RESULTS AND DISCUSSION

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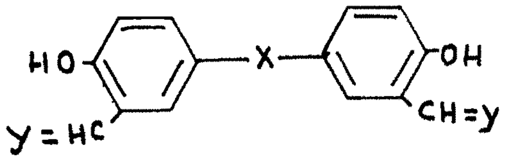
III 1. Bis-azo disalicylaldehyde and its transition metal complexes.

Coordination polymers of bis-(salicylaldehydes) and bis-(salicylaldimines) (I) where X = CH_2 and SO_2 have been



(I)

	X =	Y =
(a)	CH_2	0
(b)	SO_2	0
(c)	CH_2	NH, NR, NR'-N
(d)	SO_2	NH, NR, NR'-N
(e)	$N_2-C_6H_4C_6H_4N_2-$	0

investigated by various investigators. Thus Terent'ev, Rode and Rukhadze[47,72] and Rode, Nekrasov and Terent'ev[147] prepared Cu, Ni, Co and Fe coordination polymers of (I-a) and (I-c) and studied their thermal stability, reflection and luminescence spectra and magnetic susceptibility. Marvel and Tarkoy[102] prepared the coordination polymers of Fe, Co, Ni, Cu and Zn with (I-a) and (I-c) and studied their thermal stability. Goodwin and Bailer (Jr.)[100] studied the coordination polymers of Fe, Co, Cu and Ni with (I-c) and (I-d). Bel'skii and Tsikunov[74] prepared Fe, Co, Ni, Zn and Cd coordination polymers of (I-c) and studied their EPR spectra. Luvisi and Chenicek[148] studied the removal of Fe, Co, Cu and Cr from organic liquids (e.g. gasoline) by treating them with polymeric (I-c). We have synthesised (I-e) by the method of Sen and Ghosh[140] and prepared its coordination polymers with Co(II), Ni(II) and Cu(II) in pyridine and with Co(II) and Cu(II) in dimethylformamide in absence of pyridine. Their magnetic moment, calculated from magnetic susceptibilities and diamagnetic corrections are given in table R-1. Ohata et al.[149] have prepared Cu(II), Ni(II) and Co(II) chelates of 5-aryl azosalicylaldehydes and their schiff bases.

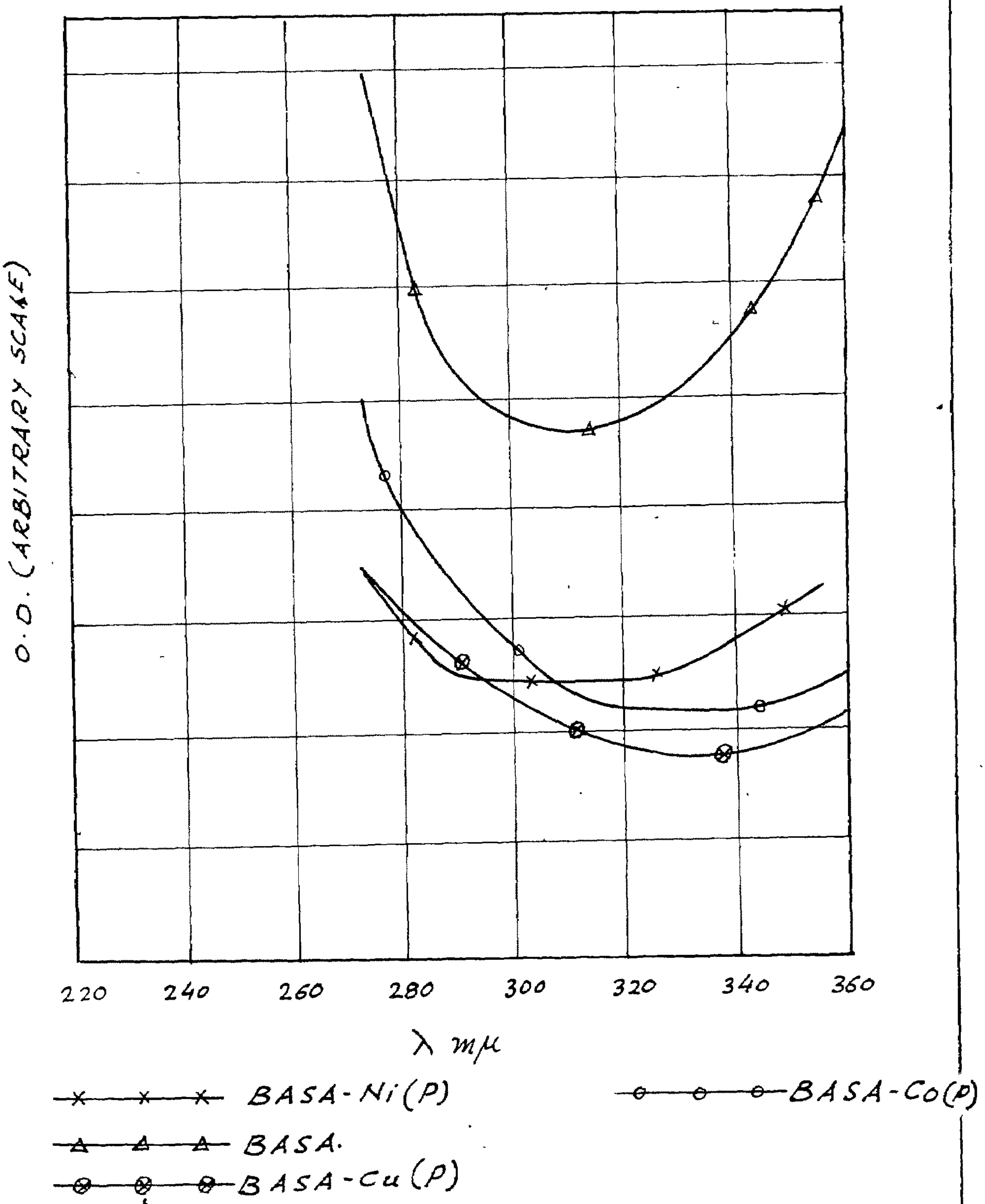
(a) 4,4'-Bis(m-formyl p-hydroxyphenylazo)biphenyl: (BASA):

