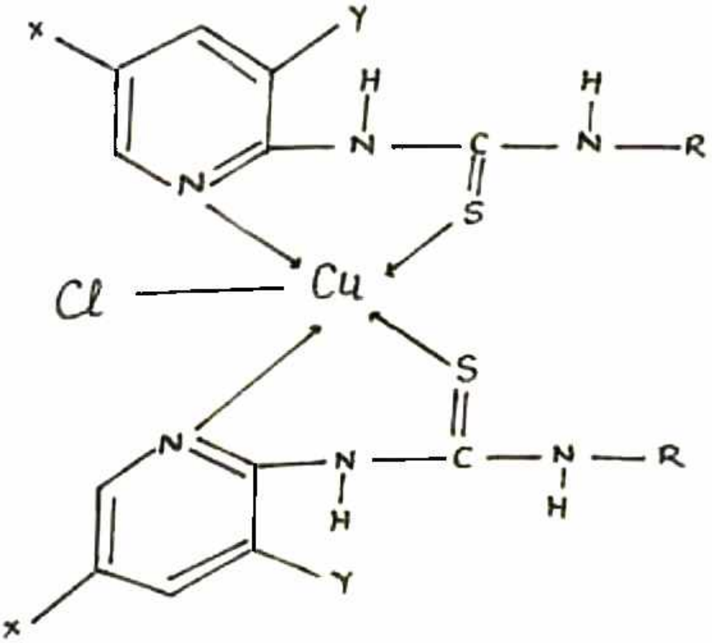


Copper (I) Chloride Complexes

Table 4.6 reports the results of the elemental analyses, molar conductance and magnetic measurements of these complexes. Elemental analysis suggest the general formula as $CuClL_2$, where L is the ligand. This suggests that Cu is present in +1 oxidation state. This is further supported by the diamagnetic nature of these complexes. The reduction of Cu(II) to Cu(I) has also been observed by other workers[37,38]. The low molar conductance range (0.9-4.1) shows that these complexes are non-electrolytes, having chlorine co-ordinated to the metal ion. In the ir spectra of the complexes (Fig. 4.12-4.14, Table 4.14) the γ(N-C-N+C=S) and γ(C=S) bands show a change in the position and/or reduction in their intensities suggesting thereby a metal to sulfur co-ordination.

Cu(I) is a soft acid according to the Pearson[68] and belongs to the (B) class of metals according to Ahrland et al.[67] Therefore, its co-ordination with a soft donor like thiocarbonyl sulfur with strong π-interaction is quite obvious.[42]

The structure of complexes may therefore be written as:



where

X = Cl, Br, I, NO_2 Y = H

Y = OH

X = H

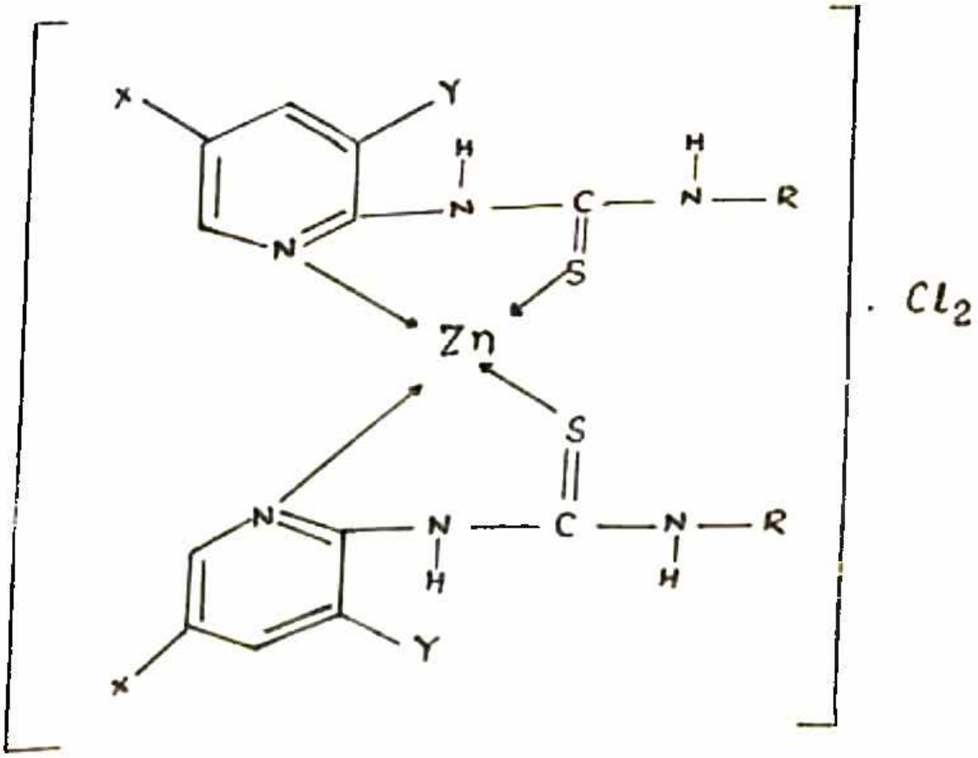
R = allyl, phenyl, o-tolyl

Complex probably is a dimer.

Zinc (II) Chloride Complexes

Elemental analysis of these complexes show that these can be represented by the general formula $ZnCl_2L_2$, where L is the ligand. The molar conductance of these complexes in DMF fall in the range of 70-80 mhos predicting these to be 1:1 electrolyte. It has been observed by Dutta Ahmed and Mandal[37] that in non-aqueous solvents the conductances of 1:2 electrolytes are less than the normal values. Similar observation are also made by Kashyap et al.[42] The magnetic measurement shows these complexes to be diamagnetic. The complexes as mentioned earlier are white in colour. In the ir spectrum, the band assigned for γ(C=C+C=N) mode is found to be shifted to lower frequencies. The γ(C=S) band is also reduced in its intensity.

The structure of the complexes, on the basis of above mentioned information could be written as:



where

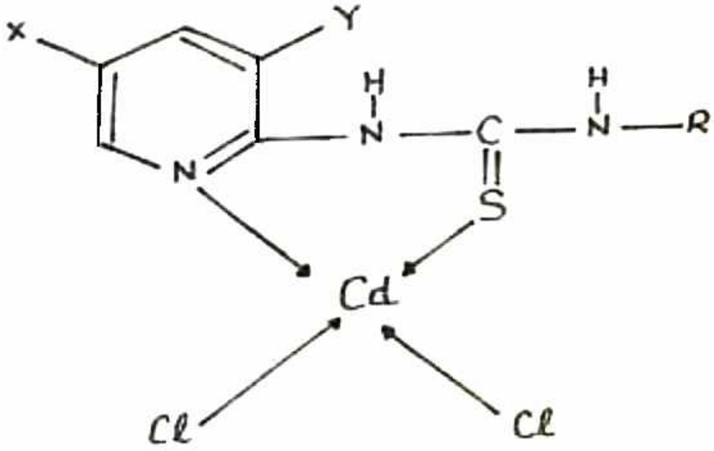
X = Cl, Br, I, NO_2; Y = H

X = H; Y = OH

R = Phenyl, o-tolyl, allyl

Cadmium (II) Chloride Complexes

Analyses of Cd(II) complexes and molar conductances are presented in Table 4.8. The general formula of the complexes could be written as $CdCl_2L$ where L is the ligand. Conductance measurements show that these complexes are non-electrolytes i.e. the chlorine atoms are co-ordinated to the metal ion. The ir spectra predicts the co-ordination through sulfur of thiocarbonyl and nitrogen of pyridyl. These informations suggest the following structure for Cd(II) complexes:



where X = Cl, Br, I, NO_2, Y = H

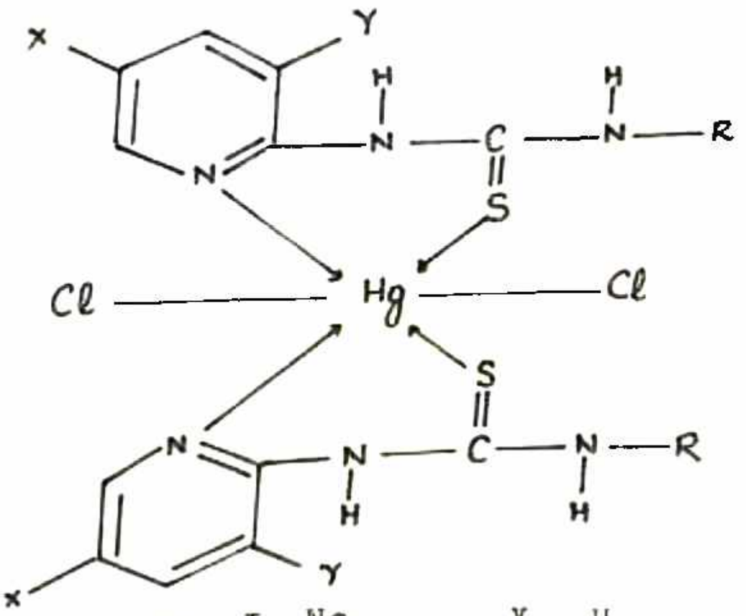
X = H, Y = OH

R = phenyl, o-tolyl, allyl.

Mercury (II) Chloride Complexes

The elemental analyses of these complexes show that their composition can be represented by general formula $HgCl_2L_2$, where L is the ligand (Table 4.9). Molar conductances of these complexes are quite low (0.2-2.8 mhos), which is indicative of the non-electrolytic nature of the complexes. Thus, the chlorine atoms are co-ordinated to the metal ion. Hg(II) is a (B) class metal and like Cu(I) should be co-ordinated to the soft donor i.e. thiocarbonyl sulfur with strong π-interaction. The γ(N-C-N+C=S) and γ(C=S) bands also show shift to lower frequency as in the case of zinc, in the ir spectra of these complexes (Table 4.12; Figs. 4.7-4.9).

On the basis of these observations the structure of the Hg(II) complexes may be represented as:



where X = Cl, Br, I, NO_2 Y = H

Y = OH

X = H

R = allyl, phenyl, o-tolyl.

TABLE 4.1

S. No.	Name of Compounds	R_f Values	
		$CHCl_3$ (Pure)	Et Ac.$CHCl_3$ (10:1 V/V)
	Thioureas		
1.	N-Benzyl, N'-2-Pyridyl-(BPT)	0.58	0.84
2.	N-p-tolyl, N'-2-Pyridyl-(PTPT)	0.62	0.86
3.	N-o-tolyl, N'-2-Pyridyl-(OTPT)	0.56	0.81
4.	N-Phenyl, N'-2-(5 chloro-Pyridyl) (PCT)	0.57	0.81
5.	N-Phenyl, N'-2-(5-Bromo-Pyridyl) (PBT)	0.62	0.81
6.	N-Phenyl, N'-2-(5-Iodo-Pyridyl) (PIT)	0.62	0.76
7.	N-o-tolyl N'-2-(5-Chloro-Pyridyl) (TCT)	0.57	0.81
8.	N-o-tolyl-N'-2-(5-Bromo-Pyridyl) (TBT)	0.60	0.81
9.	N-o-tolyl-N'-2-(5-Iodo-Pyridyl) (TIT)	0.58	0.81
10.	N-Phenyl, N'-2-(5 nitro-Pyridyl) (PNT)	0.74	0.92
	Mustard Oils		
11.	Phenyl	-	0.81
12.	Ethyl	-	0.83
13.	Allyl	-	0.84
14.	O-tolyl	-	0.81
15.	n-butyl	-	0.82
	2-Amino Pyridines		
16.	5-Chloro-	0.18	0.38
17.	5-Bromo-	0.20	0.34
18.	5-Iodo-	0.17	0.38
19.	5-nitro-	0.17	0.16
20.	5-H	0.18	0.38

TABLE 4.2

Solvent System: Et Ac:CF; 10:1 (V/V)

S. No.	Mixture	R_f	
		Mustard oil	Amino Pyridine
1.	Phenyl isothiocyanate + 2 Amino Pyridine	0.81	0.38
2.	Allyl isothiocyanate + 5 Chloro-2 Amino Pyridine	0.84	0.38
3.	Ethyl isothiocyanate + 5 Bromo-2 Amino Pyridine	0.83	0.34
4.	Phenyl isothiocyanate + 5 nitro-2 Amino Pyridine	0.81	0.16^y

y = Yellow

TABLE 4.3

Solvent System: Et Ac:CF; 10:1 (V/V)

S, No.	Thioureas + 2 Amino Pyridines	R_f	
		Thioureas	Amines
1.	PCT + 5 Chloro	0.80	0.38
2.	PBT + 5 Bromo	0.81	0.33
3.	PIT + 5-Iodo-	0.16	0.36
4.	TCT + 5-Chloro-	0.79	0.37
5.	TBT + 5 Bromo-	0.81	0.31
6.	TIT + 5 Iodo-	0.80	0.38
7.	TNT + 5 nitro-	0.92	0.16

TABLE 4.4

Substituted thiourea complexes of Co(II) Chloride

Substituted Thiourea	Complex	Molar Conductance (mhos)	Magnetic Moment (BM)	% Cobalt		% Sulphur		% Chlorine	
				Cal.	Found	Cal.	Found	Cal.	Found
ACPT	$CoCl_2[C_9N_3H_{10}SCl]_2$	10.8	4.76	10.09	9.98	10.94	10.79	-	-
ABPT	$CoCl_2[C_9N_3H_{10}SBr]_2$	12.6	4.80	8.75	8.54	9.50	9.32	-	-
AIPT	$CoCl_2[C_9N_3H_{10}SI]_2$	17.6	4.78	7.68	7.72	8.33	8.21	-	-
AHPT	$CoCl_2[C_9N_3H_{11}SO]_2$	15.2	4.81	10.76	10.62	11.68	11.53	12.96	13.01
ANPT	$CoCl_2[C_9N_4O_2H_{10}S]_2$	18.2	4.72	9.74	9.62	10.56	10.34	11.71	11.61
PHPT	$CoCl_2[C_{12}N_3H_{11}SO]_2$	10.4	4.60	9.52	9.34	10.32	10.26	11.45	11.23
PNPT	$CoCl_2[C_{12}N_4H_{10}SO]_2$	9.6	4.59	8.75	8.64	9.50	9.46	10.53	10.46
OHPT	$CoCl_2[C_{13}N_3H_{13}OS]_2$	6.5	4.69	9.11	8.91	9.88	9.73	10.96	10.87
ONPT	$CoCl_2[C_{13}N_4H_{12}O_2S]_2$	7.2	4.79	8.41	8.29	9.12	9.01	10.12	10.00

TABLE 4.5

Substituted thiourea complexes of Ni(II) chloride

Substituted Thiourea	Complex	Molar Conductance (mhos)	Magnetic Moment (BM)	% Nickel		% Sulphur		% Chlorine	
				Cal.	Found	Cal.	Found	Cal.	Found
ACPT	$NiCl_2[C_9N_3H_{10}SCl]_2$	4.5	3.21	10.09	9.78	10.94	10.99	-	-
ABPT	$NiCl_2[C_9N_3H_{10}SBr]_2$	5.1	3.27	8.75	8.54	9.50	9.62	-	-
AIPT	$NiCl_2[C_9N_3H_{10}SI]_2$	4.2	3.20	7.68	7.52	8.33	8.21	-	-
AHPT	$NiCl_2[C_9N_3H_{11}SO]_2$	6.3	3.40	10.76	10.59	11.68	11.51	12.96	12.87
ANPT	$NiCl_2[C_9N_4O_2H_{10}S]_2$	9.2	3.31	9.74	9.58	10.56	10.43	11.71	11.60
PHPT	$NiCl_2[C_{12}N_3H_{11}SO]_2$	3.6	3.12	9.52	9.46	10.32	10.21	11.45	11.34
PNPT	$NiCl_2[C_{12}N_4H_{10}SO_2]_2$	8.9	3.26	8.75	8.61	9.50	9.45	10.53	10.39
OHPT	$NiCl_2[C_{13}N_3H_{13}SO]_2$	5.7	3.21	9.11	8.97	9.88	9.69	10.96	10.79
ONPT	$NiCl_2[C_{13}N_4H_{12}SO_2]_2$	8.2	3.41	8.41	8.31	9.12	9.01	10.12	10.27

TABLE 4.6

Substituted thiourea complexes of Cu(I) chloride

Substituted Thiourea	Complex	Molar Conductance (mhos)	Magnetic Moment (BM)	% Copper		% Sulphur		% Chlorine	
				Cal.	Found	Cal.	Found	Cal.	Found
ACPT	$CuCl\,[C_9N_3H_{10}SCl]_2$	1.3	Diamagnetic	11.46	11.40	11.55	11.41	-	-
ABPT	$CuCl\,[C_9N_3H_{10}SBr]_2$	2.1	-do-	9.88	9.67	9.95	9.78	-	-
AIPT	$CuCl\,[C_9N_3H_{10}SI]_2$	0.9	-do-	8.62	8.51	8.72	8.81	-	-
AHPT	$CuCl\,[C_9N_3H_{11}OS]_2$	3.2	-do-	12.00	12.10	12.00	11.84	6.87	6.71
ANPT	$CuCl\,[C_9N_4O_2SH_{10}]_2$	2.5	-do-	11.04	10.92	11.10	10.96	6.17	6.01
PHPT	$CuCl\,[C_{12}N_3H_{10}SOH]_2$	4.1	-do-	10.78	10.67	10.82	10.90	6.03	6.12
PNPT	$CuCl\,[C_{12}N_3H_{10}SNO_2]_2$	2.1	-do-	9.97	9.82	10.05	9.96	5.57	5.46
OHPT	$CuCl\,[C_{13}N_3H_{12}SOH]_2$	3.5	-do-	10.29	10.11	10.37	10.21	6.02	6.12
ONPT	$CuCl\,[C_{13}N_3H_{12}SNO_2]_2$	1.2	-do-	9.46	9.36	9.56	9.48	5.40	5.29

TABLE 4.7

Substituted thiourea complexes of Zn(II) chloride

Substituted Thiourea	Complex	Molar Conductance (mhos)	Magnetic Moment (BM)	% Zinc		% Sulphur		% Chlorine	
				Cal.	Found	Cal.	Found	Cal.	Found
ACPT	$ZnCl_2[C_9N_3H_{10}SCl]_2$	72.05	Diamagnetic	10.10	9.95	14.21	14.21	-	-
ABPT	$ZnCl_2[C_9N_3H_{10}SBr]_2$	76.18	-do-	9.56	9.43	9.21	9.41	-	-
AIPT	$ZnCl_2[C_9N_3H_{10}SI]_2$	71.27	-do-	8.40	8.25	10.85	11.02	-	-
AHPT	$ZnCl_2[C_9N_3H_{11}SO]_2$	80.25	-do-	11.81	11.51	11.28	11.01	12.71	12.65
ANPT	$ZnCl_2[C_9N_4O_2H_{10}S]_2$	78.45	-do-	10.69	10.42	10.45	10.41	12.80	12.62
PHPT	$ZnCl_2[C_{12}N_3H_{11}SO]_2$	70.21	-do-	10.46	10.45	10.22	10.12	11.31	11.42
PNPT	$ZnCl_2[C_{12}N_4H_{10}SO_2]_2$	76.11	-do-	8.75	8.62	8.55	8.24	9.49	9.52
OHPT	$ZnCl_2[C_{13}N_3H_{13}OS]_2$	72.20	-do-	8.28	8.20	8.07	8.12	8.98	8.59
ONPT	$ZnCl_2[C_{13}N_4H_{12}SO_2]_2$	76.15	-do-	8.46	8.21	8.26	8.01	9.16	9.27

		Conductance (mhos)	Moment (BM)	% Cd		% Sulphur		% Chlorine	
				Cal.	Found	Cal.	Found	Cal.	Found
ACPT	$CdCl_2[C_9N_3H_{10}SCl]$	18.13	Diamagnetic	32.79	32.51	9.43	9.65	-	-
ABPT	$CdCl_2[C_9N_3H_{10}SBr]$	15.02	-do-	29.17	29.00	8.33	8.42	-	-
AIPT	$CdCl_2[C_9N_3H_{10}SI]$	20.52	-do-	25.40	25.21	7.26	7.42	-	-
AHPT	$CdCl_2[C_9N_3H_{11}SO]$	16.22	-do-	25.48	26.02	8.16	9.21	18.09	19.10
ANPT	$CdCl_2[C_9N_4O_2H_{10}S]$	10.15	-do-	26.67	26.43	7.59	7.32	16.85	16.39
PHPT	$CdCl_2[C_{12}N_3H_{11}SO]$	19.21	-do-	26.29	26.36	7.47	7.31	16.58	16.33
PNPT	$CdCl_2[C_{12}N_4H_{10}SO_2]$	15.12	-do-	24.57	24.27	6.99	7.05	15.52	15.31
OHPT	$CdCl_2[C_{13}N_3H_{13}OS]$	18.19	-do-	24.40	24.13	9.34	9.16	16.05	15.98
ONPT	$CdCl_2[C_{13}N_4H_{12}O_2S]$	20.02	-do-	23.94	23.81	6.82	6.89	15.12	14.98

TABLE 4.9

Substituted thiourea complexes of Hg(II) chloride

Substituted Thiourea	Complex	Molar Conductance (mhos)	Magnetic Moment (BM)	% Hg		% Sulphur		% Chlorine	
				Cal.	Found	Cal.	Found	Cal.	Found
ACPT	$HgCl_2[C_9N_3H_{10}SCl]_2$	0.19	Diamagnetic	27.61	27.52	8.80	8.26	-	-
ABPT	$HgCl_2[C_9N_3H_{10}SBr]_2$	0.18	-do-	24.64	24.62	7.85	7.92	-	-
AIPT	$HgCl_2[C_9N_3H_{10}SI]_2$	0.20	-do-	22.15	22.05	7.04	7.00	-	-
AHPT	$HgCl_2[C_9N_3H_{11}SO]_2$	1.40	-do-	36.62	36.46	9.28	9.10	10.30	10.21
ANPT	$HgCl_2[C_9N_4O_2H_{10}S]_2$	2.82	-do-	26.83	23.59	8.56	8.31	9.50	9.41
PHPT	$HgCl_2[C_{12}N_3H_{11}SO]_2$	1.25	-do-	26.34	26.12	8.41	8.11	9.32	9.21
PNPT	$HgCl_2[C_{12}N_4H_{10}SO_2]_2$	0.54	-do-	24.60	24.56	7.85	7.62	8.71	8.61
OHPT	$HgCl_2[C_{13}N_3H_{13}OS]_2$	0.98	-do-	31.99	31.71	8.11	8.24	8.99	8.70
ONPT	$HgCl_2[C_{13}N_4H_{12}O_2S]_2$	1.21	-do-	23.78	23.82	7.59	7.44	8.42	8.02

TABLE 4.10

IR Spectral Peaks of Ligands

ACPT	ABPT	AIPT	PHPT	OHPT	AHPT	PNPT	ONPT	ANPT
3440 3200	3240 3140 3050	3200 3130 3000	3525 3550 3000	3500 3250 3100 2025	3410 3310 3050	3500 3450	3200 3025	3500 3460 3210 3050
1640	1640	1635	1640	1620	1650	1650 1625	1630	1645 1630
1600	1600	1600	1610 1590	1600	1610 1580	1580	1590	1590
1560	1550	1550	1560	1560		1560	1560	1570
1530	1525	1525	1525	1525				
1475	1470	1460	1475	1490	1475	1460	1475 1460	1480 1470
1400			1450	1460	1425	1410	1410	1410
1350	1340	1350	1370	1350		1370		
1300	1300	1300	1330 1300		1300	1325	1325	1325
1260	1265	1260	1275	1280	1275	1275	1275	1275
1225	1220	1225		1250	1200			
1190	1180	1190	1180	1175	1160			1155
1125	1125	1120	1125	1150	1125	1110	1110	1115
1100	1090	1075 1000	1075	1100	1025			
950	925	960						
900	910 900	925	900					
810	825 810	850 810	875 825	850 825	875 810 825	825		
740	740	745	730	780 725	775 740	750 700	775 730	760 730

TABLE 4.11

IR Spectral Peaks of Cadmium Complexes

ACPT	ABPT	AIPT	PHPT	OHPT	AHPT	PNPT	ONPT	ANPT
3500 3365 3200 3130	3400 3260	3420 3325	3450 3350 3240 3100	3350	3400 3300	3350 3050	3500 3425 3350	3450 3350 3230
			1650	1630	1645	1640	1630	1640
1600	1600	1610	1600	1590	1610	1615	1610	1610
1575 1525	1550 1525	1575 1530 1500	1560 1515	1550	1535	1575	1580 1560	1575
1490 1470	1475 1400	1450	1480 1460 1410	1400	1410	1500 1425	1480 1460 1420	1500 1425
1395 1350 1300	1390 1350 1300	1325	1375 1330			1340 1325	1330	1340
1270	1265	1275 1250	1280 1250	1275	1275	1280	1280	1290
1180 1130 1105	1175 1125 1100	1200 1150 1100	1175 1150	1175 1150	1190 1150	1150 1120	1150 1120	1155 1120
		1075	1080			1000		1000
900		925	915			925		925
800	825	875 825	880		880	820		810
	775 725	775	750 725	725 750	770 710			740

TABLE 4.12

IR Spectral Peaks of Mercury Complexes

ACPT	ABPT	AIPT	PHPT	OHPT	AHPT	PNPT	ONPT	ANPT
3600 3450 3350 3250	3350 3325	3400 3300	3350	3450	3600 3450 3350	3500 3460 3200 3025	3530 3500 3460 3200 3025	3500 3450 3200 3010
1620	1625	1635	1665	1650	1640	1640	1630	1625
1600	1590	1600	1600	1610	1625	1630	1600	
1575 1550	1550	1545	1575	1575	1590 1570	1585 1570	1575	1580 1560
1500	1470	1520 1475		1500	1490 1470	1490 1470	1480 1475	1480 1470
1420	1400	1415	1400	1450	1405	1410	1400	
1350	1350	1350	1325	1330	1325	1325	1325	1325
1300	1300	1300			1290	1290	1310 1290	1310 1290
1275 1250	1270 1240	1275 1250	1250 1200	1250	1275	1275	1275	1275
1175 1125	1180	1180	1150		1150 1115	1150 1120	1150 1115	1150 1120
1090 1060	1090 1000	1090 1010						
		900			925		925	975 940
825	825		825		825	810	825	825
750					750	730	750	750

TABLE 4.13

IR Spectra Peaks of Zinc Complexes

ACPT	AHPT	OHPT	AHPT	ONPT	ANPT
3400 3300	3400 3300	3500 3450 3300	3450 3350	3500 3400-3350	3410 3320
				3050	3210 3050
1600	1650 1600	1650	1630	1600 1650	1650 1625
1550 1525	1575 1550 1500	1575 1525	1575 1550	1590 1560 1525-1425	1575
1460	1465 1450 1430 1410	1440-1430	1440	1425	1445 1425
1330 1300	1360 1340 1325 1310	1300	1300	1360-1300	1350 1310
1260	1250 1210	1225	1225	1275	1275
1140	1160 1100		1160 1125	1170-1010	1100-1050
1050	1025		1075		
950	970 905				925
859	885 875			860 825	850 825
750	775 760 740 710 675		750-725	750 750	

TABLE 4.14

IR Spectral Peaks of Copper Complexes

ACPT	ABPT	AIPT	PNPT	OHPT	PHPT	ONPT	ANPT
3450 3210	3100 3075 3000	3200 3000	3160 3100 3010	3500-3350 3000-2900	3150 2950	3475 3350 3200 3100	3150-2900
1600	1590	1590	1600	1650 1625 1600	1585	1650 1610	1640 1610
1510	1550-1525	1525-1500	1540	1575 1550	1560	1560	1560
1460	1460	1450	1480 1460 1440 1425	1425	1475 1400-1425	1490 1425	1490 1425
1375 1360	1340	1330	1375 1340	1350		1350 1325	1325
1300	1300	1280	1310 1280	1310 1275	1300		
1250	1235	1250 1225	1215	1220			
1180 1170	1180 1175	1180 1160	1180	1175	1175-1110	1150	1150
1095	1090	1050	1100	1075		1100	
		975	1025			910	925
825			850 810			810	810
		775	760 725 675	775 750		750	

TABLE 4.15

IR Spectral Peaks of Nickel Complexes

ACPT	ABPT	AIPT	PNPT	ONPT	ANPT	OHPT	AHPT
3250 3200 3050	3475 3450 3350	3450 3300 3150	3450 3300 3150	3480 3440 3350	3450 3350	3475 3150	3450 3200
1635 1610	1650	1590	1630	1650 1610	1650 1610	1650 1625	1660 1625
1580 1535	1580 1540	1570 1525	1560 1500	1560	1575	1590 1560 1525	1550 1525
1480 1450	1475	1460	1410	1500 1425	1500 1425	1475 1460	1425
1390 1330	1350 1300	1375 1325	1330	1340	1350	1350	1300
1290 1270	1260	1270	1275	1280	1285	1280	
1235 1210	1225 1190	1225 1175	1150	1150	1160	1210 1160	1210 1160
1130 1100	1130 1100	1125	1110	1100	1110	1100	1100
	960	1000		980			1050
	900			925			900
830	800	820	810	830 800	810		
750			740	740	750	750 710	725

TABLE 4.16

IR Spectral Peaks of Cobalt Complexes

ACPT	ABPT	AIPT	PHPT	AHPT	PNPT	ANPT
3300 3100	3300 3100	3400 3200 3000	3400 3200	3300 3100	3500 3050	3400 3200 3000
1600 1580	1640 1610	1620 1590	1625	1600	1600 1610	1600 1610
1550	1525	1540	1565	1540	1540	1540
1470 1450 1410	1480 1425 1400	1490 1440 1420	1490 1440	1475 1450	1490 1450 1425	1470 1440 1410
1350 1310	1375 1310	1360 1340 1310	1365 1350	1375 1325	1375 1350	1360 1310
1255 1220	1250 1235 1220	1240	1270 1250	1260 1240 1220	1260 1250	1260 1240
1180	1155 1140	1100	1150 1110	1150 1125	1150 1100	1160 1150 1100
1050	1040	1040	1050 1010	1075 1050	1050	1040
990 950	990 950	990	960	990 950	1000	1000 950
875 855	860	840 820	880 865	880 860	875 860 815	875 860 820
770 735 700	770 730 700	770 740	780 740 700	770 730 700	785 735	775 730