The above ligand (BASA)-(I-e) was prepared by the action of tetrazotised benzidine on salicylaldehyde. The ultra-violet and visible absorption spectra of the ligand are given in figs. R-1 and R-2 ; and some important IR bands are given in table R-2. The ligand has absorption bands at 418 mμ and 510 mμ in the visible spectrum. Normally azo compounds would have absorption bands at 280-90 mμ and 350-60 mμ. The red shift of the bands is an indication that there is "through conjugation" between phenyl rings through N_2 groups. Thus the phenyl rings and N_2 groups of the ligand molecule are considered to be coplanar. Further, azo-hydrazone tautomerism is well established in many cases.[150-53] Long wavelength band will be weaker in azo compounds, but much stronger in hydrazones. The present observations indicate the existance of tautomerism(II) (a and b) for the ligand in dimethylformamide solution and may include the intermediate form (II-c).

Table R-1

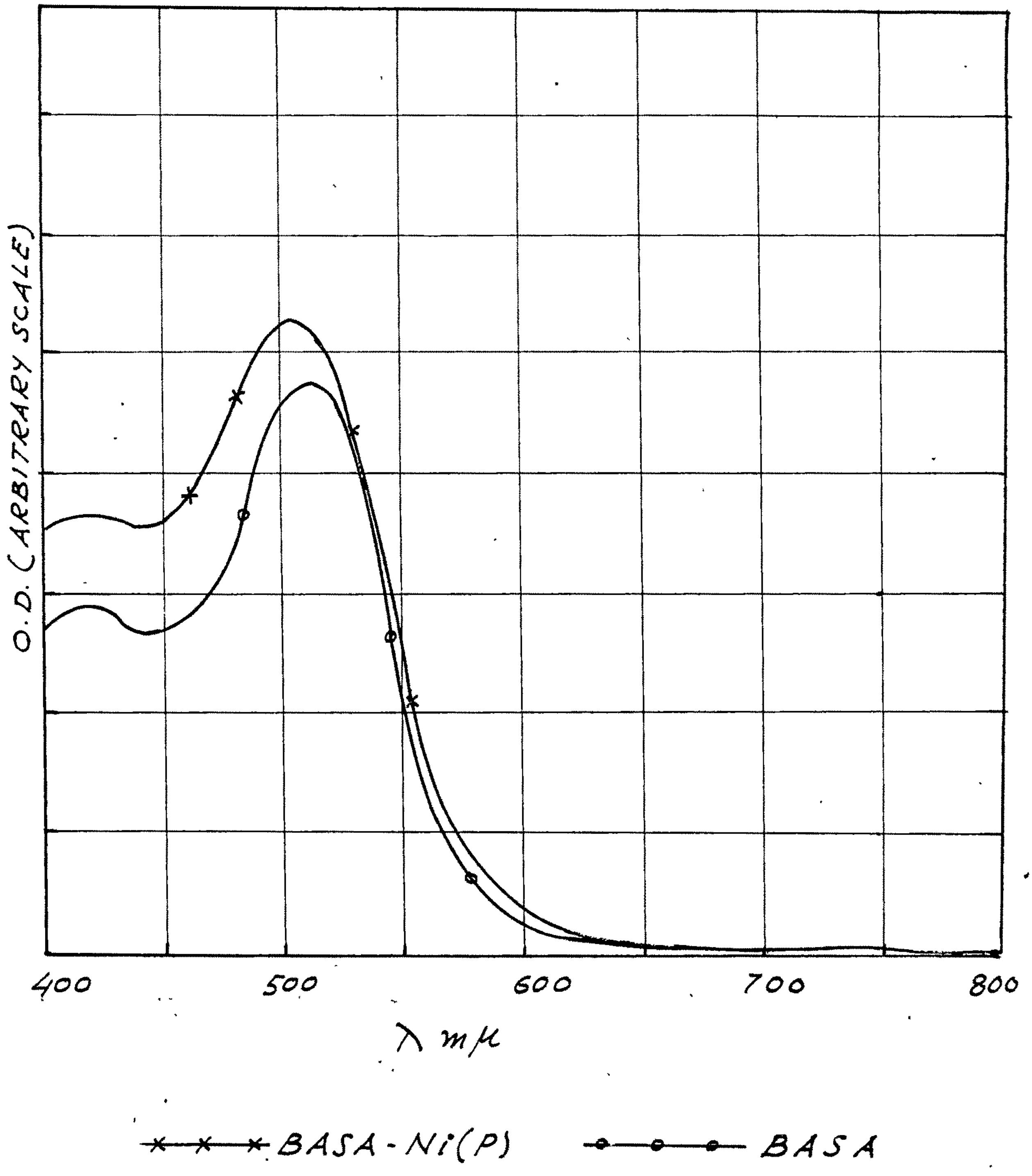
Magnetic moments of chelates and chelate polymers of azo ligands

No.	Compound	Molar magnetic susceptibility (per-metal atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per-metal atom) $X'_m \times 10^6$	Magnetic moment (per-metal atom) μ (B.M.)
1	BASA-Co (p)	8468	8792	4.74
2	BASA-Cu (p)	1756	2102	2.27
3	BASA-Ni (p)	2859	3374	2.86
4	BASA-Co (D)	9638	10221	5.00
5	BASA-Cu (D)	2181	2459	2.44
6	BASAO-Ni	2841	3126	2.75
7	AAC-Cu	1697	1918	2.16
8	BAAC-Cu	2053	2439	2.43



U.V. ABSORPTION SPECTRA OF BASA AND ITS CHILATE POLYMERS

FIG. R-1



VISIBLE ABSORBTION SPECTRA OF BASA
AND BASA-Ni(P)

FIG. R-2

Table R - 2

Some characteristic IR frequencies (cm^{-1}) of BASA and its coordination polymers

(a) BASA

3150 (m)
1650 (vs)
1620 (m)
1570 (m)
1470 (s)
1375 (m)
1300 (m)
1275 (s)
1240 (w)
1200 (m)
1175 (m)
1140 (m)
1100 (m)
1000 (w)
950 (w)
900 (w)
840 (m)
830 (m)
810 (w)
765 (w)
740 (m)

(b) BASA-Co (p)

3400 (w) b
1610 (s)
1500 (m)
1450 (m)
1430 (sh)
1400 (m)
1400 (m)
1250 (w)
1200 (w)
1185 (m)
1135 (m)
1100 (m)
1000 (w)
900 (w)
835 (m)
740 (w) b

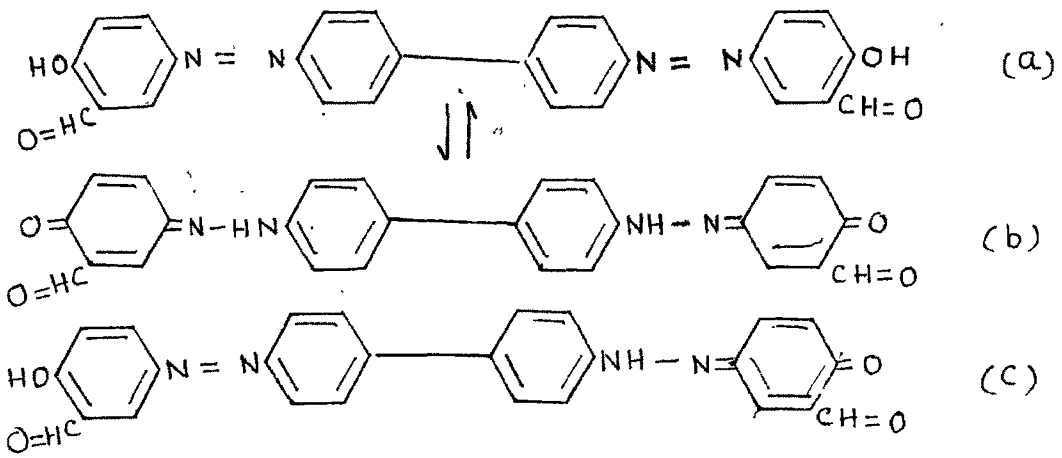
Table R-2 (contd).

(c) BASA-Cu (p)

3470 (m)
1605 (vs) b
1525 (m)
1430 (m)
1375 (s)
1320 (m)
1280 (m)
1240 (w)
1180 (m)
1140 (m)
1100 (m)
1000 (w)
950 (w)
900 (w)
825 (m)
740 (w)

(d) BASA-Ni (p)

3450 (w)
1650 (sh)
1610 (s)
1510 (w)
1450 (w)
1400 (m)
1340 (w)
1290 (w)
1190 (w)
1140 (w)
1100 (m)
1000 (w)
900 (w)
830 (m)
740 (w)

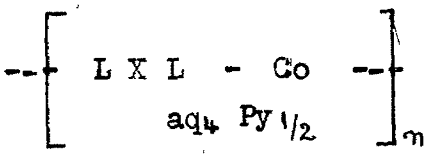


(II)

The IR spectrum of the ligand has bands at 1650 cm^{-1}, and 3150 cm^{-1} which may be attributed to chelated carbonyl and chelated hydroxyl groups respectively. The band at 1005 cm^{-1} is attributed to conjugated azo group.

(b) Coordination polymer of Co with BASA in pyridine : BASA - Co (P):

The cobalt complex prepared in presence of pyridine gave, on analysis, the ratio of metal to nitrogen as 1:4.5 ; hence it is formulated as a linear chain (III), with the association of water and pyridine molecules.



$$-\!-\left[\begin{array}{l} L\ X\ L\ -\ Co\ -\!- \\ \qquad aq_4\ Py_{1/2} \end{array}\right]_n$$

(III)