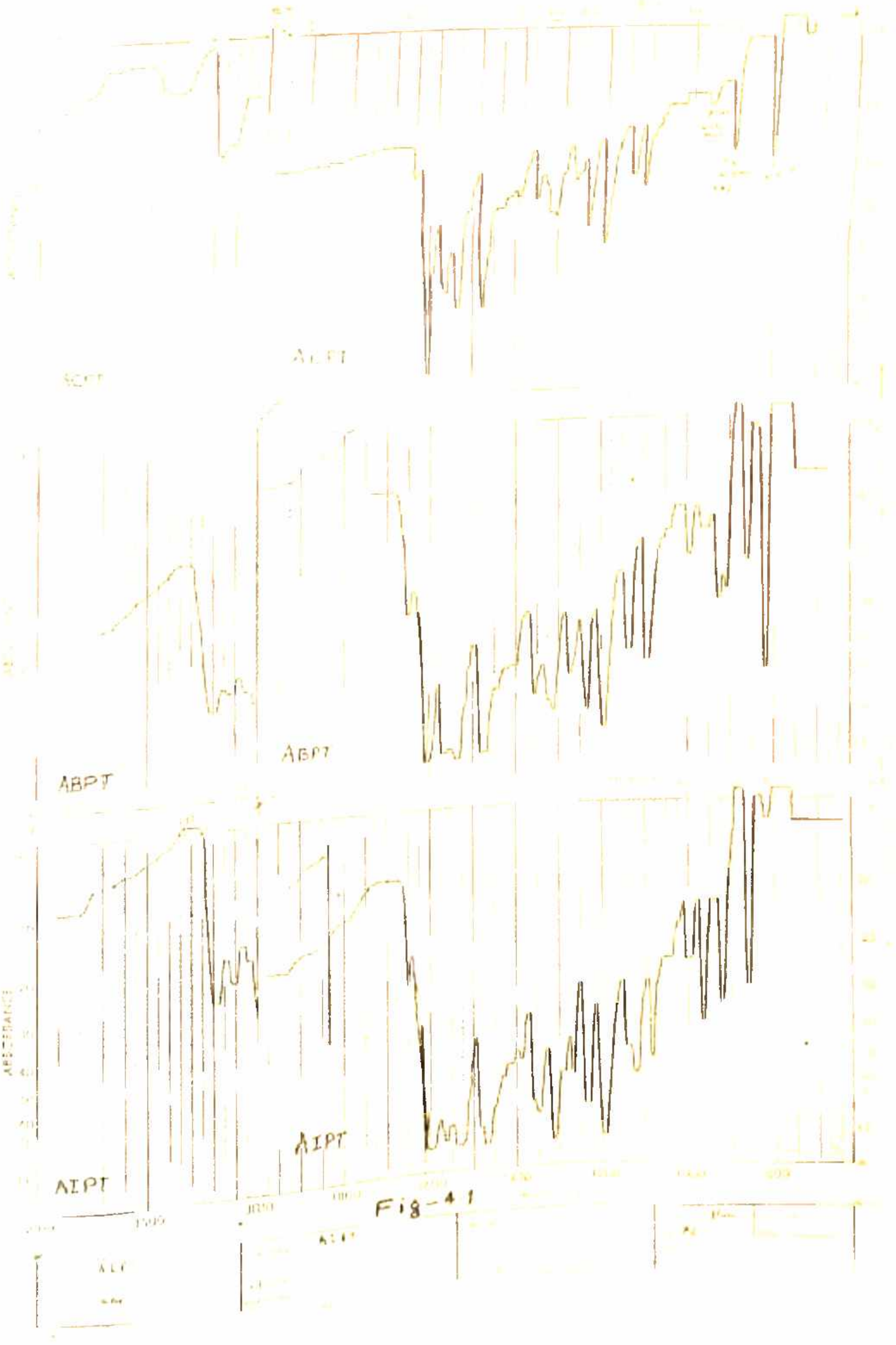


Fig-4.1

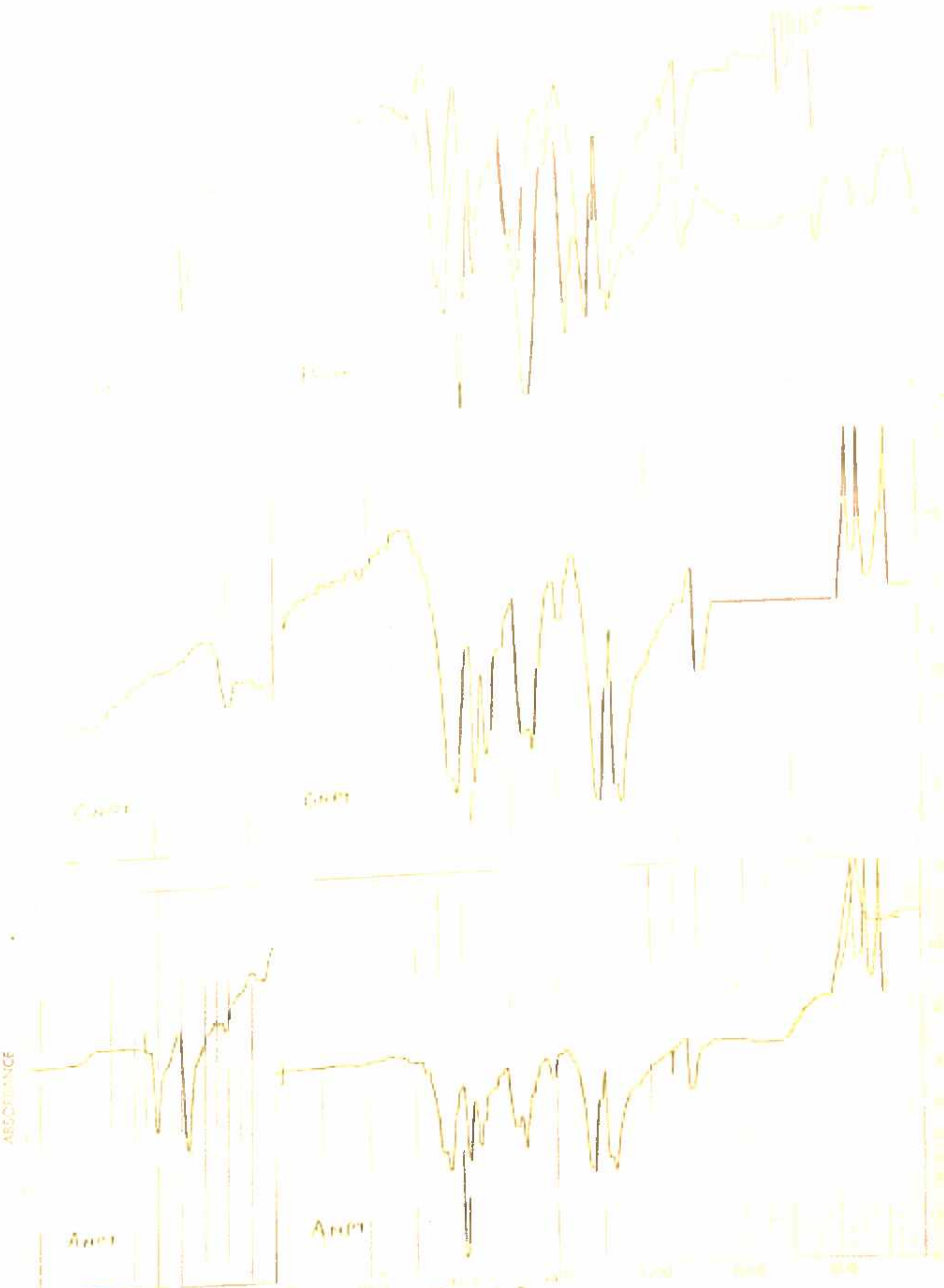


Fig 4 2

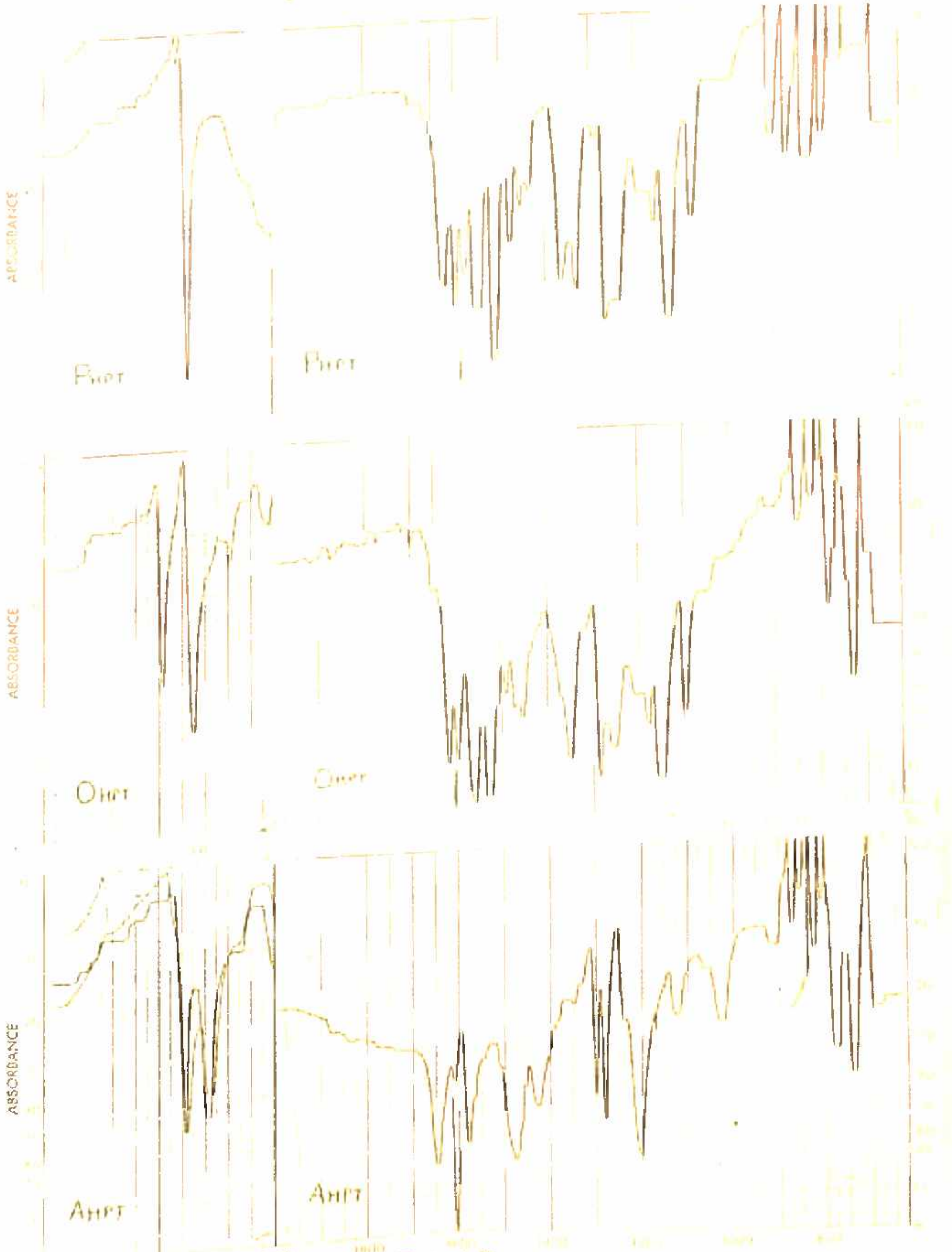

ABSORBANCE
PHPT
PHPT
ABSORBANCE
OHPT
OHPT
ABSORBANCE
AHPT
AHPT

Fig 4.3

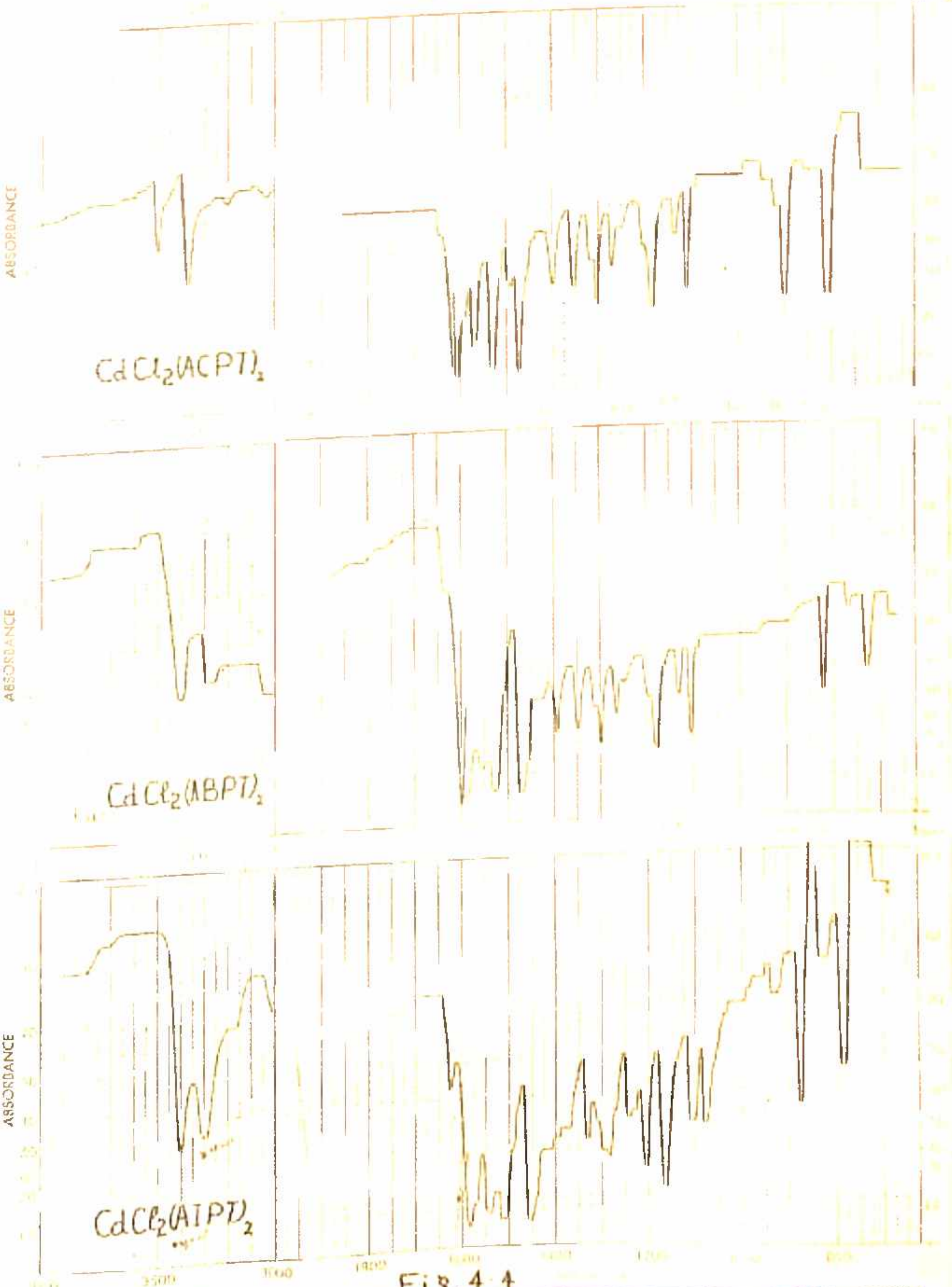

ABSORBANCE
CdCl2(ACPT)2
ABSORBANCE
CdCl2(ABPT)2
ABSORBANCE
CdCl2(AIPT)2
3500
3000
1800
1600
1400
1200
800

Fig 4.4

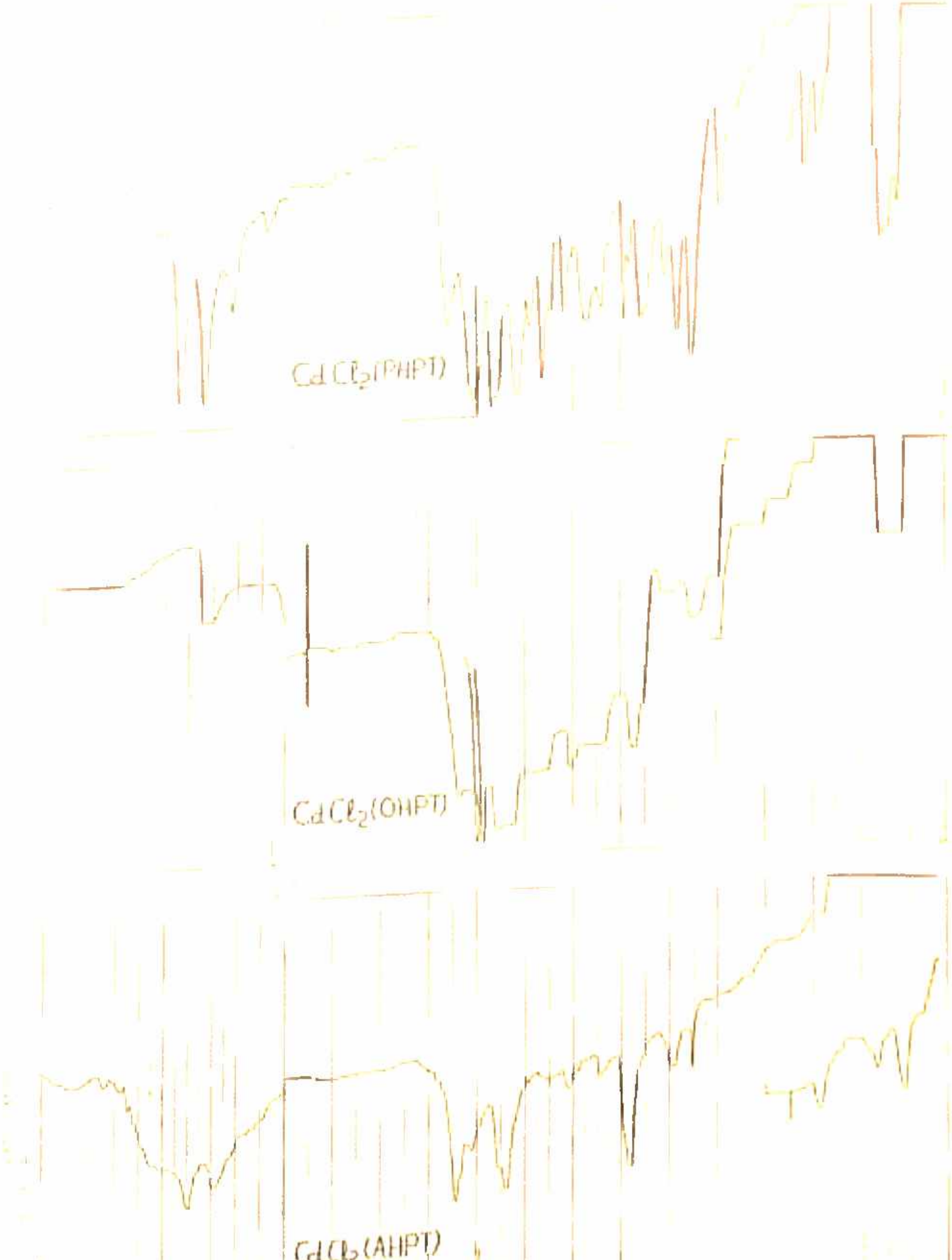


Fig-4.5

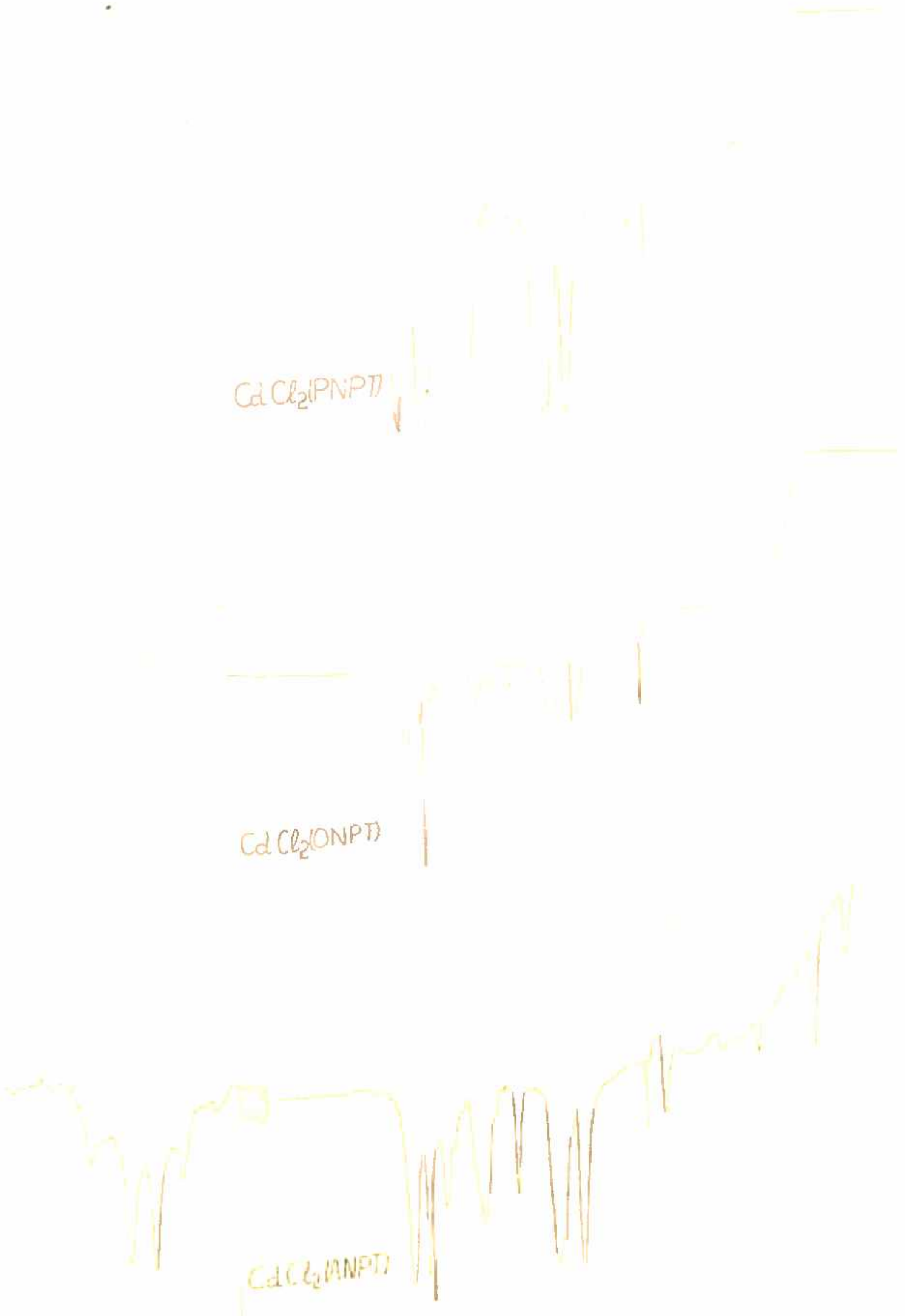


Fig 4.6

Fig. 4.7

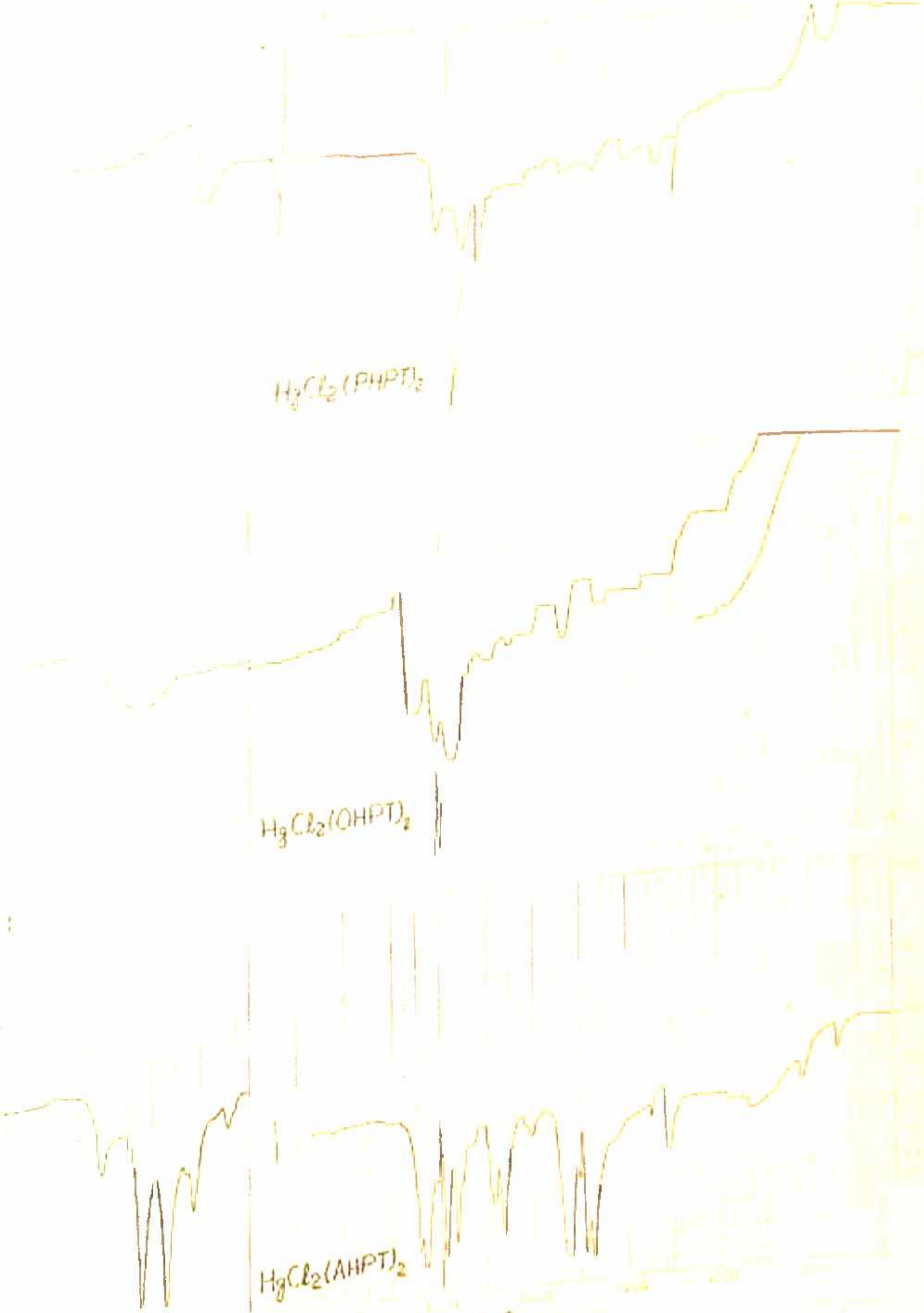


Fig 48

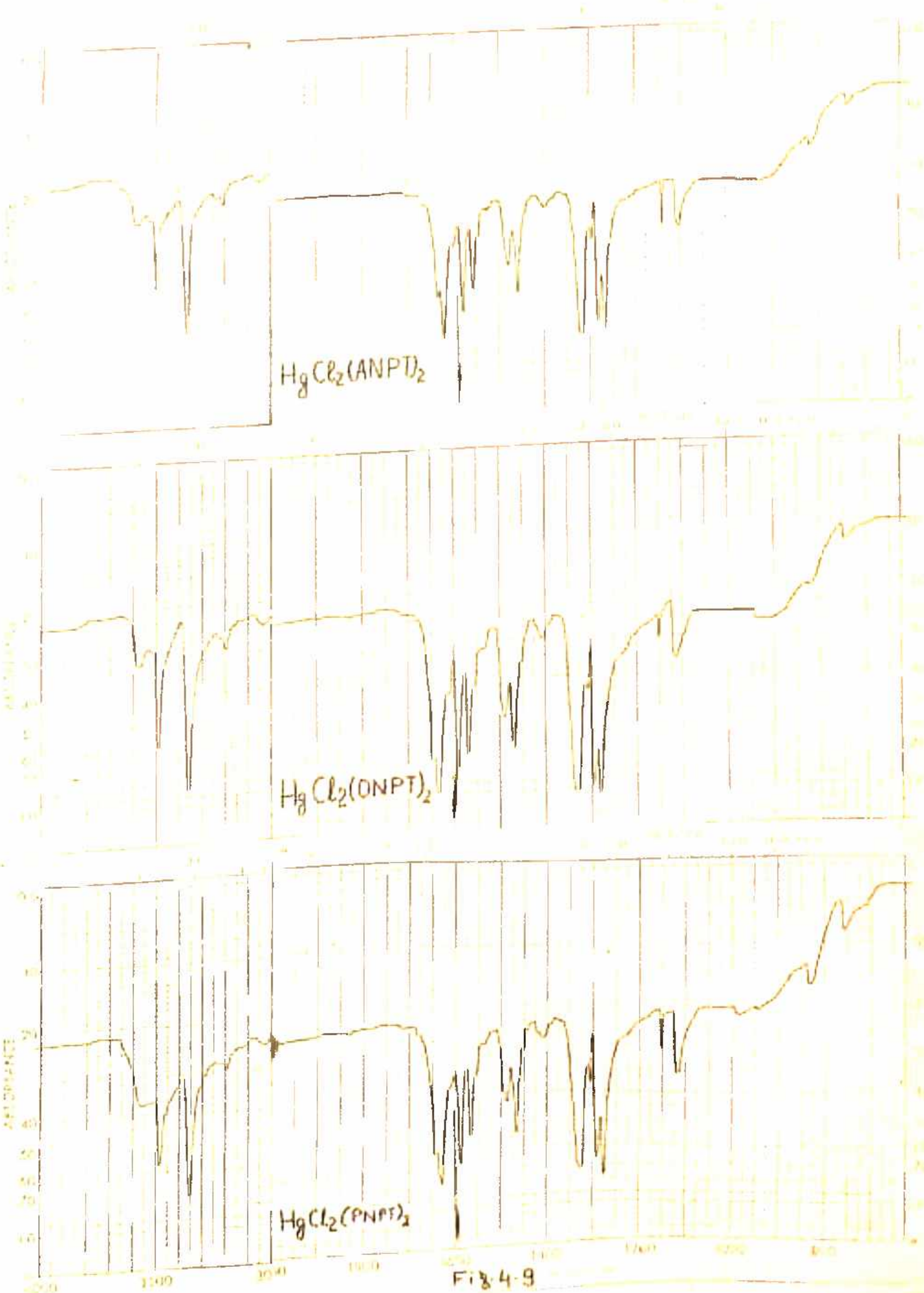


Fig. 4.9

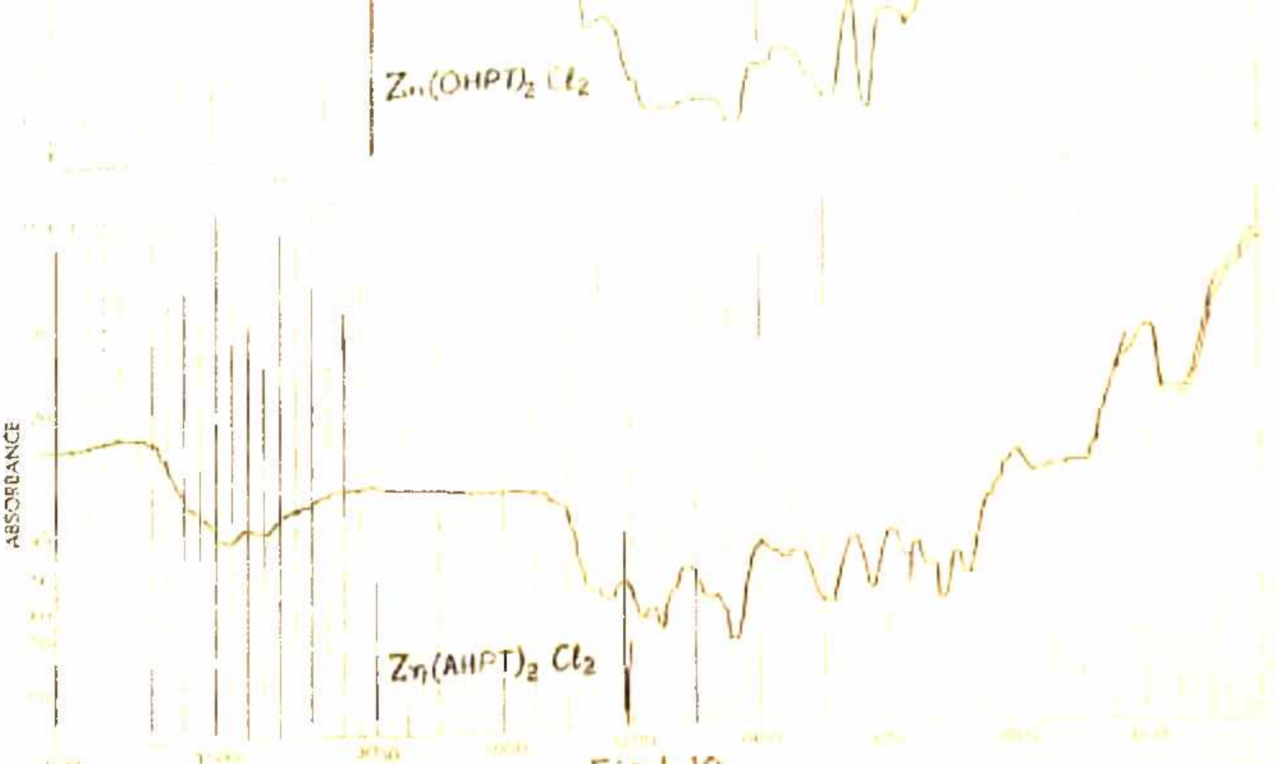


Fig 4·10


ABSORBANCE
Zn(PHPT)$_2$ Cl$_2$

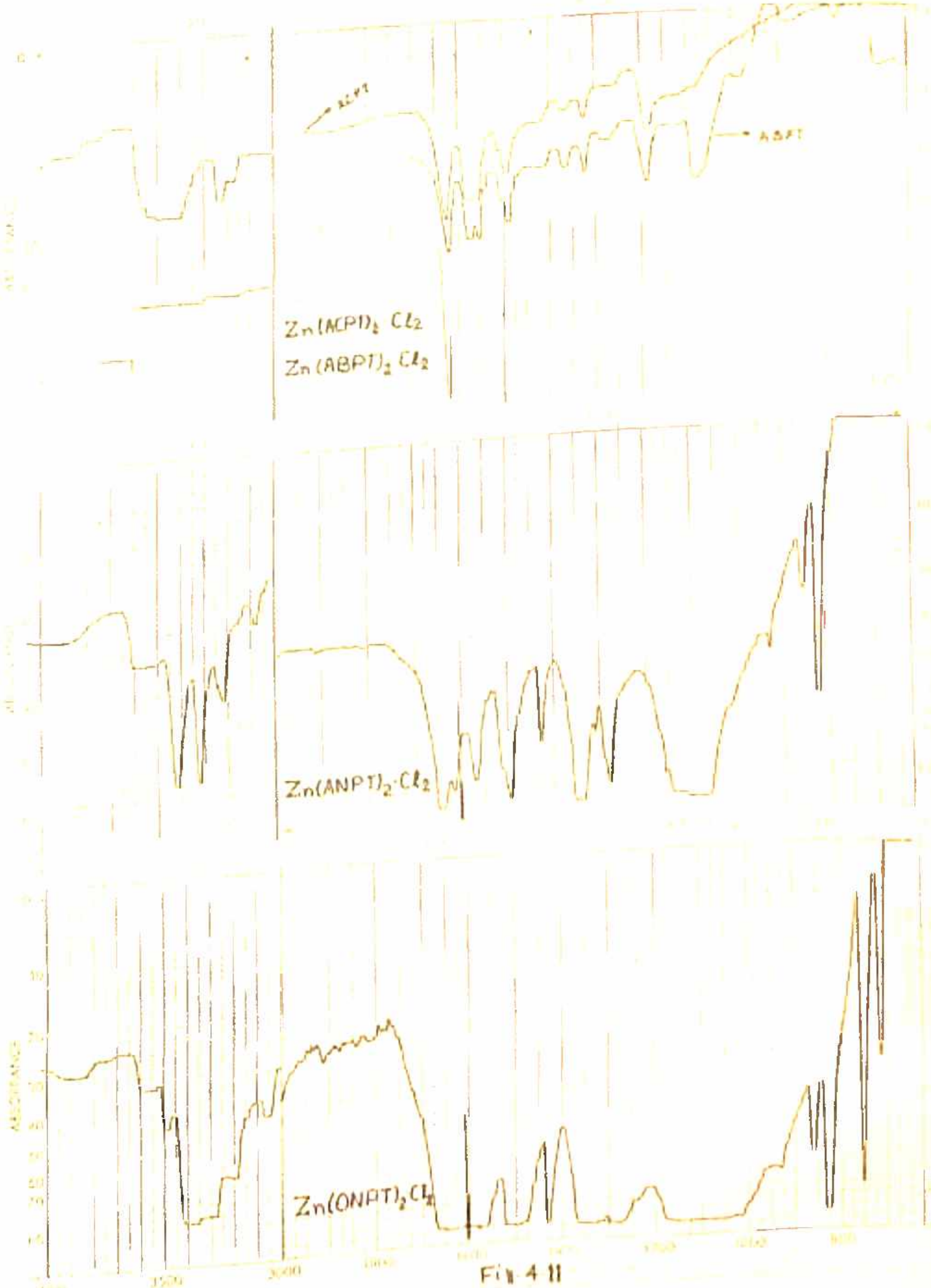

ACPT
ABPT
Zn(ACPT)$_2$ Cl$_2$
Zn(ABPT)$_2$ Cl$_2$
Zn(ANPT)$_2$·Cl$_2$
Zn(ONPT)$_2$Cl$_2$
ABSORBANCE
3500
3000
800

Fig 4.11

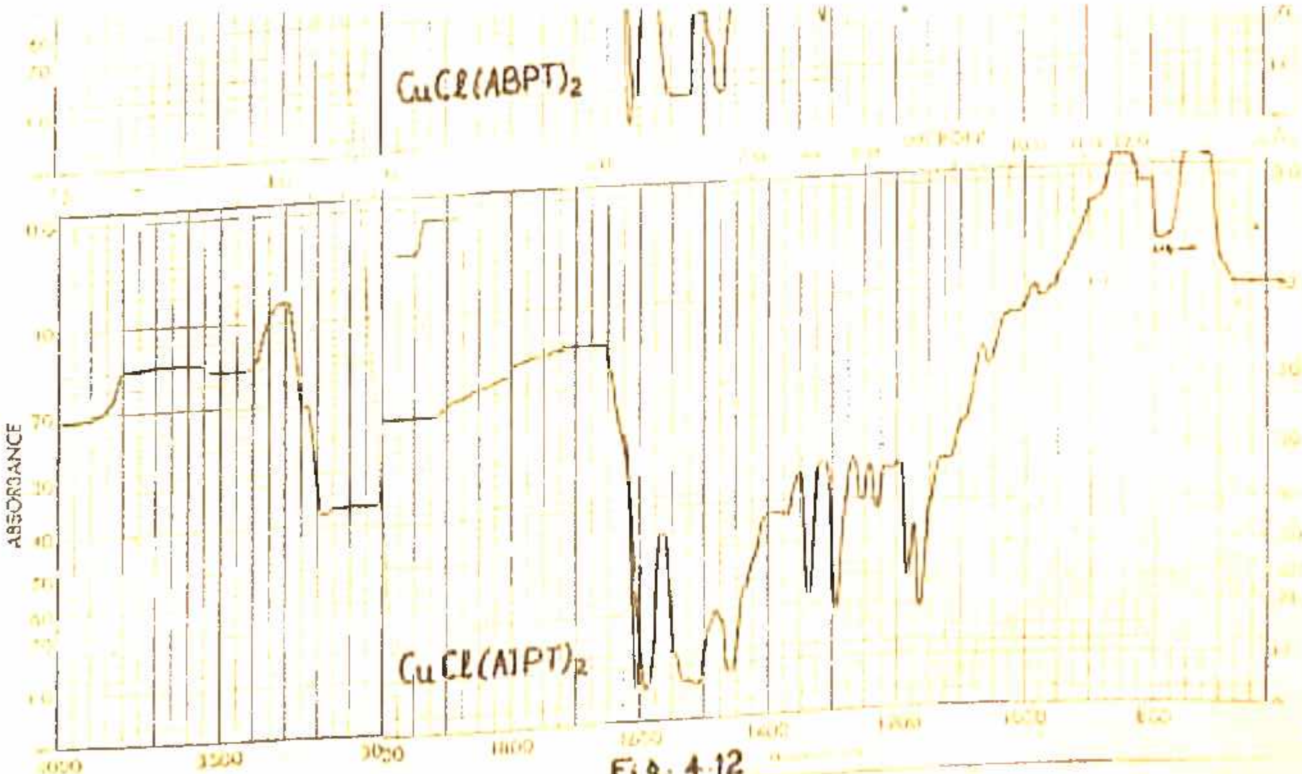
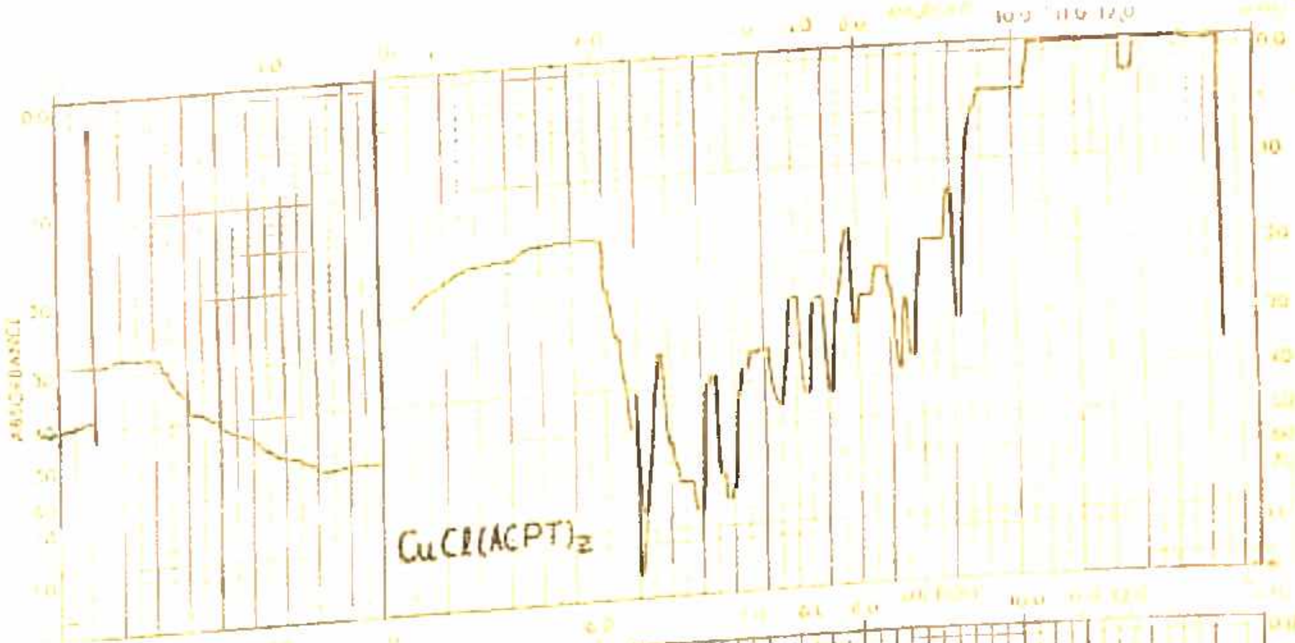
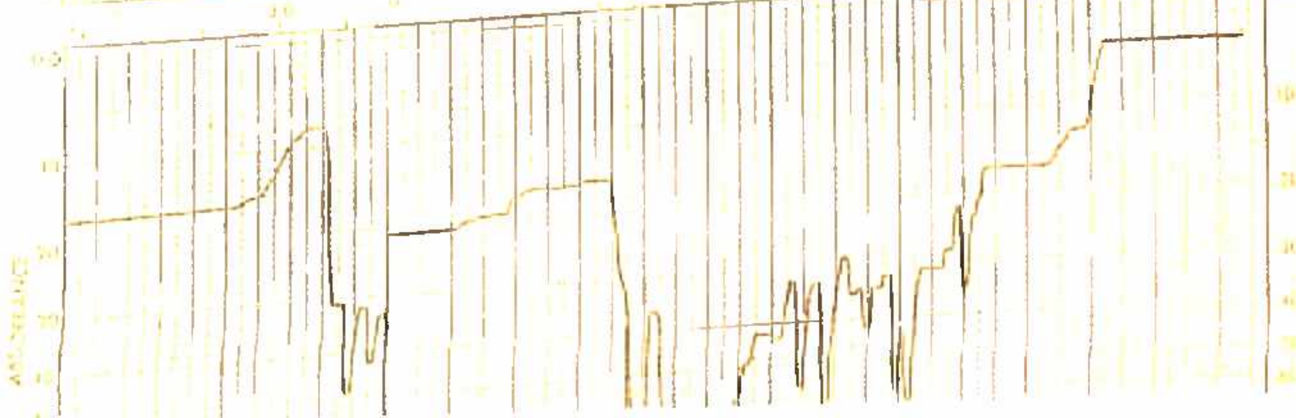


Fig. 4.12


ABSORBANCE
CuCl(ACPT)₂


ABSORBANCE

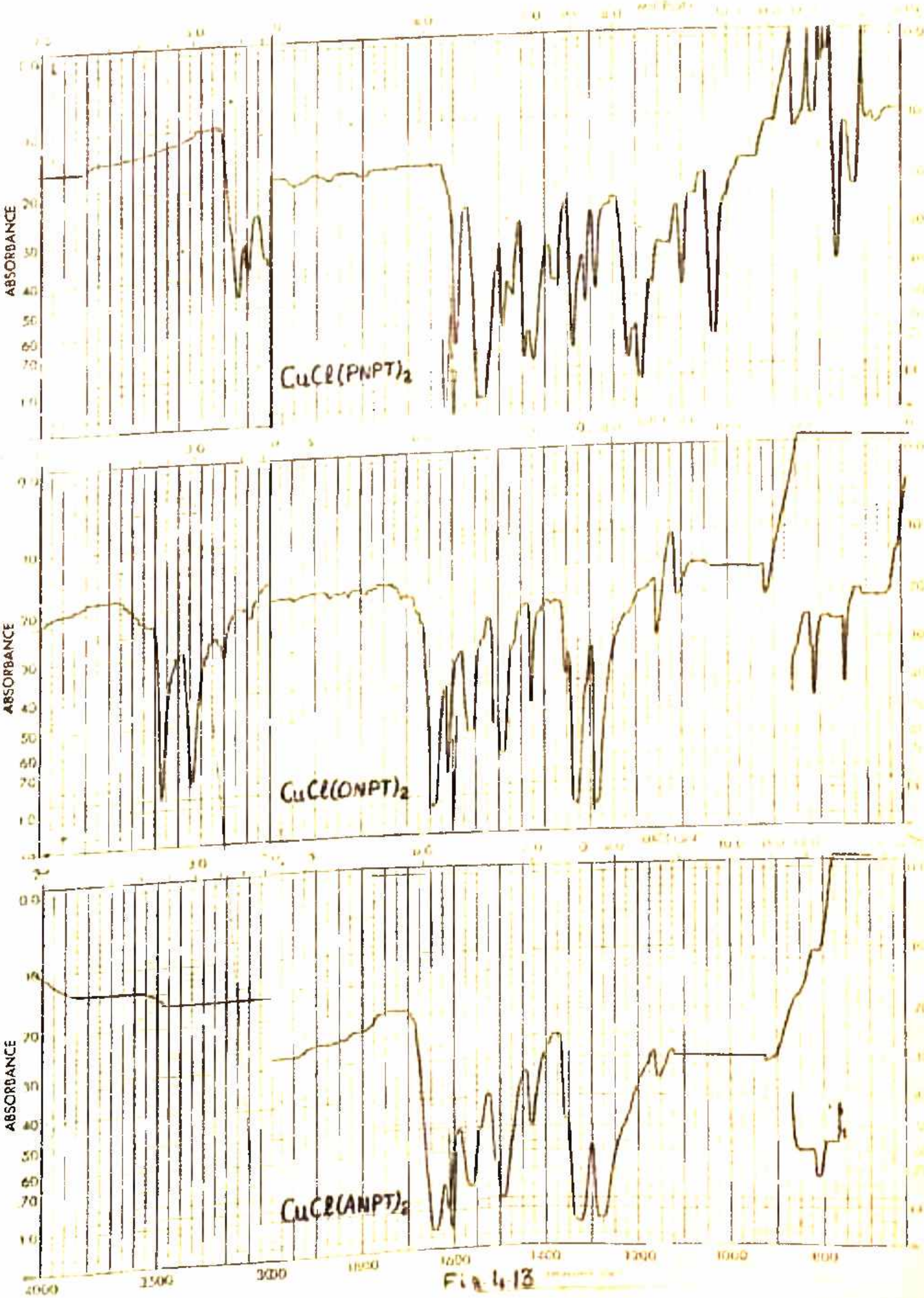

ABSORBANCE
CuCl(PNPT)₂
ABSORBANCE
CuCl(ONPT)₂
ABSORBANCE
CuCl(ANPT)₂
4000
3500
3000
1800
1600
1400
1200
1000
800

Fig. 4.13

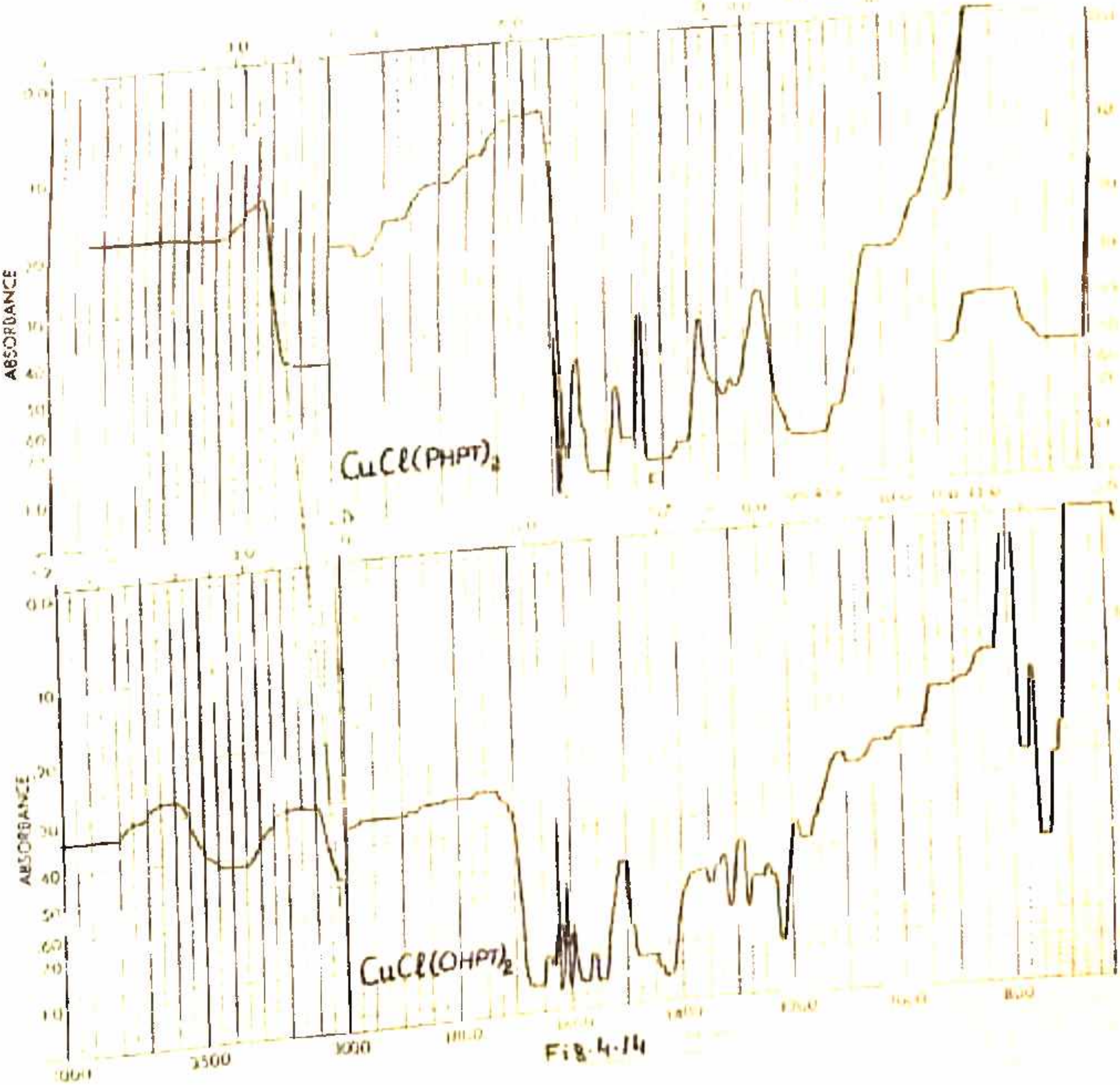

ABSORBANCE
CuCl(PHPT)$_2$
ABSORBANCE
CuCl(OHPT)$_2$
4000
3500
3000
1800
1600
1400
1200
1000
800

Fig. 4.14

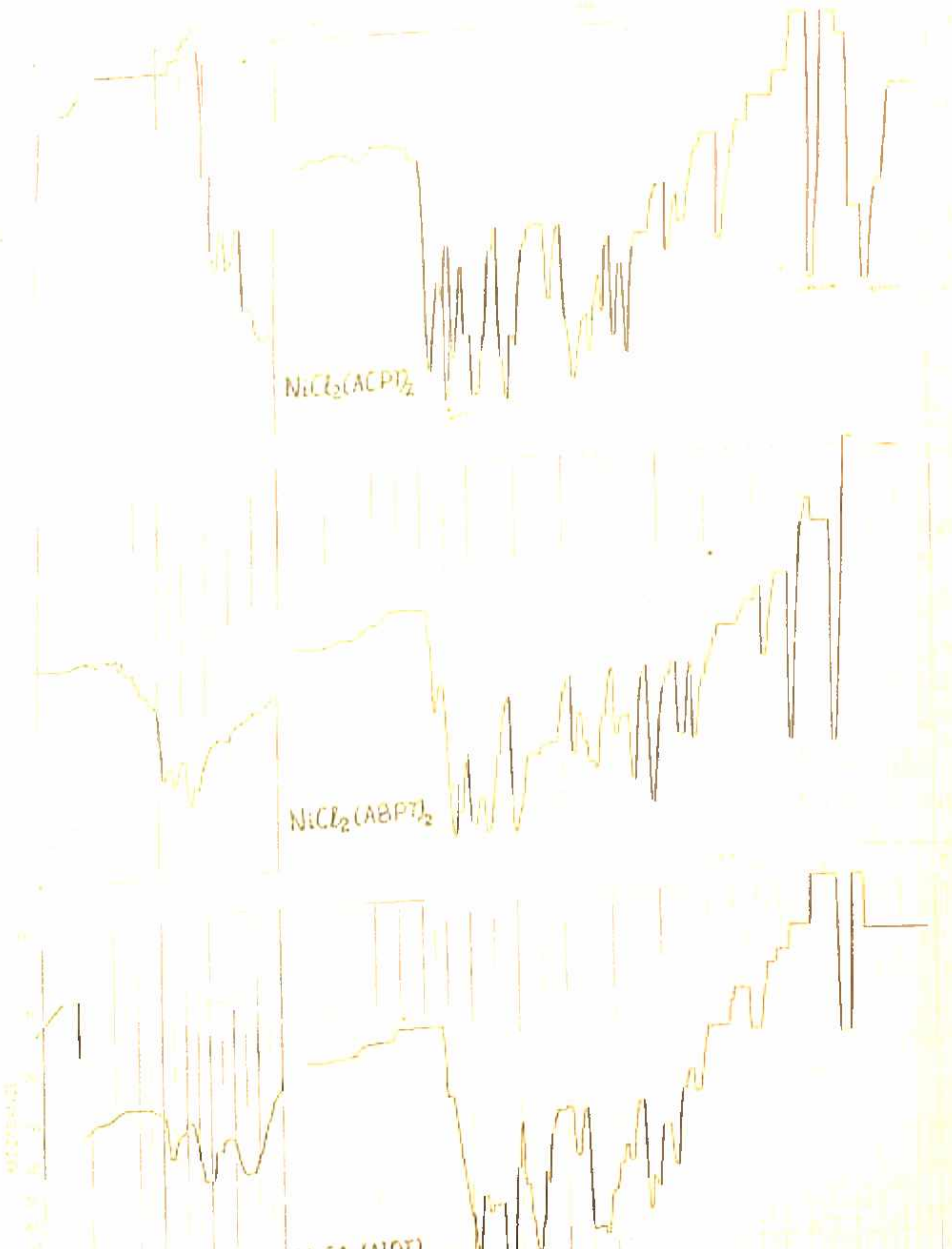


Fig 4.15

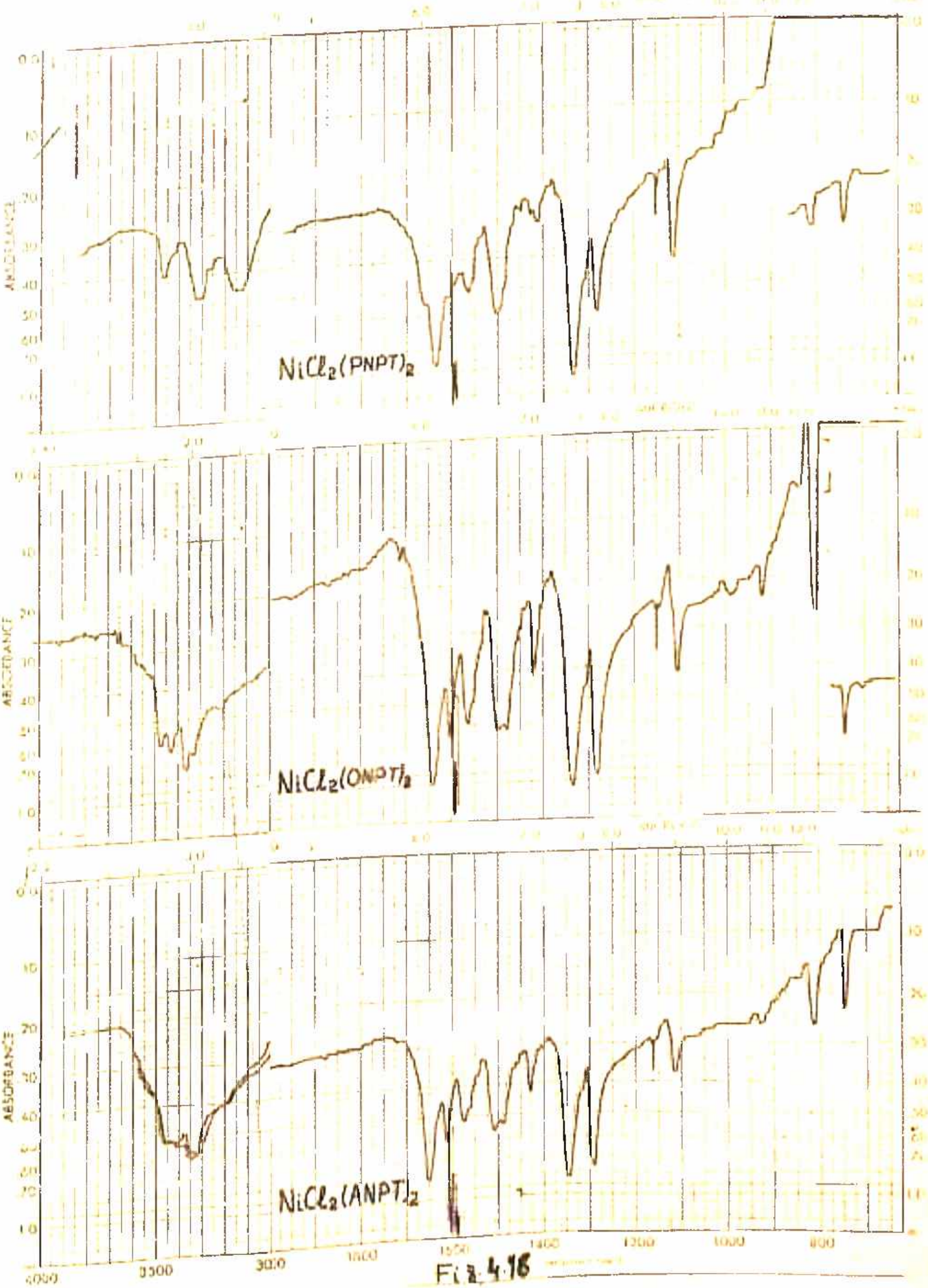

$NiCl_2(PNPT)_2$
$NiCl_2(ONPT)_2$
$NiCl_2(ANPT)_2$
ABSORBANCE
ABSORBANCE
ABSORBANCE
4000
3500
3000
1800
1600
1500
1400
1200
1000
800

Fig. 4.16

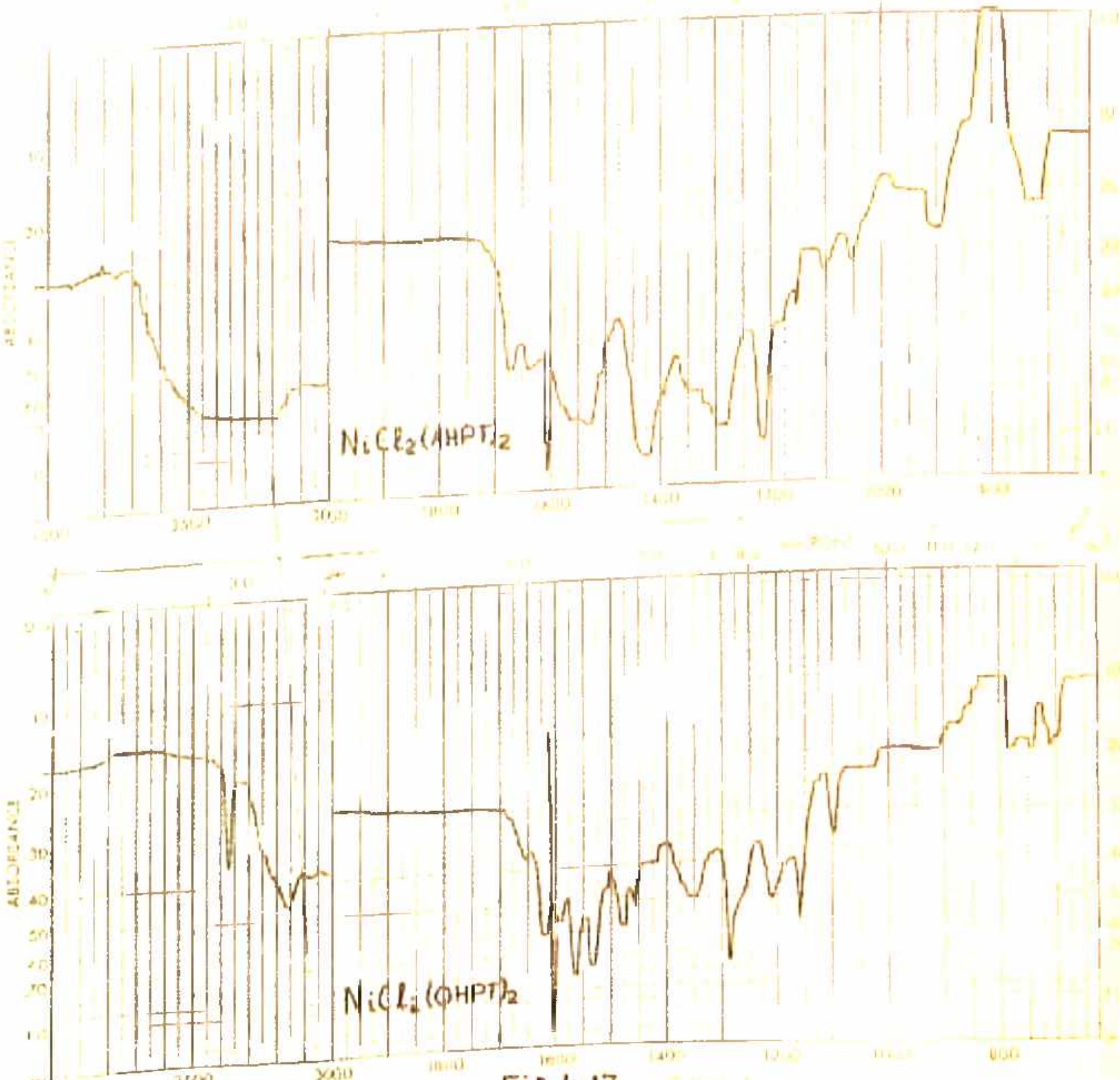

$NiCl_2(4HPT)_2$
$NiCl_2(\Phi HPT)_2$
ABSORBANCE
4000
3500
3000
1800
1600
1400
1200
1000
800