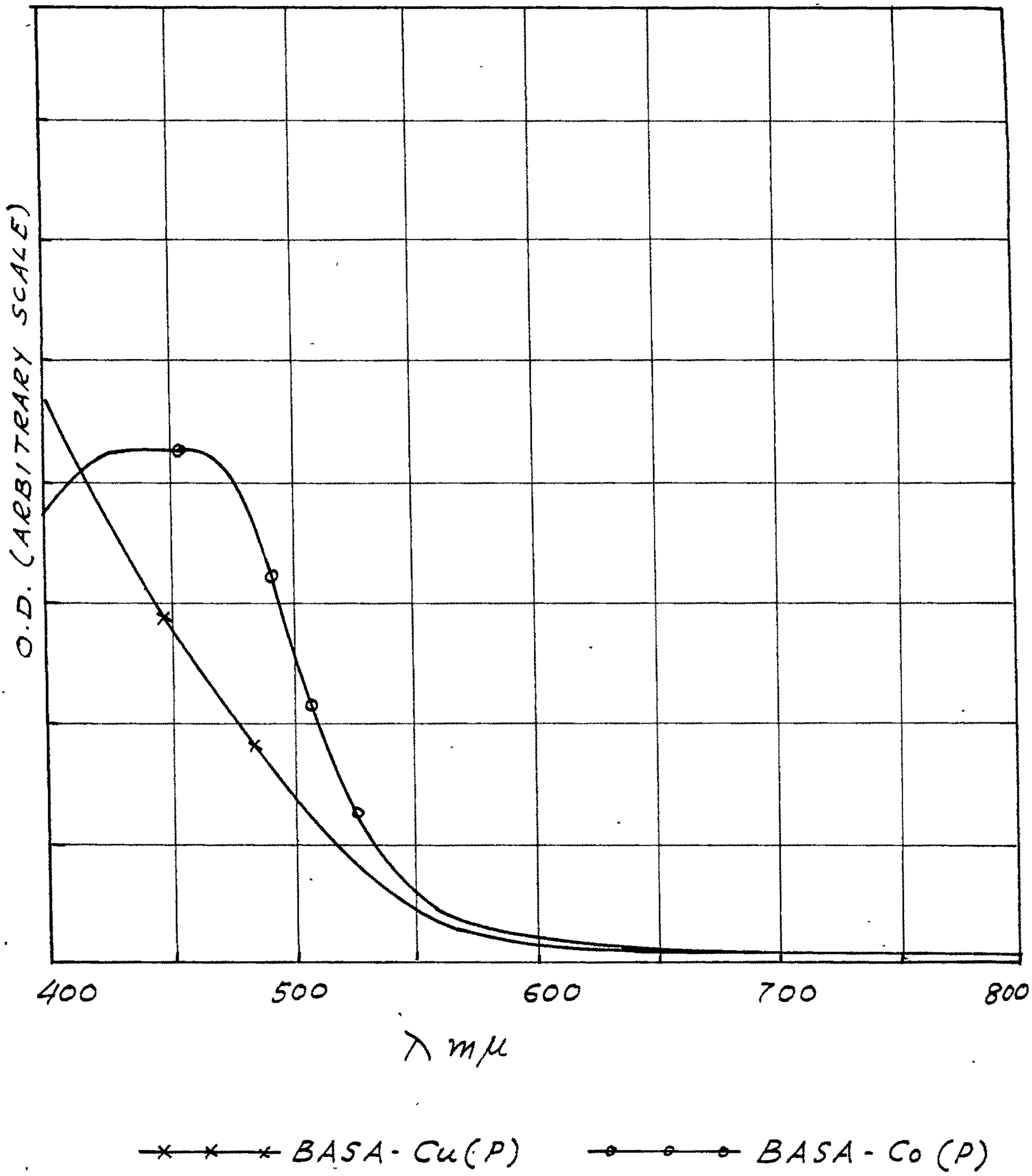
Where X $(LH)_2$ represents the ligand BASA, aq water and Py pyridine.

The polymer is slightly soluble in pyridine, dimethylformamide and nitrobenzene. A qualitative test was carried out to detect the presence of acetate; it was found absent. Further, cobalt is not precipitated from the solution by hydrogen sulphide. The pyridinated Co chelates of 5-arylazosalicylaldehydes prepared by Ohata et al., were red; the product obtained by us is reddish brown.

The absorption spectra of the polymer in the ultra-violet and visible region are presented in figs. R-1 and R-3. The band at 418 mµ observed in the spectrum of the ligand has broadened in the spectrum of the polymer (420-60 mµ); and its absorbance is much greater than that of the band at 510 mµ. Hence it is suggested that the ligand "anion" is present in the azo form in the polymer. It is likely that the broad band may include the charge transfer band (L ⟶ M) of the polymer.

Some important IR bands of the polymer are given in table R-2. The band at 1650 cm^{-1} observed in the spectrum of the ligand and attributed to the chelated carbonyl group is not observed even as a shoulder but is found shifted to 1610 cm^{-1} in the spectrum of the polymer. Hence it is considered that the ligand is not present as an end group in the polymer. The band for pyridine is found as a shoulder at 1430 cm^{-1} and indicates non-coordinated nature of pyridine in the polymer. Further a broad band for water is observed at 3400 cm^{-1}. The band for azo group is observed unshifted at 1005 cm^{-1}.