Fig. 4·17

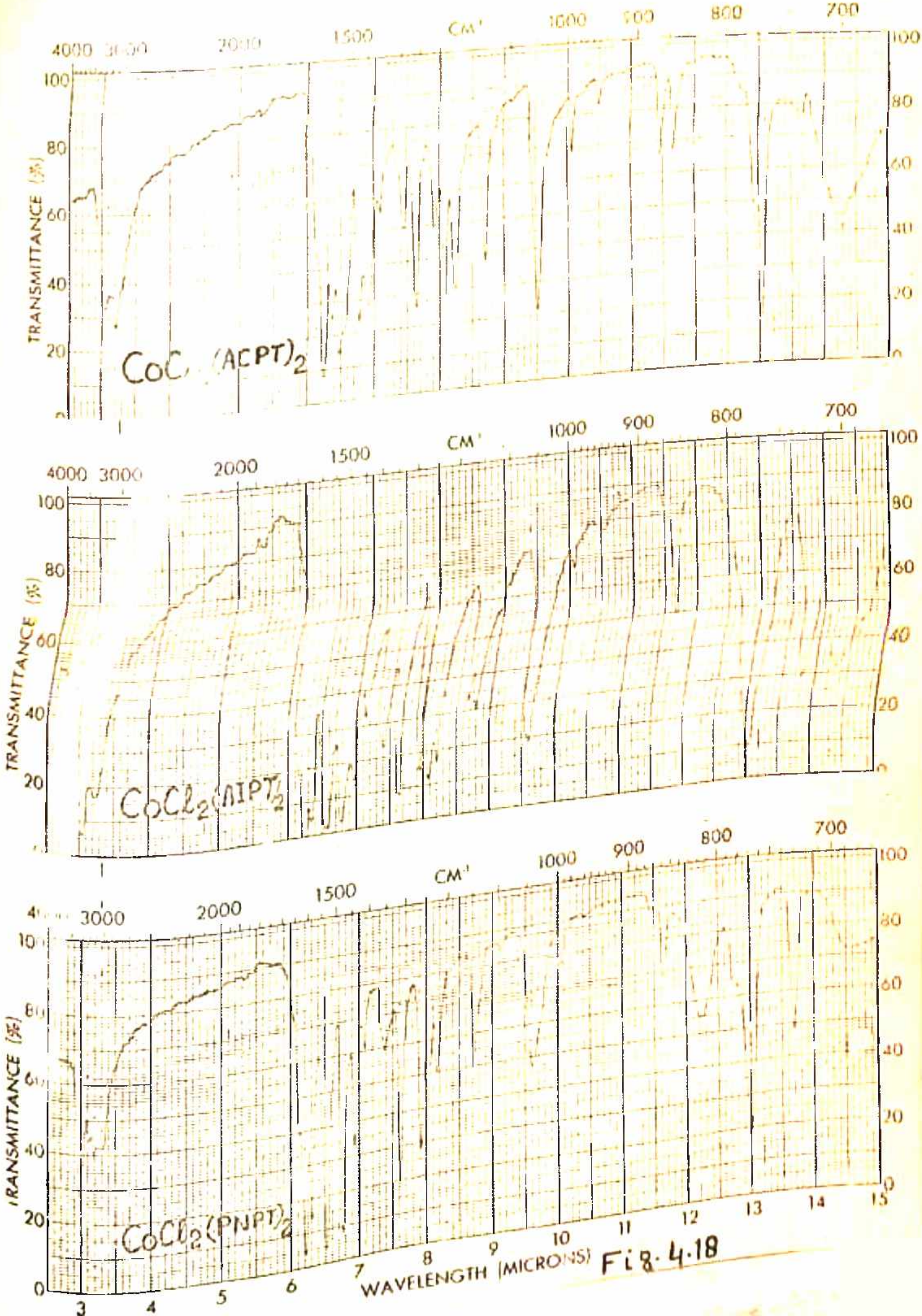

CoCl (ACPT)$_2$
CoCl$_2$(AIPT)$_2$
CoCl$_2$(PNPT)$_2$
TRANSMITTANCE (%)
CM⁻¹
4000
3000
2000
1500
1000
900
800
700
0
20
40
60
80
100
WAVELENGTH (MICRONS)
3
4
5
6
7
8
9
10
11
12
13
14
15

Fig. 4.18

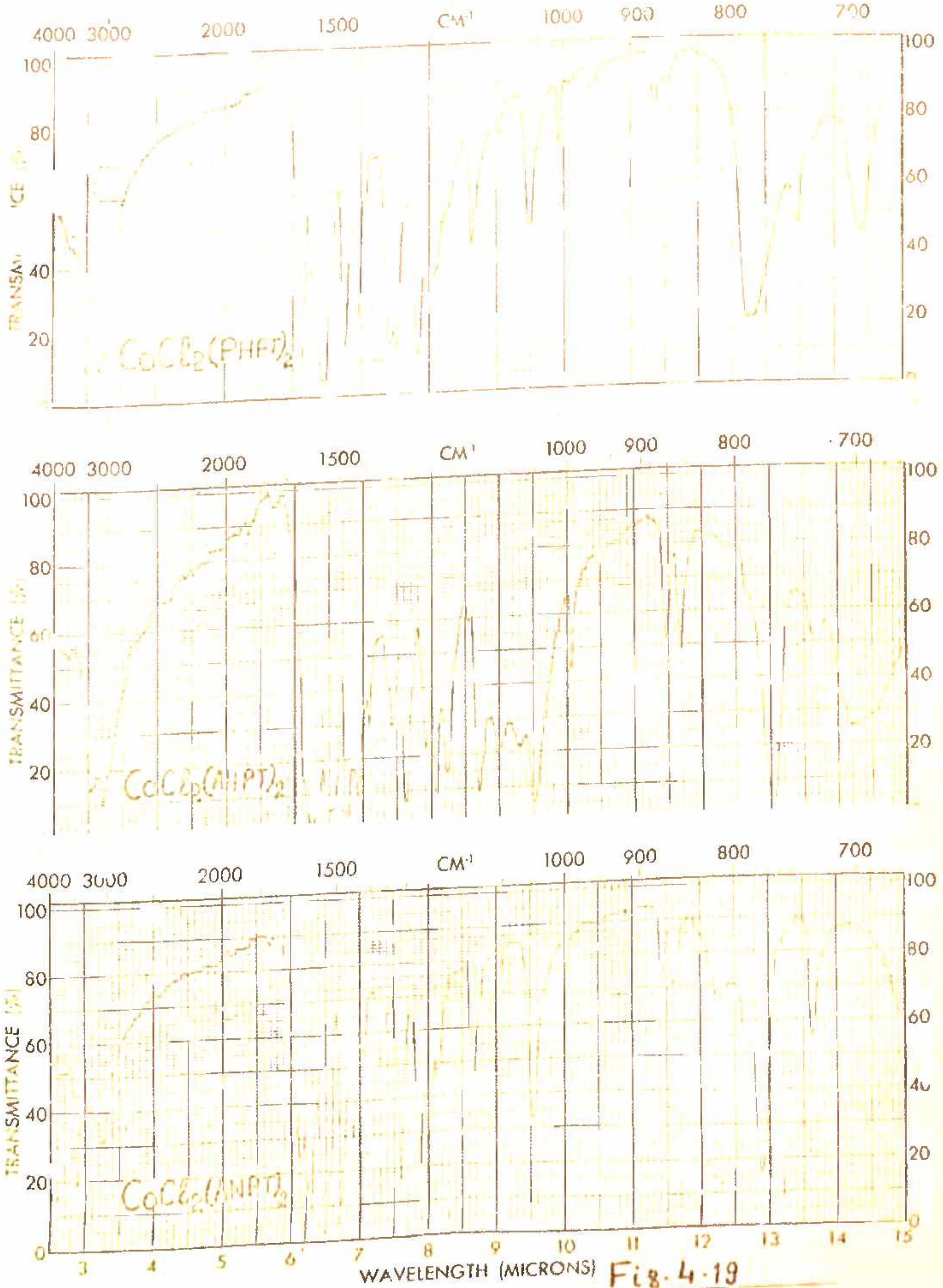

CM⁻¹
4000
3000
2000
1500
1000
900
800
700
TRANSMITTANCE (%)
0
20
40
60
80
100
CoCl₂(PHPT)₂
CoCl₂(MHPT)₂
CoCl₂(ANPT)₂
WAVELENGTH (MICRONS)
3
4
5
6
7
8
9
10
11
12
13
14
15

Fig. 4·19

REFERENCES

1. A. Werner, "Nature Anschhauungen auf dem Gebeite der anorganischen chemie", 4th Edition, F. Vieweg and Sohn, Brunswick (1920).

2. N.V. Sidgwick, "Electronic Theory of Valency", Oxford (1927).

3. T.M. Lowary, J. Chem. Soc., 433 (1941).

4. L. Pauling, "Nature of the Chemical Bond", Cornell University Press, Ithaca (1930).

5. H. Bethe, Ann. Phy., 3, 133 (1929).

6. J.H. Van Vleck, J. Chem. Phys., 3, 803 (1935).

7. W.G. Penny and R. Schlapp, Phys. Revs., 42, 666 (1932).

8. J.H. Van Vleck and W.G. Penny, Phil. Mag., 17, 961 (1934).

9. L.E. Orgel, "An Introduction to Transition Metal Chemistry - Ligand Field Theory", John Wiley and Sons, New York (1960).

10. C.J. Ballhausen, "Introduction to Ligand Field Theory', McGraw-Hill, New York (1962).

11. B.N. Figgis, "Introduction to Ligand Fields", John Wiley and Sons, London (1966).

12. J.S. Griffith, "The Theory of Transition Metal Ions", Cambridge (1961).

13. R. Rivest, Can. J. Chem., 40, 2234 (1962).

14. A. Yamagauchi et al., J. Amer. Chem. Soc., 80, 527 (1958).

15. D.S. Bystrov, T.N. Sumarokova and V.N. Filiminov, Optics and Spectroscopy, 9, 239 (1960).

16. M. Nardelli, L. Cavalca and A. Brainbanti, Gazetta, 86, 867, 1037 (1956).

17. O. Foss and S. Hauge, Acta Chem. Scand., 13, 1252 (1959).

18. M. Nardelli, Gazetta, 89, 616 (1959).

19. O. Foss and S. Hauge, Acta Chem. Scand., 15, 1616 (1961).

20. V.B. Evodokmov et al., Doklady Akad. Nauk. SSSR., 143, 1282 (1962).

21. A. Lopez-Castro and M.R. Truter, J. Chem. Soc., 1309 (1963).

22. L.F. Lindoy, S.E. Livingstone and T.N. Lockyer, Austral. J. Chem., 18, 1549 (1965).

23. M. Nardelli, A. Braibanti and G. Fava, Gazetta, 87, 1209 (1957).

24. F. Pantani and P.G. Desideri, Talanta, 5, 69 (1960).

25. R.L. Carlin and S.L. Holt, Inorg. Chem., 2, 849 (1963).

26. S.L. Holt and R.L. Carlin, J. Amer. Chem. Soc., 86, 3017 (1964).

27. M. Nardelli, I. Chiesici and A. Braibanti, Gazetta, 88, 37 (1958).

28. G.T. Morgan and F.H. Burstall, J. Chem. Soc., 143 (1928).

29. C.M. Harris and S.E. Livingstone, Rev. Pure and Appl. Chem. (Australia), 12, 16 (1962).

30. S.M. Banerjea and S.K. Sidhanta, J. Ind. Chem. Soc., 38, 747 (1961).

31. S.N. Banerjea and A.C. Sukhthanker, J. Ind. Chem. Soc., 39, 197 (1962); 40, 387 (1963).

32. B. Hirsch, J. Prakt. Chem., 12, 264 (1961).

33. O. Foss and W. Johannssen, Acta Chem. Scand., 15, 1939, 1947 (1961).

34. O. Farroq and A.U. Malik, Collect. Czech. Chem. Commun. 37(10), 3910-4 (1972).

35. Yu. Ya. Khavitonov, V.D. Brega, A.V. Ablov and N.N. Proskina, Zh. Neorg. Khim., 19183, 2166-77 (1974).

36. Rafaele Baltistuzzi and Guisseppe Marcotrigiano, Gazz. Chim. Ital., 104(5-6), 117-19 (1974).

37. A. Dutta Ahmed and P.K. Mandal, J. Inorg. Nucl. Chem., 29, 2347 (1967).

38. D. Banerjea and I.P. Singh, Ind. J. Chem., 6, 34 (1968).

39. N. Krishnaswamy and H.D. Bhargava, Ind. J. Chem., 7, 710 (1969).

40. B.C. Haldar and R.A. Nadkarni, J. Ind. Chem. Soc., 43, 429 (1966).

41. C.S.G. Prasad, Ph.D. Thesis, B.I.T.S., Pilani (1973).

42. B.C. Kashyap, Ph.D. Thesis, B.I.T.S., Pilani (1974), also B.C. Kashyap, S.K. Banerji and A.D. Taneja, J. Inorg. Nucl. Chem., 37(2), 612-15 (1974) and Curr. Sci., 45(3), 81-3 (1976).

43. M.P. Sharma, S.P. Mathur, M.R. Bhandari and T.N. Mathur, J. Inst. Chem., Calcutta, 46, Pt. I, 10 (1974).

44. P.K. Mandal, Ind. J. Chem., 12(8), 845-7 (1974).

45. Rath Mohapatra, J. Ind. Chem. Soc., 51(7), 705-6 (1974).

46. R.N. Dash, D.V. Raman Rao, Ind. J. Chem., 11(6), 603-4 (1973).

47. S.K. Bhowal, Curr. Sci., 44(5), 157-8 (1975).

48. O.M. Petrukhin, V.I. Nefedov, Ya. V. Salyn and V.N. Sherchenko, Fiz. Mat. Metody. Koord. Khim., Tezisy Dokl. V Ses Soveshch, 5th 15-16 (1974).

49. Gieuseppe, Marcotrigiano, Z. Anorg. Allg. Chem., 422(1), 80-8 (1976).

50. P.K. Mandal, Ind. J. Chem., 14A (1976).

51. A. Weissberger et al., Technique of Organic Chemistry, Vol. III, Interscience, New York (1955).

52. C.A. Kraus and R.A. Vingee, J. Amer. Chem. Soc., 56, 511 (1934).

53. Shozo Shibata et al., Anal. Chim. Acta, 50, 439 (1970).

54. C.L. Leese and H.N. Raydon, J. Chem. Soc., 4039 (1954).

55. W.T. Caldwell et al., J. Amer. Chem. Soc., 66, 1479 (1944).

56. A.I. Vogel, "Practical Organic Chemistry", Longmans, London (1962).

57. A.K. Jain and K. Rubenstein, Nature, 171, 840 (1953).

58. M. Nanda, R.B. Das Kanungo, B.C. Dash and G.N. Mohapatra, J. Ind. Chem. Soc., 49, 251 (1972).

59. H. Wagner, L. Horhammer and H. Nufer, Arznein Forsch, 15, 453 (1965).

60. S. Fisel, F. Modreanu and A. Corpov., Acad. Ropub. Pop. Rom., Fil. Iasi., Stud. cercet. Stiint., Chim., 7, 19 (1965).

61. M.B. Devani, G.J. Shishoo and B.K. Dadia, J. Chromatog., 105, 186 (1975).

62. Edt. I.M. Hais and K. Macek, "Paper Chromatography", Academic Press, New York, p. 630 (1963).

63. M.F.A. EL-Sayed and R.K. Sheline, J. Inorg. Nucl. Chem., 6, 187 (1958).

64. B. Kadzia, P.X. Armendarez and K. Nakamoto, J. Inorg. Nucl. Chem., 30, 849 (1968).

65. K. Swaminathan and H.M.H. Irving, J. Inorg. Nucl. Chem., 26, 1291 (1964).

66. A. Syamal, J. Ind. Chem. Soc., 45, 904 (1948).

67. S. Ahrland, J. Chatt and N.R. Davies, Quart. Rev., 12, 265 (1968).

68. R.G. Pearson, J. Amer. Chem. Soc., 85, 3533 (1963).

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CHAPTER V

Present chapter with a brief description of Differential Thermal Analysis, reviews the analytical chemistry applications of DTA for organic and inorganic compounds only. DTA studies of substituted thiourea and their metal complexes reveal the decomposition temperature and post heat treatment temperature for the fabrication of thin films for solar cells.

Differential thermal analysis (DTA) is a thermal technique in which the temperature of a sample compared with the temperature of a thermally inert material is recorded as a function of the sample, inert material, or furnace temperature as the sample is heated or cooled down at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic enthalpic transitions or reactions such as those caused by phase changes, fusion,crystalline structure inversions, boiling, sublimation and vaporization, dehydration or dissociation reactions, oxidation or reduction reactions destruction of crystalline lattice structure and other chemical reactions. Generally speaking, phase transitions, dehydration, reduction and some decomposition reactions produce endothermic effects, whereas crystallization, oxidation and some other decomposition reactions produce exothermic effects. The temperature changes occurring in the sample are detected by differential method.

HISTORICAL ASPECT

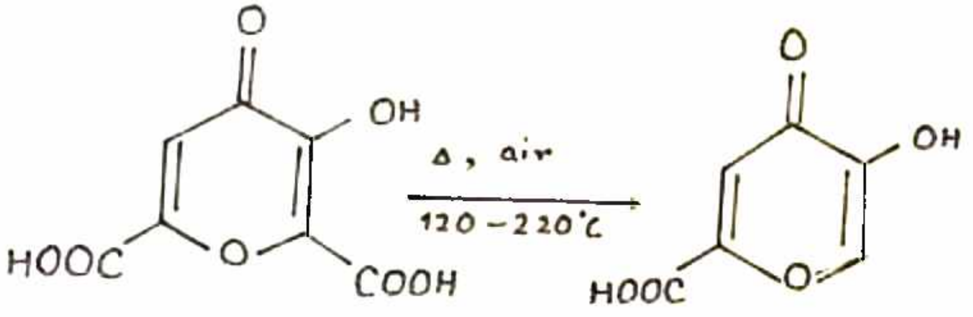
Le Chatelier[1] has been credited as the father of this technique. His early work in 1887 on clays and minerals consisted of thermal analysis determination. He embedded a thermocouple in clay sample which was heated at about 100°C/min. Response from galvanometer was measured by reflection of flashes from an induction coil from the galvanometer mirror to a photographic plate. The temperature of the sample was then displayed on the developed photographic plate as a series of lines each of which corresponded to a spark discharge which occurred at interval of 2 secs. An endothermic reaction was indicated by closely spaced lines whereas wider spacings indicated an exothermic reaction. Accordingly[2], Le Chatelier was the father of thermal analysis but not of differential thermal analysis.

Later Ashley[3], Wholin[4], Rieke[5], Wallach[6] and Mellor and Holdcroft[7] studied the thermal changes which took place in a substance as it was heated by recording its temperature, measured with thermocouple, as a function of time. Breaks in the heating curve, thus obtained, indicated dehydration, decomposition, phase transition etc. reactions. However, this heating curve method was not very sensitive to small heat effects and was adversely affected by factors such as heating rate, recording equipment etc. On account of these deficiencies Robert-Austen[8] in 1899 suggested a two thermocouple measuring system. In this one thermocouple was placed in reference and other in the sample. This enables recording of differential temperature, which is more sensitive to small temperature changes, as a function of time. In the much neglected paper, Burgess[9] discussed the merits of single and double thermocouple systems for cooling curve data. He also mentioned the various experimental techniques known at that time and presented equations for calculations of heat of transformations. Fenner[12] studied the phase transitions in silicates. Houldsworth and Cobb[11] for the first time used DTA to study the behaviour of fire clays and bauxite on heating. This initiated the numerous investigations on the thermal decomposition of clays and minerals by Norton[17], Grim[18], Berkelhamer[13], Kerr and Kulp[14], Kauffman and Dilling[15], Foldvari-Vogl[16] and Mackenzie[19].

For the chemists, the renaissance of DTA development and application occurred during 1950 as a result of the work of Stone[20] and Borchardt and Daniels[21-22]. Stone developed the first modern, high quality commercial DTA instrumentation whereas Brochardt, in his Ph.D. Thesis at the University of Wisconsin, applied the DTA technique to problems in inorganic and physical chemistry. His work on the determination of homogeneous reaction kinetics by DTA is classical one. In 1960s, DTA because of commercial instrumentation was applied with great vigour in polymer chemistry and today DTA in addition to a newly developed Differential Scanning technique is an important tool to study thermal properties of the polymers.

As Differential thermal analysis is a rapidly developing research technique, there are a number of reviews on DTA and its application to chemical problems. A few important ones are the biennial reviews since 1958 by Murphy[25], the last one of which appeared in 1972[26]. Recent books and/or book chapters on DTA include those by Smothers and Chiang[27-28], Wendlandt[23-24], Garn[29], Mackenzie[30], Gordon and Cambell[32-33], Kissinger and Newman[31], Barall and Johnson[34], David[35], Barall[36], Schultze[37], Ramachandran[38], Wunderlich[39], Porter and Johnson[40-41], Schwenker and Garn[42] and Wendlandt[43]. In the following paragraph only analytical chemistry applications of DTA for inorganic compounds are included.

The applications of DTA technique to organic compounds are quite diverse and have been extensively reviewed[44-50]. The thermal decomposition of a number of organic acids has been studied by Wendlandt and Hoiberg[50-51]. As acids were decomposed in an Argon atmosphere only endothermic peaks were obtained. These peaks were caused by reactions such as dehydration, decarboxylation, sublimation, decomposition and phase transitions from the solid to the liquid state. The only acid studied containing water of hydration is oxalic acid dihydrate which has dehydration peaks with ΔT_{min} values of 110, 120 and 125°C respectively. DTA was also used to establish the best preparative conditions for the conversion of meconic acid (I) (3 hydroxy-4-oxo-4H-pyrane-2,6 dicarboxylic acid) to comenic acid (II)[53]



It was found that comenic acid is formed by decarboxylation of meconic acid in a reaction giving an exothermic peak at ΔT_{max} of 240°C. At and above this temperature the product sublimes. Brancone and Ferrari[54] obtained qualitative information concerning purity, solvation, structural configuration and polymorphism of a number of pharmaceutical compounds.

The precise determination of melting and boiling points by DTA was first discussed in detail by Vassallo and Harden[55]. Precision of ±0.3°C over a wide range of heating rates and temperature range from -150-450°C was obtained. This is further discussed by Barrall[56], Kerr and Landis[57] have described a microboiling and melting point procedure by DTA. The 2-5 µl samples were trapped at the exit port of a GC column and transferred with a 10 µl syringe to a capillary tube.

Chiu[58] investigated the formation of an organic derivative by DTA whereas Harmelin et al.[59] have studied the Diels-Alder diene synthesis using maleic anhydride and anthracene.

Thermal properties of explosives and propellant compositions are widely studied. Fauth[60] recorded the DTA curves of some hydrazine, guanidine and guinidinium picrates, styphnates and sulfates. Other picrates with Th, ammonium, tetramethyl ammonium, and tetraethylammonium were studied by Stammler[61]. David[62], Bohon[63] examined the thermal behaviour of explosives and propellants under various external pressures upto 3000 p.s.i.g using DTA. Graybush et al.[64] have described decomposition of primary explosives using remotely operated DTA cell.

A wide variety of organic reactions such as Cis-trans isomerization of stilbene and oleic acid, polymerization of styrene, Diels-Alder reactions etc. were studied by Santoro and coworkers[65-68] using sealed tube. Koch[69] made use of the technique to detect unstable intermediates in an organic reaction. Degradation of hydrocarbon liquids[70-72] and quality control of grease[73-74] are also studied by DTA. Other applications of DTA in clays and minerals, polymers, biological materials etc. are reviewed by Wendlandt[43].

A large number of DTA applications to inorganic compounds are reviewed by Mackenzie et al.[75] Stone[76] had suggested a rapid method for the determination of the moisture content of nearly powdered substances. Effect of potassium chlorate impurity on the thermal stability of ammonium perchlorate has been studied by

Petricciani et al.[77] Wendlandt et al.[78] have studied the thermal decomposition of the thorium, uranium and rare-earth metal oxalate hydrates and mixture of rare-earth oxalate hydrates. Erdey and Paulik[79] in simultaneously DTA-TG study, investigated the thermal decomposition of Ba, Sr, Mn(II), Ca, Mg and Zn oxalates in air and N_2 atmospheres. They found that evolved CO_2 in the reaction inhibit the progress of the reaction and shift the peak temperature to higher values. Mesmer and Irani[80] had determined changes in ethalpy which occur when $CaHPO_4.2H_2O$ is heated upto 1300°C.