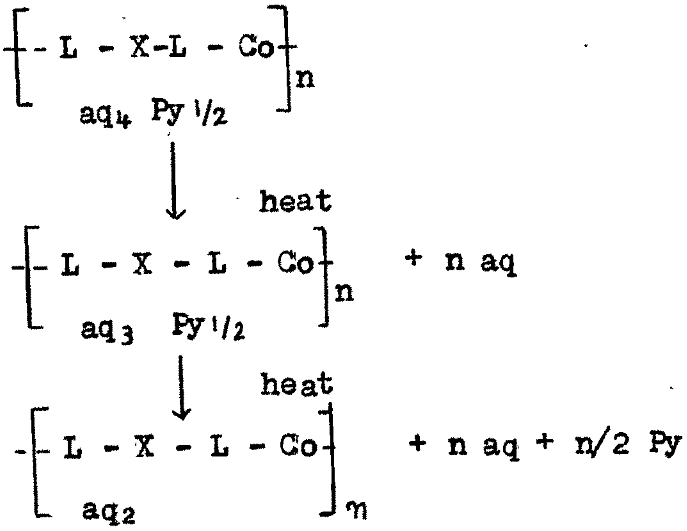
The thermograms (D.T.A. and T.G.A.) of the polymer



VISIBLE ABSORPTION SPECTRA OF BASA-Co(P) AND BASA-Cu(P)

FIG. R-3

are presented in fig. R-4. It can be suggested from the wt. loss and the endothermic peaks that (i) the polymer losses one molecule of water per monomeric unit over a temperature range of 90-130°C. (ii) losses further amounts of water and pyridine at higher temperature and (iii) melts (or depolymerises) at a temperature of 625-30°C. The results indicate high thermal stability of the polymer. The thermal decomposition reactions may be represented as follows :



$$\begin{array}{l} \left[-\underset{aq_4\ \ Py\,1/2}{L - X - L - Co}-\right]_n \\ \qquad\Big\downarrow \text{heat} \\ \left[-\underset{aq_3\ \ Py\,1/2}{L - X - L - Co}-\right]_n + n\ aq \\ \qquad\Big\downarrow \text{heat} \\ \left[-\underset{aq_2}{L - X - L - Co}-\right]_n + n\ aq + n/2\ Py \end{array}$$

The magnetic moment of the polymer per Co-atom is calculated as 4.74 B.M. It suggests octahedral stereochemistry of Co- in the monomeric unit.

The electrical resistivity of the polymer has been studied over a small range of temperature and the results are shown graphically (log resistivity vs reciprocal temperature) in fig. R-5. A straight line is obtained, satisfying the relation

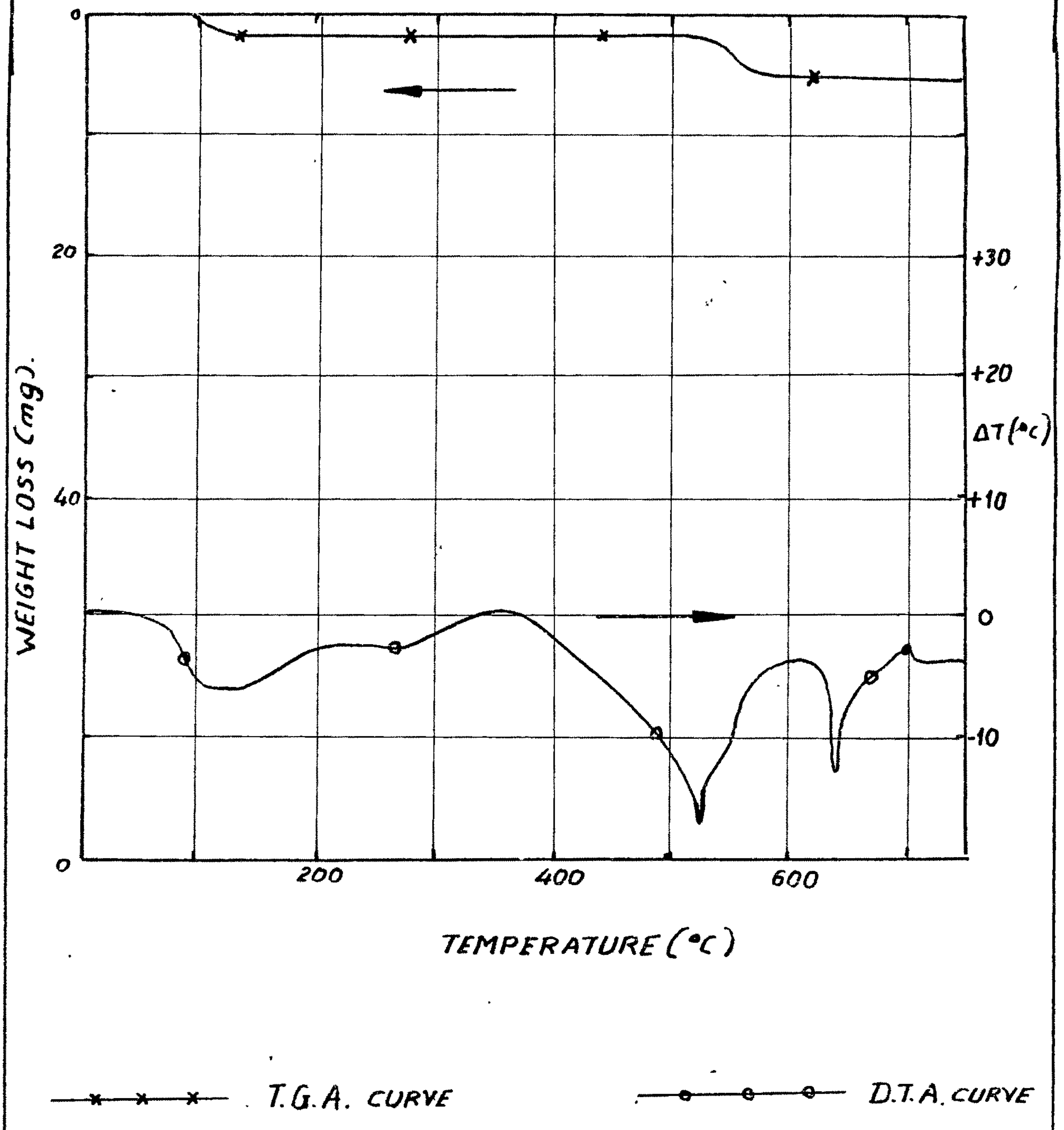