Heats of transitions of a number of inorganic compounds were determined using several new methods of quantitative DTA.[81-82] Wendlandt[83] found that by using the sealed tube technique, heat of dehydration of metal salt hydrates could be obtained which would be impossible using conventional open tubes or crucibles. Similar studies were made on the deaquation of $Cr(NH_3)_5.H_2O\ X_3$ and $Co(NH_3)_5.H_2O\ X_3$ complexes.[84-85] Chiu[86] recorded the DTA curve of sulfur. He found that enantiotropic change from rhombic to monoclinic sulfur corresponds to a peak at 113°C. Melting, transformation in liquid sulfur and finally boiling occurs at 124, 179 and 446°C respectively. Organic contamination in ammonium nitrate was detected by Du Pont Co.[87] Macak and Malecha[88] determined metallic nickel in catalysts. From the area of DTA curve determination of palladium and platinum in various catalysts was calculated.[89] Garn[90] has reported

DTA curves for a number of inorganic compounds used as standards. The amount of tricalcium silicate in Portland cement can be obtained from a large reversible transition which occurs at 915°C[91]. Ramachandran[92] has described the determination of chloride content in concrete composition. Chamberlin and Skarman[93] used DTA for finding decomposition temperature. For a particular 1:1 S to Cd ratio complex an endothermic DTA curve is obtained.

The literature survey shows that no work has so far been done on substituted thioureas and their transition metal complexes using DTA methods of analysis. The following substituted thioureas were selected for these studies to obtain greater information.

1. N-Methyl, N'-pyridyl
2. N-Allyl, N'-5 nitro 2-pyridyl
3. N-Benzyl, N'-2-Pyridyl
4. N-Phenyl, N' 2-Pyridyl
5. N-Phenyl, N'-5 chloro-2-Pyridyl
6. N-Phenyl, N'-5 bromo-2-Pyridyl
7. N-Phenyl, N'-5-iodo-2 Pyridyl
8. N-o-tolyl, N'-2-Pyridyl
9. N-o-tolyl, N'-5 chloro-2 Pyridyl
10. N-o-tolyl, N'-5 bromo-2 Pyridyl
11. N-o-tolyl, N'-5 iodo-2 Pyridyl
12. N-o-tolyl, N'-5 Nitro-2 Pyridyl
13. N-o-tolyl, N'-3 hydroxy-2 Pyridyl

INSTRUMENTATION

A Differential Thermal Analyser DTA 02 (German Make) was used. Nickel cylindrical sample tubes with a block in between and open ends were employed as sample holders.

Alumina (for TLC) BDH was used for the reference.

All weight measurements were made on single pan electrical balance

Differential thermal analysis is a dynamic temperature technique and hence has a large number of factors which can affect the resulting experimental curves[93]. To avoid discrepancies due to these factors the following standard conditions were maintained throughout the whole series:

1. Heating rate - 10°C/min
2. Sample amount - 5-10 mg.
3. No dilution was used
4. Amplification factor - 100
5. Paper speed ~ 3 mm/minute
6. Temperature range - 25°C to 800°C

RESULTS AND DISCUSSION

The DTA curve obtained for different compounds are represented in Figs. 5.1-5.10. The important peaks are also recorded in Table 5.1. The Table contains the nature of the peak (endothermic or exothermic), the temperature at which peak starts T_s, the maxima ΔT_{max} for exothermic or minima ΔT_{min} for endothermic peaks, the peak height and the peak width all in terms of degree centigrade. It also lists the number of major peaks observed.

In case of methyl, 2-pyridyl thiourea three peaks were observed. The first peak which was started at lowest temperature ($T_s \simeq 40^\circ C$) was found to be exothermic in nature and was broadest. The peak area of this was also largest among the three peaks observed for this compound. The peak reaches its maximum around $60^\circ C$ and $\Delta T_{max} \simeq 120^\circ$ (peak height).

The second peak, endothermic in nature, had starting temperature around $160^\circ C$. Peak area for this though smaller than first, was greater than the third one. The minimum of this occurred around $175^\circ C$ and ΔT_{min} had a value of $\simeq 70^\circ C$.

The third peak, though not very well defined had $T_s \simeq 360^\circ C$ and was endothermic. Minima of this occurred around $365^\circ + 30^\circ = 395^\circ$ and had $\Delta T_{min} = 15^\circ C$.

Allyl, 5-nitro-2-pyridyl thiourea, another compound containing an aliphatic group (Allyl) as substituent showed almost similar pattern as observed for methyl pyridyl thiourea. The first peak in former, as in the case of later, was exothermic in nature, had $T_s \simeq 40^\circ C$ and was broadest. The maxima of peak was around 30+[illegible] $100^\circ C$ and $\Delta T_{max} \simeq 130^\circ C$.

The second peak was found endothermic in nature and started at around 200°C. The minima occurred around 260°C with $\Delta T_{min} \simeq 65°C$. The third peak could not be observed in this case because of some instrumental defect that crept in.

In case of Benzyl pyridyl thiourea, a sharp departure from base line takes place at the lower temperature. In fact, a steep rise towards exothermic side starts at around 40°C and after about 95°C the ΔT becomes constant. A small peak starting at 490°C and endothermic in nature was observed. The peak had minima at 490°C, is very weak in nature and $\Delta T_{min} = 20°C$. This peak is followed by another which though endothermic, is sharper than earlier one. The minima ($\Delta T_{min} = 40°C$) is observed at 500°C.

In Phenyl pyridyl thiourea unlike methyl or allyl substituent an endothermic peak was observed at lower temperature. This peak started around 40°C and had $\Delta T_{min} = 70°C$ around 60°C. The peak is followed by two exotherms, the first of them appearing between 100°C-230°C had $\Delta T_{max} = 80°C$ at around 160°C and covering largest area. This is followed by the third one, covering least area and the parameters $\Delta T_m = 30°C$ at 300°C and $T_s = 270°C$.

Phenyl Iodo pyridyl thiourea also shows three peaks. All the three are endothermic. The first one, appearing at the lowest temperature starts around 40°C and reaches its minimum at 120°C with $\Delta T_{min} = 320°C$. It covers the largest area. The second peak starts at 520°C. The minima for this occurs around 580°C with $\Delta T_{min} \simeq 110^{\circ}C$. Third peak appears at 650°C with its minimum at 695°C with $\Delta T_{min} \simeq 130^{\circ}C$.

In case of o-tolyl-2-pyridyl thiourea only one peak could be located. This starts around 40°C and reaches its minimum at 130°C with $\Delta T_{min} = 530^{\circ}C$. The peak is endothermic in nature. The heat change involved here is so much that it almost goes out of the range of instrument.

Similar pattern is observed in case of ortho tolyl-5 chloro-2 pyridyl thiourea. The first peak had the parameters $T_s = 40^{\circ}C$, $\Delta T_{min} = 210^{\circ}C$ at 210°C. However, in this a second peak followed by very weak third peak, both endothermic in nature are also observed. The second peak started at 840°C and has $\Delta T_{min} = 25^{\circ}C$ at 870°C.

Ortho tolyl, 5-bromo pyridyl thiourea also gave the similar pattern. Here three peaks are observed too. All of them being endothermic. First, like earlier one started at 40°C, is broadest reached its $\Delta T_{min} \simeq 320^{\circ}C$ at 115°C. The second peak started at 380°C and showed its $\Delta T_{min} \simeq 50^{\circ}C$ at 470°C. Third the weakest one starts at 580°C and reached its minimum $\Delta T = 15^{\circ}C$ at 610°C.

Ortho-tolyl 5-nitro-2-pyridyl thiourea also gave similar pattern. The first peak though weaker than in other cases atarts at 40°C reaches its minimum $\Delta T = 30^\circ C$ at 80°C. The second one is endothermic too. It starts at 200°C and reaches its minimum $\Delta T = 40^\circ C$ at 250°C. However, the third peak, at higher temperature, could not be located due to instrumental defect.

The pattern showed by ortho-tolyl, 3 hydroxy-2-pyridyl thiourea is interesting in the sense that an exothermic peak in addition to the pattern shown by above mentioned complexes is observed at the beginning of the experiment. This peak appears as soon as the experiment is started. It reaches its maximum $\Delta T = 40^\circ C$ at 37°C ($< 40^\circ C$). The first peak corresponding to above mentioned compounds though could not be established with certainty, it follows almost the same pattern. Around 680°C a peak pattern starts. The first peak here starts at 680°C, reaches its minimum $\Delta T = 40^\circ C$ at 775°C followed by a second endothermic peak with starting temperature at 760°C and $\Delta T_{min} = 45^\circ C$ at 805°C.

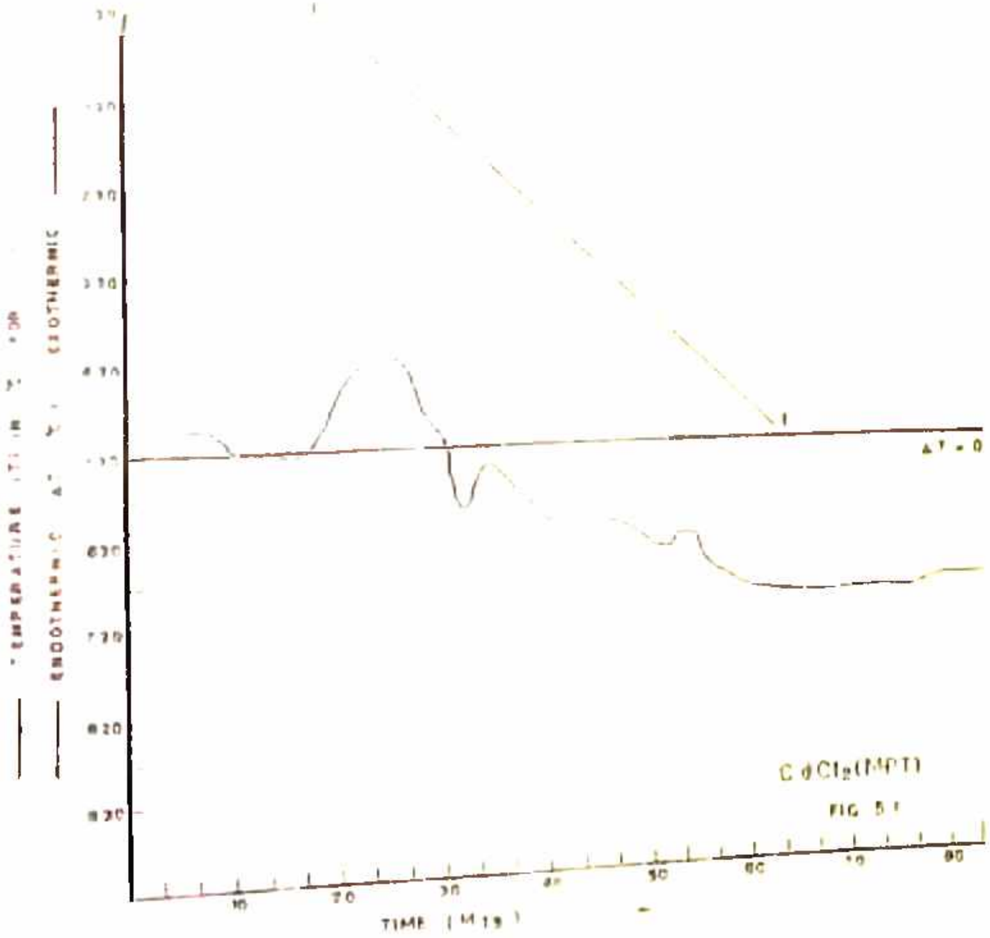
The behaviour of these complexes as shown by DTA curve is quite complex as is to be expected for complex compounds with a ligand containing more than one potential co-ordinating atom i.e. a multidentate ligand.[75] In such cases apart from a desolvation peaks and a decomposition peak, the other peaks represent a series of oxidation and fusion processes too complex to be resolved. Therefore, only qualitative interpretation can be attempted.

The results as compiled in Table 5.1 show that the DTA curves, in general, contain two or three major peaks. The first peak starts around 40°C and reaches its maximum or minimum below 100°C. In case of hydroxy substituent a very weak peak at 7°C was observed which was associated with the decomposition of the hydrogen bond between nitrogen of thiourea and oxygen of hydroxyl group.

Applied to the decomposition of CdS for the deposition of thin films it shows that thermal decomposition completes below 600°C in most of the cases and hence the deposited CdS films should be given the post heat treatment below 600°C only. This fact is supported by the work of K.L. Chopra et al.[94] They have shown that the photoconductivity gain of sprayed films increases as the temperature of post heat treatment increases. However, beyond 550°C it again starts decreasing, and as has been observed in the DTA analysis, the post heat treatment of the films should never be done beyond 600°C to obtain good and consistent results.

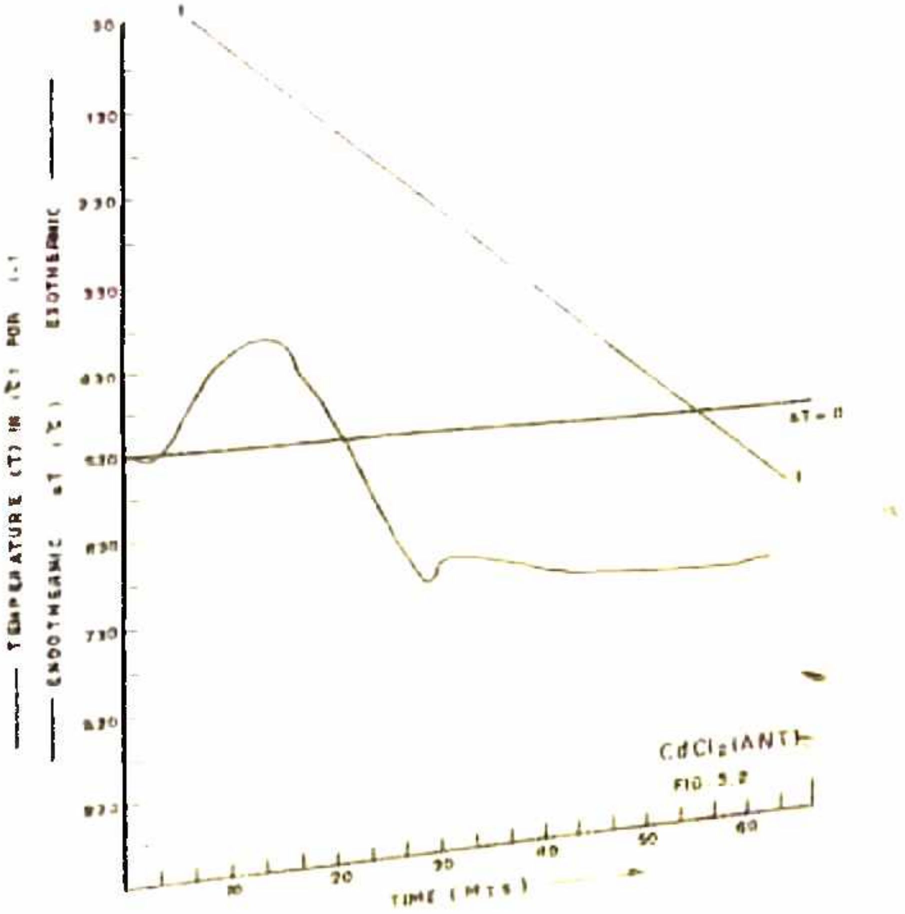
Table 5.1 (contd.)

Substituted thiourea	Complex	No. of peaks	Nature of peaks	Peak maxima or minima temperature (^{o}C)	Peak width	Peak height (ΔH)
N-o-tolyl,N'(2-pyridyl) thiourea	$CdCl_2(C_{13}H_{13}N_3S)$	1	i) Endothermic	130	120	530
N-o-tolyl,N'(5 chloro-2-pyridyl) thiourea	$CdCl_2(C_{13}H_{12}N_3SCl)$	2	i) Endothermic	210	360	210
			ii) Endothermic	870	60	25
N-o-tolyl,N'(5-bromo-2-pyridyl) thiourea	$CdCl_2(C_{13}H_{12}N_3SBr)$	2	i) Endothermic	115	340	320
			ii) Endothermic	470	150	50
N-o-tolyl,N'(5-nitro 2-pyridyl) thiourea	$CdCl_2(C_{13}N_4H_{12}O_2S)$	2	i) Endothermic	80	60	30
			ii) Endothermic	250	80	40
N-o-tolyl,N'(3-hydroxy-2-pyridyl) thiourea	$CdCl_2(C_{13}N_3H_{13}OS)$	2	i) Exothermic	37	10	40
			ii) Endothermic	805	50	40



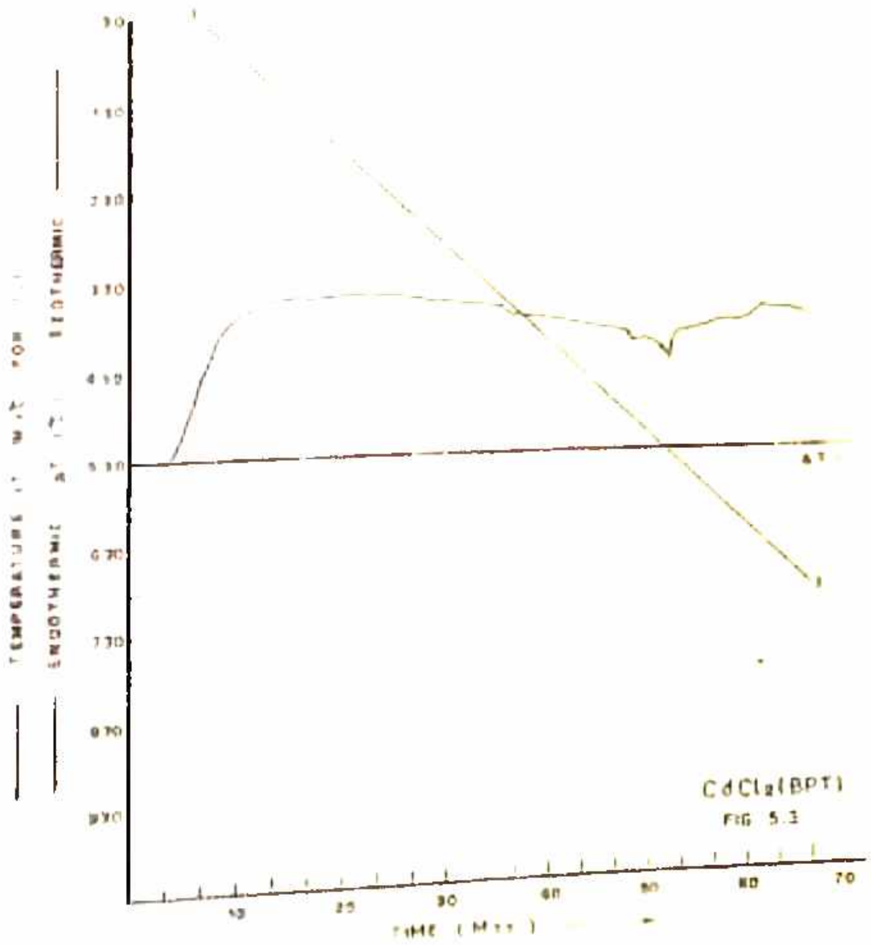
CdCl₂(MPT)

FIG. 5.1

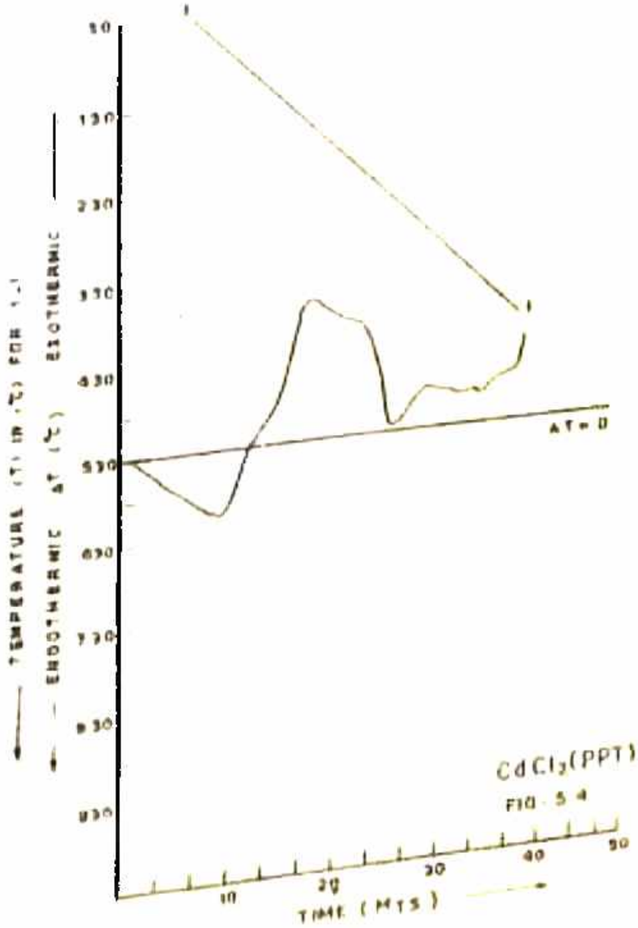


CdCl₂(ANT)