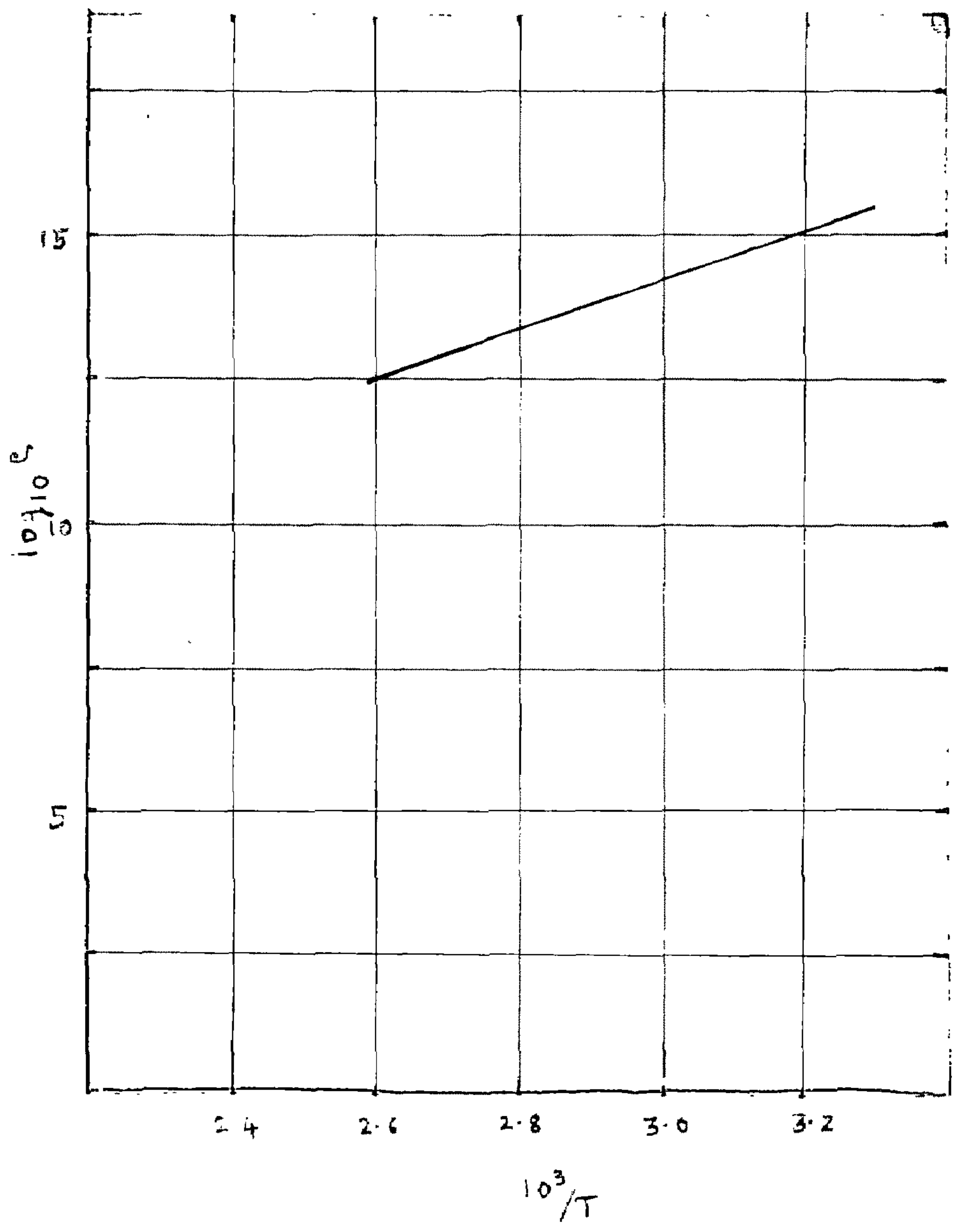