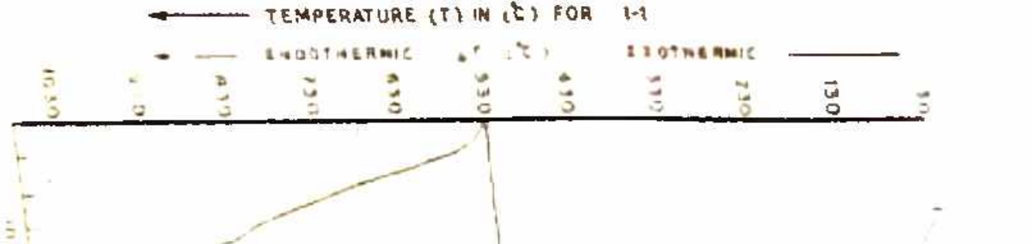
FIG. 5.2



CdCl₂(BPT)
FIG. 5.3

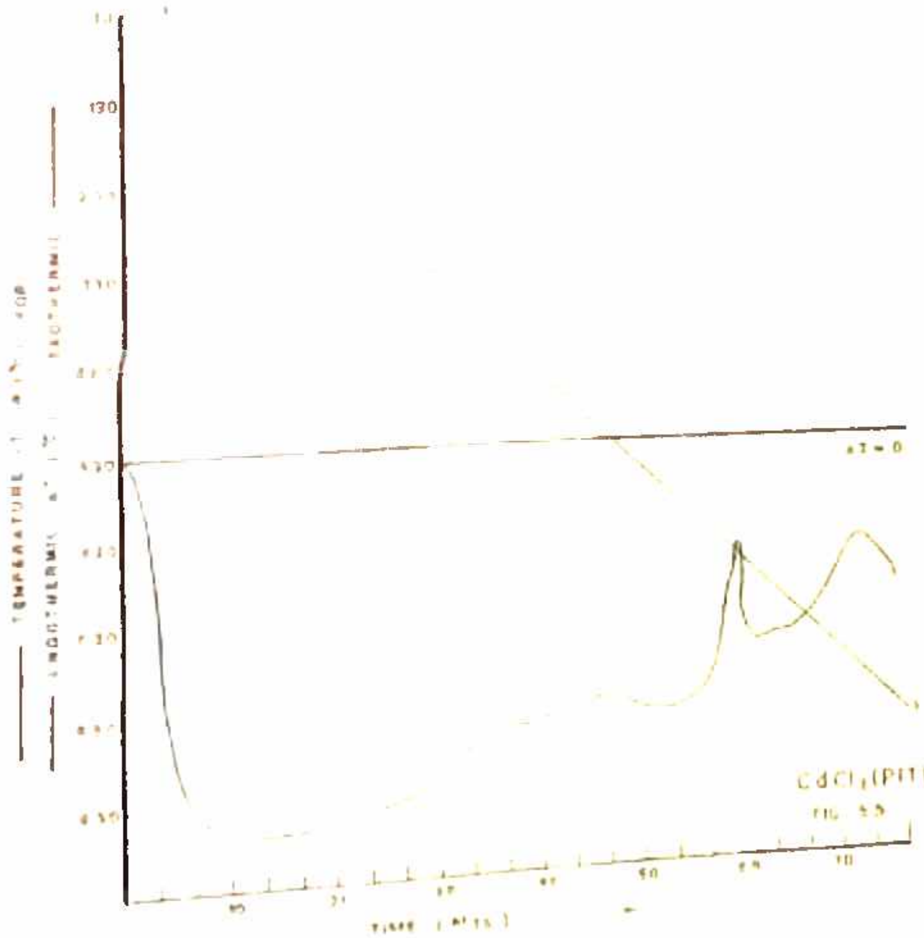


CdCl₂(PPT)
FIG. 5.4


TEMPERATURE (T) IN (°C) FOR 1-1
ENDOTHERMIC ΔT (°C) EXOTHERMIC
1030
930
830
730
630
530
430
330
230
130
30

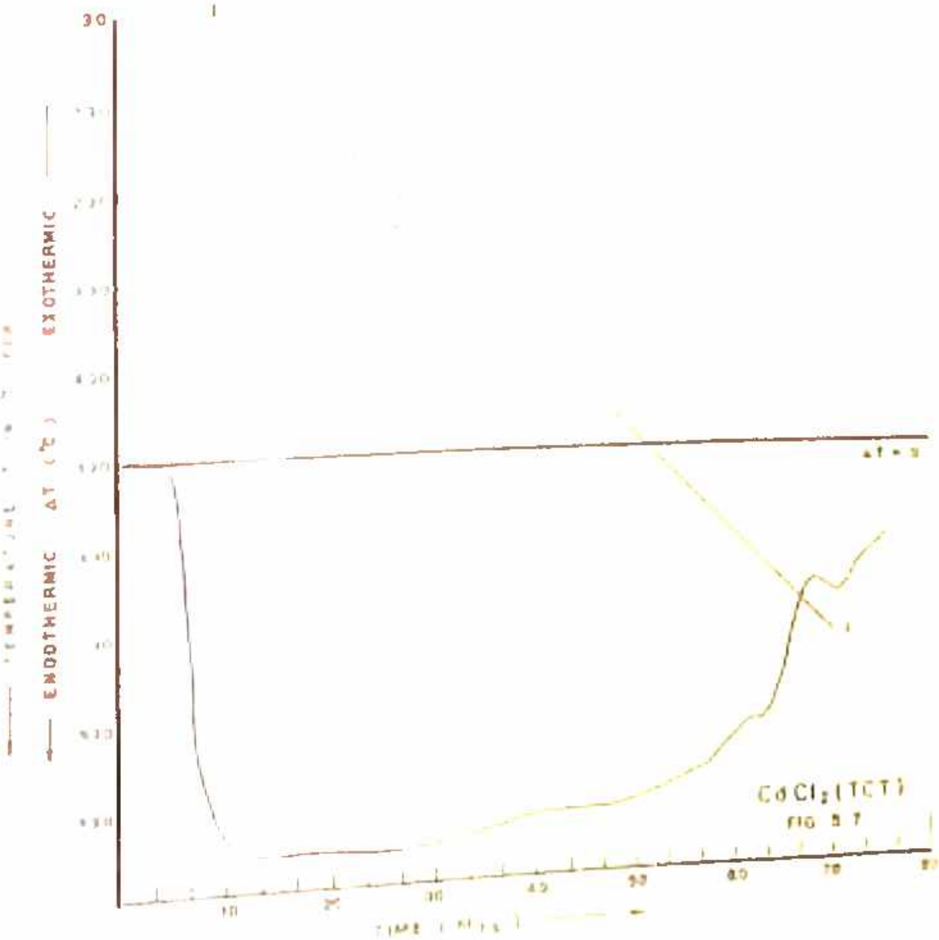
$CdCl_2(OTPT)$

FIG. 56

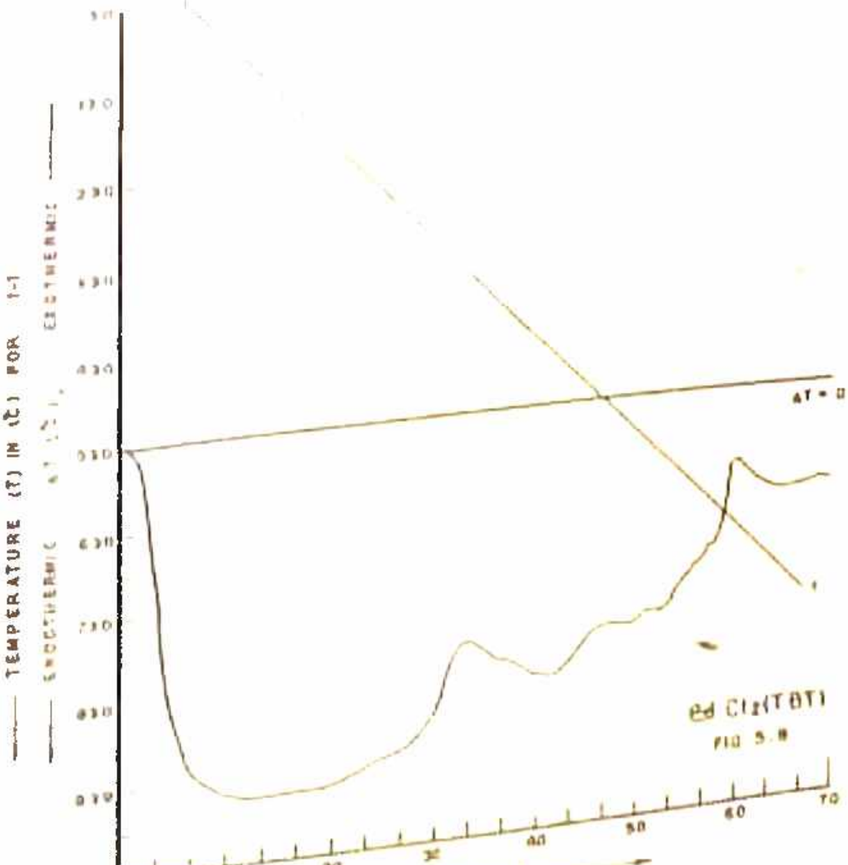


CdCl₂(PIII)

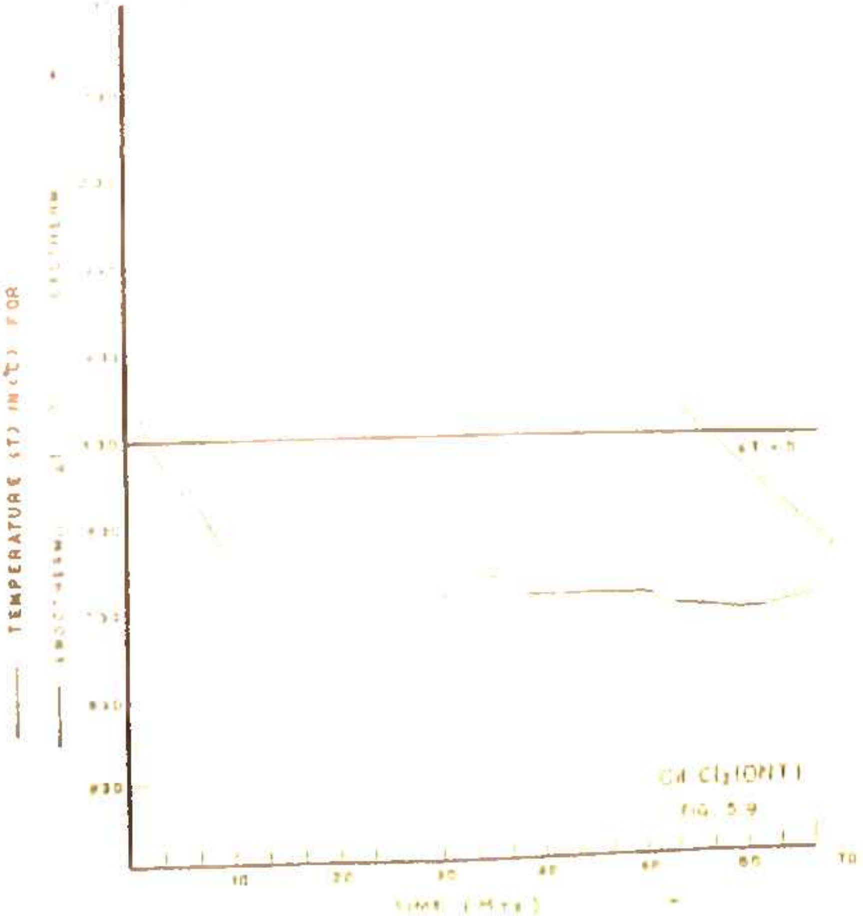
FIG. 55



Cd Cl2 (TCT)
FIG 5.7

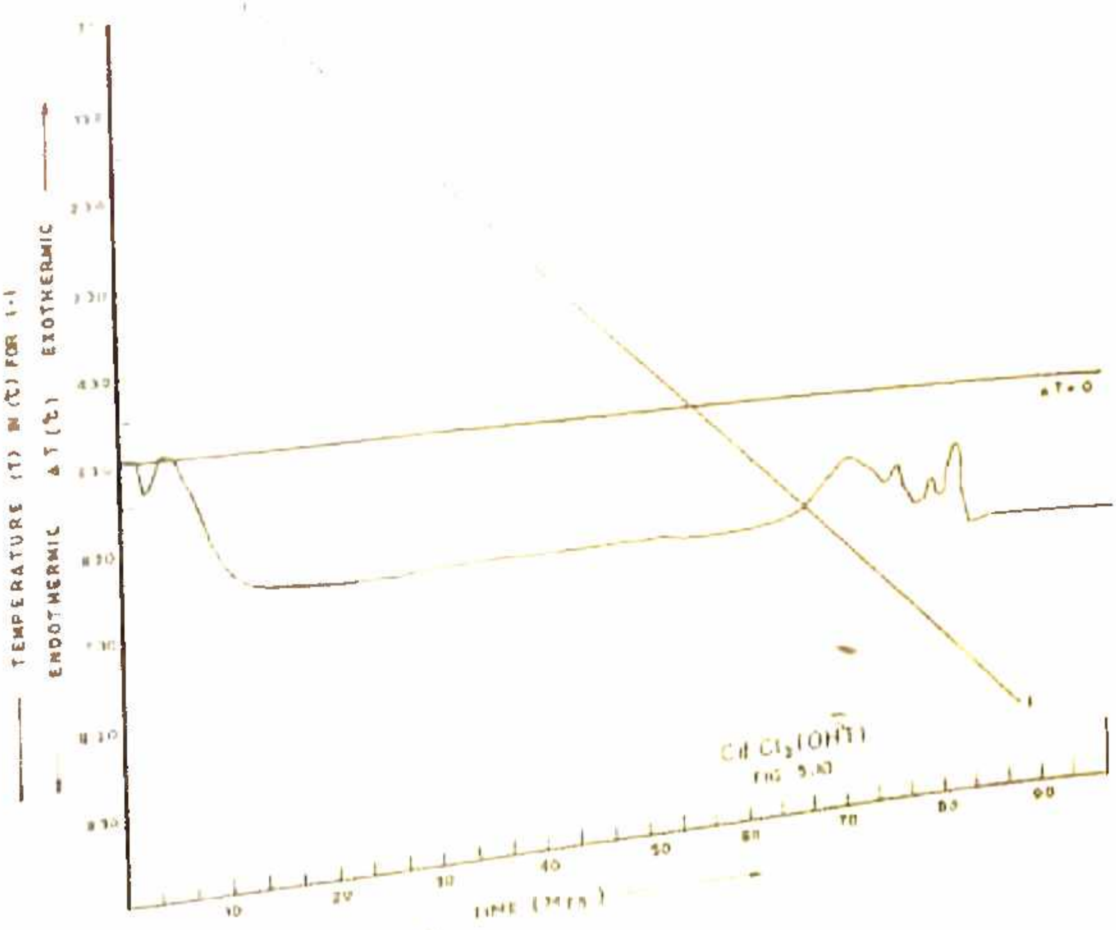


Cd Cl2 (TBT)
FIG 5.8



Cd Cl$_2$(ONT)

FIG. 5.9



Cd Cl$_2$(OHT)

FIG. 5.10

REFERENCES

1. Le Chatelier, H., Bull. Soc. Franc. Mineral, 10, 203 (1887).

2. Murphy, C.B., Minerals Sci. Eng., 2, Oct., 51 (1970).

3. Ashley, H.E., Ind. Eng. Chem., 3, 91 (1911).

4. Wholin, R., Sprechsaal, 46, 749, 767, 781 (1913).

5. Rieke, R., Sprechsaal, 44, 637 (1911).

6. Wallach, H., Compt. Rend., 157, 48 (1913).

7. Mellor, J.W. and Holdcraft, A.D., Trans. Brit. Ceram. Soc., 10, 94 (1910-1911).

8. Roberts-Austen, W.C., Proc. Inst. Mech. Engrs., London (1899); Metallographist, 2, 186 (1899).

9. Burgess, G.K., Nat. Bur. Std. (U.S.) Bull., 5, 199 (1908-1909).

10. Speil, S., L.H. Berkelhamer, J.A. Pask and B. Davis, U.S. Bur. Mines, Tech. papers, 664 (1945).

11. Holdsworth, H.S. and Cobb, J.W., Trans. Brit. Ceram. Soc., 22, 111 (1922-1923).

12. Fenner, C.H., Am. J. Sci., 36, 331 (1913).

13. Berkelhamer, L.H., U.S. Bur. Mines, Rept. Invest., R13762 (1944).

14. Kerr, P.F. and Kulp, J.L., Am. Minerologist, 33, 387 (1948).

15. Kauffman, A.J. and Dilling, E.D., Econ. Geol., 45, 222 (1950).

16. Foldvari-Vogl, M., Acta Geol. Acad. Sci.Hung. 5, 1 (1958).

17. Norton, F.H., J. Am. Ceram. Soc., 22, 54 (1939).

18. Grim, R.E., Ann. N.Y. Acad. Sci., 53, 1031 (1951).

19. Mackenzie, R.C., Differential Thermal Analysis of Clays, Central Press, Aberdeen, Scotland, 1957.

20. Stone, R.L., J. Am. Ceram. Soc., 35, 76 (1952).

21. Borchardt, H.J. and Daniels, F., J. Phys. Chem., 61, 917 (1957).

22. Borchardt, H.J. and Daniels, F., J. Am. Chem. Soc., 79, 41 (1957).

23. Wendlandt, W.W., in Techniques of Inorganic Chemistry, Vol. 1, H.B. Jonassen and A. Weissberger, eds., Interscience, New York, 1963, p. 209.

24. Wendlandt, W.W., J. Chem. Educ., 49, A623 (1972).

25. Murphy, C.B., Anal. Chem., 30, 867 (1958).

26. Murphy, C.B., Anal. Chem., 44, 513R (1972).

27. Smothers, W.J. and Y. Chiang, Differential Thermal Analysis: Theory and Practice, Chemical Publishing Co., New York, 1958.

28. ibid., 2nd Edn.

29. Garn, P.D., Thermoanalytical Methods of Investigation, Academic Press, N.Y., 1965.

30. Mackenzie, R.C., ed., Differential Thermal Analysis, Academic Press, London, Vol. I, 1970.

31. Kissinger, H.E. and S.B. Newman, in Differential Thermal Analysis in Analytical Chemistry of Polymers, Vol. XII, Part II, G.M. Kline, ed., Interscience, N.Y., 1962.

32. Gordon, S., in Encyclopedia of Science and Technology, Vol. 13, McGraw-Hill, New York, 1960, 556-559.

33. Gordon, S. and C. Campbell, in Handbook of Analytical Chemistry, L. Meites, ed., McGraw-Hill, N.Y., 1963.

34. Barall, G.M. and Johnson, J.F., in Techniques and Methods of Polymer Evaluation, P.E. Slade and L.T. Jenkins, eds., Vol. I, Marcel-Dekker, N.Y., 1966, Chapt. 1.

35. David, D.J., ibid., Chapt. 2.

36. Barall, E.M., in Guide to Modern Methods of Instrumental Analysis, T.G. Gouw, ed., Wiley-Interscience, N.Y., 1972, Chapt. 12.

37. Schultze, D., Differential Thermoanalyze, Deutscher Verlay der Wissenschaften, Berlin, 1969.

38. Ramachandran, V.S., Differential Thermal Analysis in Cement Chemistry, Chemical Publishing Co., N.Y., 1969.

39. Wunderlich, B., in Physical Methods of Chemistry, A. Weissberger and B.W. Rossiter, eds., Vol. 1, Part V, Wiley-Interscience, N.Y., 1971, Chapt. VIII.

40. R.S. Porter and J.F. Johnson, eds., Analytical Calorimetry, Vol..1, Plenum, N.Y., 1968.

41. ibid., Vol. 2, 1970.

42. R.F. Schwenker and P.D. Garn, eds., Thermal Analysis, Academic Press, N.Y., Vols. 1 and 2, 1969.

43. Wendlandt, W.W., Thermal Methods of Analysis in Chemical Analysis, Vol. 19, Wiley-Interscience, N.Y., 1974.

44. Mitchell, B.D. and Birnie, A.C., in Differential Thermal Analysis, R.C. Mackenzie, ed., Academic Press, London, 1970, Chapt. 22.

45. Manning, M., Industrial Res., Feb. 18 (1966).

46. Gray, A.P., Am. Lab., Jan., 43 (1971).

47. Murphy, C.B., Anal. Chem., 38, 443R (1966).

48. ibid., 40, 380R (1968).

49. ibid., 42, 268R (1970).

50. ibid., 44, 513R (1972).

51. Wendlandt, W.W. and Hoiberg, J.A., Anal. Chim. Acta, 28, 506 (1963).

52. ibid., 29, 539 (1963).

53. Atkinson, G.F. and Itzkovitch, Anal. Chim. Acta, 49, 195 (1970).

54. Brancone, L.M. and Ferrari, H.J., Microchem. J., 10, 370 (1966).

55. Vassallo, D.A. and Harden, J.C., Anal. Chem., 34, 132 (1962).

56. Barrall, E.M., Thermochim. Acta, 5, 377 (1973).

57. Kerr, G. and P.S. Landis, Anal. Chem., 44, 1176 (1972).

58. Chiu, J., Anal. Chem., 34, 1841 (1962).

59. Hermelin, M., Duval, C. and Xuong, N.D., Proceedings of the Third Analytical Chemical Conference, Budapest, 1970, Akademiai Kiado, 1970, p. 325.

60. Fauth, M.I., Anal. Chem., 32, 655 (1960).

61. Stammler, M., Explosivevstoffe, 7, 154 (1968).

62. David, D.J., Anal. Chim. Acta, 36, 2162 (1964).

63. Bohon, R.L., Anal. Chem., 35, 1845 (1953).

64. Graybash, R.J., May, F.G. and Forsyth, A.C., Thermochim. Acta, 2, 153 (1971).

65. Barrett, E.J., H.W. Hoyer and Santoro, A.V., Mikrochim Acta, 1970, 1121.

66. ibid., J. Thermal Anal., 2, 461 (1970).

67. ibid., Tetrahedron Letters, 5, 603 (1968).

68. ibid., 19, 2295 (1968).

69. Koch, E., Angew. Chem. Inter. Ed., 9, 288 (1970).

70. Krawetz, A.A., and Tovrog, T., I and EC Prod. Res. Dev., 5, 191 (1966).

71. Cross, C.K., Am. Oil. Chem. Soc., 47, 229 (1970).

72. Bsharah, L., I and EC Prod. Res. Dev., 6, 246 (1969).

73. Vamos, E., Schmierstoffe Schmierungstech., 1966, 84.

74. Trzebowski, N., Freiberger Forschungsh., A367, 257 (1955).

75. R.C. Mackenzie, ed., Differential Thermal Analysis, Academic Press, N.Y., 1970, Chapts. 7-15.

76. Stone, R.L., Anal. Chem., 32, 1582 (1960).

77. Petricciani, J.C., Wimberley, S.E., W.H. Bauer and Clapper, T.W., J. Phys. Chem., 64, 1309 (1960).

78. Wendlandt, W.W., George, T.D. and Horton, G.R., J. Inorg. Nucl. Chem., 17, 273 (1961).

79. Erdey, L. and Paulik, Acta Chim. Acad. Sci. Hung., 7, 27 (1955).

80. Mesmer, R.E. and Irani, R.R., J. Chem. Eng. Data, 8, 530 (1963).

81. Ozawa, T., Momota, M. and Isozaki, H., Bull. Chem. Soc., Japan, 40, 1583 (1967).

82. Ozawa, T., Isozaki, H. and Negishi, A., Thermochim Acta, 1, 545 (1970).

83. Sokolov, V.A. and Schmidt, N.E., Izr. Sekt. Fiz. Khim. Anal., Inst. Obsh. Neorg. Khim., Akad. Nauk. SSR, 27, 217 (1956); Chem. Absts., 50, 15200b (1956).

84. Wendlendt, W.W., D'Ascenzo, G. and Gore, R.H., Thermochim. Acta, 1, 488 (1970).

85. ibid., J. Inorg. Nucl. Chem., 32, 3404 (1970).

86. Chiu, J., Anal. Chem., 35, 933 (1963).

87. DuPont DTA Apparatus Bulletin, DuPont Co.

88. Macak, J. and Makcha, J., Anal. Chem., 41, 442 (1969).

89. DuPont Application Brief, No.9001331, July, 1970.

90. Garn, P.D., Anal. Chem., 41, 447 (1969).

91. Ramachandran, V.S., J. Thermal. Anal., 3, 181 (1971).

92. ibid., Materoaux et. Constructions, 4, 3 (1971).

93. Chamberlin, R.R. and Skarman, J.S., J. Electrochemical Society, 113, 84 (1966).

94. Gogna, P.K., Malhotra, L.K. and Chopra, K.L., Research and Industry, 22, 74 (1977).

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CHAPTER VI

This chapter presents the attempts to fabricate a thin film solar cell by non-vacuum chemical methods.

INTRODUCTION

It has been shown in earlier chapters that thin film solar cells are possibly most attractive of all the types fabricated so far. These cells are fabricated by employing various heterojunction combinations of semiconductors, the most established among these being the CdS-Cu_2S heterojunction. In recent years this Cu_2S-CdS heterojunction has been studied extensively, especially with respect to photovoltaic energy conversion for terrestrial applications.

The fabrication of CdS solar cells has been achieved by dipping single crystal (or vacuum evaporated thin films of CdS) in a cuprous chloride solution.[1,2] More recently Chamberlin and Skarman[3], Vedel et al.[4], Jordon[5], Martinuzzi et al.[6] and Bougnot et al.[7] have shown that it is possible to obtain cells from a CdS layer produced with a chemical reactive atomizer i.e. a spray, without affecting conversion efficiency. Chemical precipitation i.e. deposition of photosensitive films from solutions containing thiourea has also been used by various workers.[8-10]

Thin film CdS-Cu_2S solar cells have been successfully used in space applications.[11] It is the terrestrial application of these cells which is of a recent interest.[12-18] The biggest hurdle for mass production of these cells is their high cost. The cost of production could be reduced by employing purely chemical methods such as spray and chemical deposition. The following paragraphs, therefore, present our attempts in this direction.

EXPERIMENTAL

Chemicals

All the chemicals such as cadmium chloride, cadmium sulphate, thiourea and ammonia were of high purity (BDH) grade. Cuprous chloride (A.R.) was obtained from Johnson and Sons, London. The green colour impurities of this compound (due to hydroxides of Cu(II)) were removed by the following procedure:

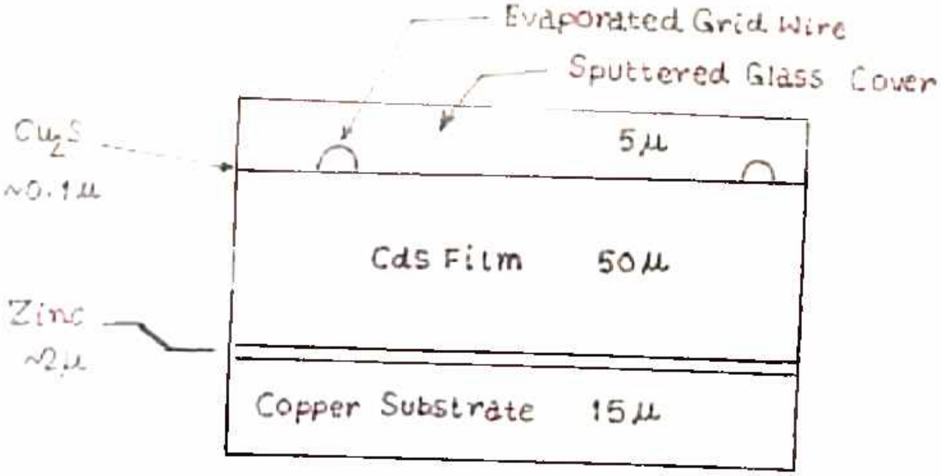
About 10 gms of CuCl was grinded in a mortar with enough 1M sulfuric acid to form a paste. This paste was stirred into a large quantity of dilute sulfurous acid (white powder settles down). This was then suction filtered and washed with 20-25 ml of glacial acetic acid. During washing process full care was taken to suck liquid so slowly that a thin layer always covered the salt before new portions of washings were added. Walls of funnel were also washed simultaneously. After glacial acetic acid 3, 30 ml. washings of absolute alcohol and six, 15 ml washings with anhydrous ether in exactly same way, as described above, were carried over. After the last portion of ether was sucked for about 30 seconds the white solid was quickly transferred to a well dried watch glass and kept in oven at (75-100°C) for about 25-30 minutes. The white powder so obtained was preserved in an air-tight bottle.

Cu(I) chloride is unaffected by air or light in absence of moisture. It develops a violet or blue tint in the presence of moisture. Moist air converts it into dark-green material that is probably a mixture of Cu(II) chloride and basic Cu(II) chloride.

Cu(I) chloride is slightly soluble in water. In NH_3 and HCl it forms colourless complex salts. These solutions readily absorb carbon monoxide from atmosphere. A maximum of 1 molecule of gas/atom of Cu is absorbed and a complex with $(CuCl.CO).2H_2O$ could be isolated. In order to avoid all these difficulties a fresh saturated solution has always been used.

CELL FABRICATION

The cell design attempted for fabrication in present study is basically the same as developed by Clevite Corporation and later described by Shirland et al.[1,13-18] The schematic represented of present cells could be shown as:



Terrestrial CdS Cell

The stepwise fabrication is given below:

(a) Substrate Material

It has ~~been~~ long been recognised that the material of the substrate is a key factor in the quality of the CdS thin film solar cells which can be formed on it. However, it remains difficult to relate variations in cell quality quantitatively to specific characteristics of the substrate.

Space CdS cells, in general, are fabricated using light weight metallized plastic such as Kapton or Mylar, substrates. For terrestrial cells the metallic foil substrates were considered more advantageous as they are expected to provide impermeability and thus exclude oxygen, water vapour and other contaminants that might react with the semiconducting layers. Moreover, the elimination of all polymeric materials is expected to improve the long term physical stability of the structure.

Many high output CdS thin film solar cells have been fabricated on Mo foil, electroformed Zn foil, electroformed Zn on Cu foil and a number of other materials.[14] However, in view of constraints of availability and economy all precious metals and other expensive materials were avoided and only following materials were tried as substrate materials:

(a) Aluminium,
(b) Brass,
(c) Copper, and
(d) Electroformed Zn on Cu foil.

The pure zinc could not be used as it is found difficult to prepare foils with a thinness required for these purposes.

(b) Substrate Preparation

Substrate is the 2x2 cm^2 and about 0.001" thick metal foil. The materials were obtained from and cut into shape at the Central Workshop. The substrate is cleaned by degreasing using commercial degreaser, followed by a light etch in warm (40-45°C) 1:3 HNO_3 solution. After water rinsing and drying with absolute alcohol and acetone, the substrate is used immediately (within one hour) for CdS film deposition. Zinc was electroplated on Cu using zinc-acid-sulphate solution ($ZnSO_4.7H_2O$ - 360 g/l; NH_4Cl - 30 g/l; Sodium Acetate - 15 g/l and glucose - 120 g/l, temperature - 20-30°C, current density - 1.5-3.0 amp/sq.dm or 1-2 amp/in^2).

(c) CdS Film Deposition

Both spray and chemical precipitation were used to deposit a thin CdS film.

(i) CHEMICAL PRECIPITATION

The method followed was that of Propov and Shulman.[10] Anhydrous cadmium sulfate solution (1M-25ml) was taken in a beaker. Glass plates were dipped at 45°C. A thiourea solution (1M) is then mixed with constant stirring. The metal to ligand ratio of 1:1.5 to 1:1 was maintained. Few drops of 4.5M NH_3 solution were also mixed. After vigorous stirring (using magnetic stirrer) the solution is allowed to settle down. The reaction was carried out both at room temperature as well as at 80°C. In former case the reaction takes about an hour to precipitate yellow or reddish yellow deposit on glass plate as well as on the walls of the beaker, whereas in later case it takes only 10-20 minutes. The plates were then removed from the beaker and washed with distilled water and dried in air oven for 20-30 minutes at $\sim$120°C. The thickness of films was determined by weighing.

The deposited films appeared transparent and uniform but when seen under microscope appeared like the scattered dark clouds. These films were soluble or washable with dil HCl or HNO_3.

(ii) SPRAY DEPOSITION

The apparatus needed to carry out the chemical spray process consists basically of a device to atomize the spray solution and some sort of substrate heaters. Figure 6.1 shows a typical experimental set-up. Since neither the gas used to atomize the spray nor the ambient atmosphere contributes to the composition of film being deposited, a single-fluid nozzle is used in which atomization is achieved by pressurizing the liquid.

(iii) SPRAY NOZZLE

A pyrex glass conical flask was used as spray bottle. The capacity of flask was 100 ml. However, only 50 ml. solution could be handled conveniently at a time.

(iv) CARRIER GAS

Air was used as carrier gas. Compressed air was passed at the controlled pressure of 40-50 kg/cm^2. Most of the experiments were made at ~ 50 kg/cm^2.

To control the spray rate and uniform deposition an adjustment was made by varying the height of the spray nozzle from the substrate. This height varies from 9"-14" for different pressures applied.

As cadmium forms as 1:1 metal to ligand complex (thioureas being ligand) 1:1 thiourea and cadmium chloride solution mixture were prepared. Concentrations of metal and ligand solutions were varied from 0.1M to .001M. Metal complex solutions (0.01M) were also sprayed.

A hot plate (Tempo-Toshniwal) was used as heater. The temperature of substrate was varied from 250-350°C. In case of electroplated Zn on copper foils a lower substrate temperature was used. The highest temperature used was around 450°C. Solution was sprayed in stages initially ~10% and subsequently rest 90%.

After spraying all the required solution, plates were heated for another 10 minutes to ensure complete volatilization of other decomposed products such as NH_3, H_2O, CO_2, HCl etc. A yellow colour deposit at lower temperature and chocolate brown colour at higher temperature is clearly seen after deposition. These foils are then removed and cooled down at room temperature.

(d) Deposition of Cu_2S Barrier Layer

To form the Cu_2S carrier, following steps were followed.

(i) HCl etching. Deposited CdS films were dipped for a second or two in very dilute hydrochloric acid (10^{-5}N-10^{-6}NHCl).

(ii) CuCl dipping. After HCl etching, the CdS films were dipped into a freshly prepared CuCl solution. Few drops of HCl were added in the aqueous solution to avoid the formation of Cu^{+2} ions. Optimization of the CuCl dipping process ~~has~~ like other steps had to be done empirically. The temperature dip around 80°C and time of dipping around 5-10 seconds were determined in present study. At this stage the yellow colour plate immediately turns into blackish brown. In some of the cases a thick precipitate also separates out damaging the CuCl solution.

(iii) Rinsing. Plates were rinsed with de-ionized water (triple distilled) after CuCl dip. Normally three rinsings of 5 seconds duration each were used.

(iv) Drying. Plates were dried in an air oven for 20-30 minutes at 30-40°C and finally at higher temperature ~100-120°C. Cells dried at higher temperature does not give current.

(v) Ohmic contacts. Finally the ohmic contacts to the two sides were made by mechanically pressing and current measurement were made with the help of micro-galvanometer (least count 2 μA).

RESULTS AND DISCUSSION

Currents more than 50 µA but less than a mA were observed in dark and sunlight. In some of the cases there was an increase in current on exposure to sunlight. The current so produced decays to zero value, within 10-15 minutes. This effect was also observed in dark (i.e. when cells were not exposed to light). However, in few cases the rate of decay was slower when cells were illuminated than they were tested in dark. Unfortunately, some of these results are not reproducible and only ten to fifteen per cent of the cells fabricated show such effects.

This led to a detailed examination of the factors which possibly are responsible for this. These have been discussed hereinafter.

The prime factor appears to be a fuller understanding of the reactions involved in the process of formation of CdS from the mechanistic point of view. In Chapters III, IV and V, a detailed study has been made of this. The conclusions arrived at from the experimental results should be considerable use in preparing thin film CdS cells by these methods.

The other factors, which have been detailed out are:

Zinc plating: CdS makes a blocking contact to copper and silver and a few other metals, with copper substrates. A zinc interlayer has been used to obtain an ohmic contact. Other metals such as cadmium, aluminium chromium and tin have been tried with a degree of success, but zinc has given the best overall results and has become standard in spite of the fact that it has some undesirable characteristics for such applications. However, zinc has given best results only when electroplated from a fluoborate bath under a rather narrow range of conditions arrived at empirically. Vacuum deposited zinc interlayers, and zinc electroplated from acid or cyanide plating baths always gave cells with lower outputs.

Some of these observations were generally confirmed in this study. When copper or aluminium or brass foils were used as substrates no current was observed either in dark or when illuminated with 1500 watt tungsten light or placed in direct sunlight. Moreover, the yellow colour deposit of CdS is very poorly adhered to the aluminium and brass foils. The zinc plated Cu was the only substrate material to give the well adhered films and current of few micro amperes.

The zinc plating on Cu foil substrates appears to be fulfilling several functions. First, it provides a low resistance ohmic contact, second it acts as a diffusion barrier[8] to prevent the migration of copper from the substrate into the CdS film as it forms, and third it appears to cover minor structural inhomogeneities of the surface of the copper foil substrate to yield a more homogeneously structured CdS film. This latter factor is probably a result of the well known superior "throwing power" of the fluoborate over other types of electroplating baths.

It is found that higher the substrate temperature better is the appearance of CdS deposit. Film looks more uniform and bright in colour. However, when electroplated zinc on Cu is used the temperature has to be kept around 300°C as Zn melts and volatalizes at higher temperature.

The control of spray rate is another difficulty which is faced during spray deposition. It has been observed experimentally, that slower is the deposition, better is the result. There are three parameters which determine the spray rate in present set-up experiments:

(a) The pressure at which the carrier gas is supplied.

(b) The height of spray nozzle from the substrate and

(c) The solution concentration of cadmium chloride and thiourea or their metal complex.

It is obvious that the concentration of solution should be kept as low as possible for slower deposition. But some practical difficulties are encountered while using very dilute solutions. It not only takes longer time to spray required amount but also the spray is to be carried out in stages. The reason for this is quite obvious. As more and more solution falls on the substrate the temperature of the substrate goes on decreasing. It might drop well below the decomposition temperature of the complex to give CdS. Moreover, as the temperature decreases, the rate of volatilization of other decomposed products such as NH_3, H_2O etc. and solvent also decreases. This allows solvent to remain on the substrate which is undesirable because when this solvent is allowed to evaporate at such a high temperature the bubbling caused by boiling of the liquid damages the uniformity of the film. Therefore, care must be taken that the solution drops must evaporate the moment they fall on the substrate. This is only possible when spray rate is kept as low as possible.

Contrary to this is the effect of degree of atomization of the solution. It is observed, higher is the degree of atomization, better are particles spread.[3] In present case, more is the air pressure applied more is the degree of atomization. Increase in carrier gas pressure also increases the spray rate which is contrary to above observation. Chamberlin and Skarman[3] have suggested 20 ml/sec. as the ideal spray rate for (10^{-2}-10^{-3}M) solution concentration. This could be achieved in present case by supplying carrier gas around 45-50 kg/cm^2 pressure and then finally adjusting the height of spray nozzle between 9"-14". In most of the cases the height was kept at 14". Concentration of solution used was 10^{-2}M and around 200 ml. of total solution was sprayed. Thickness of the film was measured by weighing on micro-single pan electrical balance.

The principal function of HCl pre-etch appears to be to texture the CdS surface so that the cell surface acts as a light trap. The etch also appears to open the boundary region between CdS grains so that the Cu_2S penetrates the grain boundary region. Both effects result in increased absorption of the incident light and hence should give higher cell currents. However, it has not been possible to characterize the cadmium sulfide films to determine what parameter is varying and thus to determine a priori the optimum conditions for etch, CuCl dip and rinsing.

In addition to these, the proper ohmic contacts to the cells is another difficulty faced in present work. In absence of vacuum evaporation, the contacts were made by mechanical press method. During measurements it was found that there were a few points on the Cu_2S layer where the current was comparatively more than the other places. This may be due to two reasons:

(a) Improper contacts to the p-Cu_2S layer or

(b) non-uniformity of the film.

It seems more probable that the CdS film is not uniform throughout as a result of which more than one discrete n-p junctions are formed on the substrate. This means there would be some points where no current would be observed and at some points currents of different magnitude would be obtained.

CONCLUSION

The outgoing discussion suggests that the various parameters such as substrate temperature, solution concentration, cleaning, rinsing, HCl etching and CuCl dip conditions, post-heat treatment, purity of raw material etc. are to be optimized first in order to get the reproducible results. Moreover, once determined they must be strictly followed. The optimization of all these parameters is more or less empirical in nature, and therefore, requires the characterization of film growth at each step. This makes the above mentioned film deposition techniques more or an art rather than a science. Therefore, though as pointed out earlier, the techniques show great potential and promise for mass production, they must be mastered first before a solar cell fabrication is attempted. However, because of the constraints of availability of film growth characterization facilities and binding of time the attempts in this direction could not be extended further.

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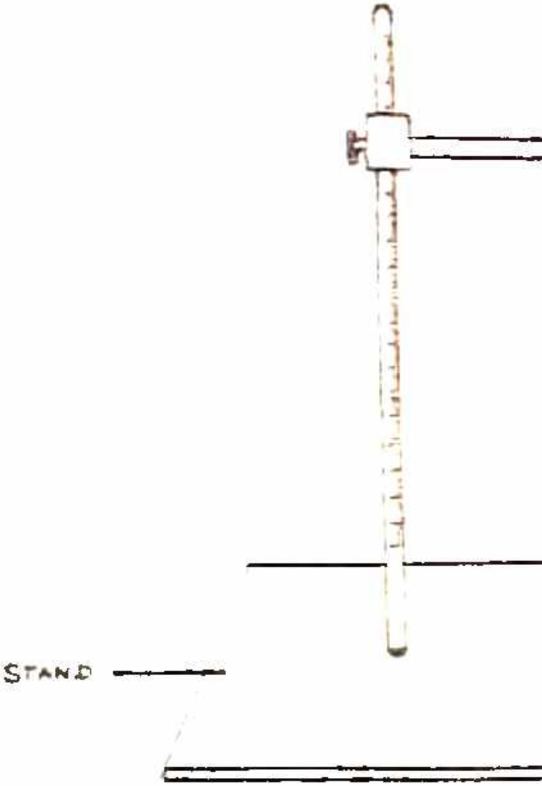

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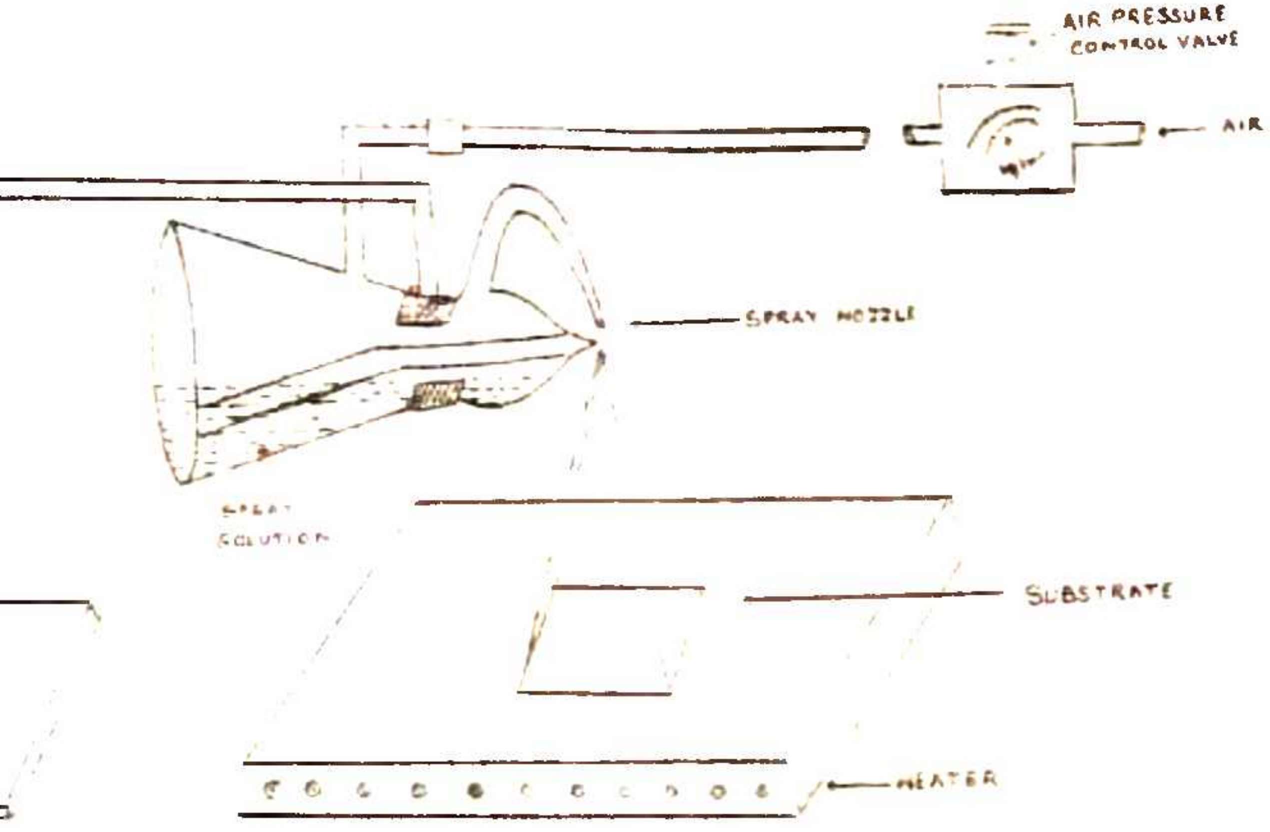

EXPERIMENTAL SET UP

Fig 6.1

REFERENCES

1. Fred A. Shirland, Adv. Energy Conv., 6, 201-22, 1966.

2. F.A. Shirland, W.J. Biter, E.W. Greeneich, A.J. Simon and T.P. Brody, Report NSF/RANN/SE/AER74-14918 A01/ FR/76 (1977).

3. R.R. Chamberlin and J.S. Skarman, J. Elec. Chem. Soc., 113, 85 (1966).

4. J. Vedel, E. Castel, p. 333-337, International Conference, Toulose, March 1-5 (1976).

5. J.F. Jordon, p. 508-514, IEEE, Photovoltaic Specialist Conference, Scottsdale Arizona, May 6-8 (1975).

6. S. Martinuzzi, F. Cabane-Brouty, J. Gervais, A. Mostavan, p. 303-308, International Conference, Toulouse, March 1-5 (1976).

7. J. Bougnot, M. Perotin, J. Marucchi, M. Sirkis and M. Sarelli, 12th IEEE Photovoltaic Specialist Conference, Baton Range, Louisiana, Nov. 15-18 (1976).

8. N.V. Philips, Gloeilampenfabricken CA 53:P21208f (1958), also CA 54:105506d.

9. G.A. Kiteev, S.G. Mokrushin and A.A. Uritskaya, Kolloid. Zh. 27(1) 51-6 (1965), also G.A. Kitaev et al. in ref. Chapter 2.

10. Propov, V.P. and Shulman, V.M., Sb. Nauch. Tr., Vsch. Nauch-Issled Inst. Lyuminoforov Osoba Chist. Veshchestv 3, 132-4 (1970), CA, 81: 70432 p.

11. R.J. Mytton, Comparative review of Si and CdS solar cells.

12. Thin film solar cells for Terrestrial Applications, F.A. Shirland, W.J. Biter, E.W. Greeneich, A.J. Simon and T.P. Brody, Third Quarterly Progress Report on NSF Grant AER74-14918 A01 NSF/RANN/SE/ AER 74-14918 A01/PR/7611.

13. ibid., Second Quarterly Progress Report on NSF Grant AER 74-14918 A01 NSF/RANN/SE/AER 74-14918 A01/ PR/75/4.

14. ibid., First Quarterly Progress Report on NSF Grant AER 74-14918 A01 NSF/RANN/SE/AER 74-14918 A01/PR/75/3.

15. ibid., Fourth Quarterly Progress Report on NSF Grant AER 74-14918 A01 NSF/RANN/SE/AER 74-14918 A01/PR/75/2.

16. ibid., Third Quarterly Progress Report, ibid, PR/75/1.

17. ibid., Annual Progress Report on NSF Grant AER 74-14918 NSF/RANN/SE/AER 74-14918/TR/74/4.

18. ibid., Final Report on NSF Grant AER 74-14918 NSF/RANN/SE/AER 74-14918 A01/FR/76.

* * *

SUMMARY

The present thesis embodies the work carried out on the problem entitled 'Studies on chemical deposition of thin films for solar cells by thioureas and their transition metal complexes'. The work has been presented in six chapters.

In the first chapter, a brief review of solar cells has been presented with particular reference to the needs and efficiency of thin film solar cells. It is found that the main problem facing the workers engaged in the field is to reduce the cost of solar cells so as to compete with other established sources of energy. In this context the thin film solar cells have an edge over the conventional single crystal solar cells.

Definitions and mechanism of growth of thin films are described in chapter II. Also described are the various methods of fabrication of thin films. A survey of literature reveals that though vacuum methods are good in terms of purity, well controlled growth, crystallinity and uniformity of films, they are applicable for growing thin films, only to a limited area. The non-vacuum chemical methods, on the other hand, promise a great potential for solar cells. The simplicity of these methods which include mainly chemical precipitation and spray, is the biggest boon and therefore, these are the methods which form the crux of present work. With the aim of improving the methods of CdS deposition as thin films, it has been felt necessary to study both the theoretical and experimental aspects of thioureas and their substituted forms. This would enable the exploration of newer and better reagents. The later chapters present the attempts to achieve this goal.

Chapter III describes briefly HMO method and presents the theoretical calculations on various substituted thioureas. The comparison in terms of electron indices such as ionization potential, electron affinity, charge density, heat of formation, energy of isomerization, delocalization energy etc. reveals the superiority of substituted thioureas over thiourea as they help in traping the metal ion by giving rise to a stabler complex and thus prevent the precipitation of unwanted cadmium hydroxide. The pyridyl group substitution is found to be the best in this regard.

Chemical precipitation and spray both involve the formation of a complex during the process of film deposition, the nature of which is not very well established.
Chapter IV presents the synthesis of a series of substituted thioureas and their transition metal complexes. Their characterization by ir, uv, magnetic measurements, molar conductance and elemental analysis reveals that most of these complexes have metal to ligand ratio as 1:2 (except Cd) and are non-electrolyted (except Zn). Further, they crystallize out in an octahedral environment.

The thiourea complexes of transition metals, upon decomposition give cadmium sulphide. A qualitative study of decomposition temperatures of these complexes by differential thermal analysis forms the Chapter V. The study reveals that the decomposition of most of the complexes completes below 600°C and thus the post-heat treatment of CdS films may be carried out below the 600°C.

Finally, in the last chapter our attempts to fabricate a thin film CdS-Cu_2S solar cell by the non-vacuum chemical methods utilizing the information gathered by above studies have been presented. The results indicate that the technique must be mastered by optimizing all the parameters involved, which are more or less empirical in nature, so as to get good and consistent results.

Figures and tables are numbered such that each number is preceded by a chapter number. References, together with the tables and figures for a particular chapter are given at the end of that particular chapter so as to complete each chapter in itself.

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