FIG. R-4 THERMOGRAMS OF BASA-Co. (P)



LOG RESISTIVITY VS $10^3/T$ FOR

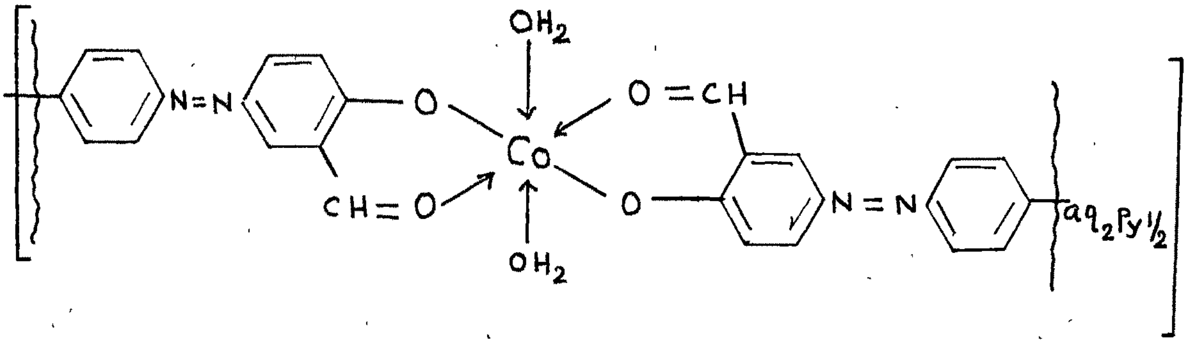
BASA-CO (P)

FIG. R-5

$$\rho = \rho_0 \; e^{E_g/2KT} \quad \text{—— (a)}$$

where Eg and ρ_0 are the energy gap and a constant respectively. Values of Eg and $\log_{10}\rho_0$ are calculated from the curve as 0.18 ev. and 12.54 respectively. The low value of Eg is an indication of the highly conjugated nature of the system; however, the mobility of charge carriers is not high as anticipated.

On the basis of the above observations, the structure of the cobalt complex in the monomeric unit may be considered to be a trans octahedral one and the monomer may be represented as (IV).



(IV)

(c) Coordination polymer of cobalt with BASA (without pyridine) : BASA - Co (D)

The product was obtained by treating cobalt acetate with the ligand BASA in dimethylformamide. It gave on analysis, the ratio of metal to nitrogen as 1:7. Hence it may be represented as (V).

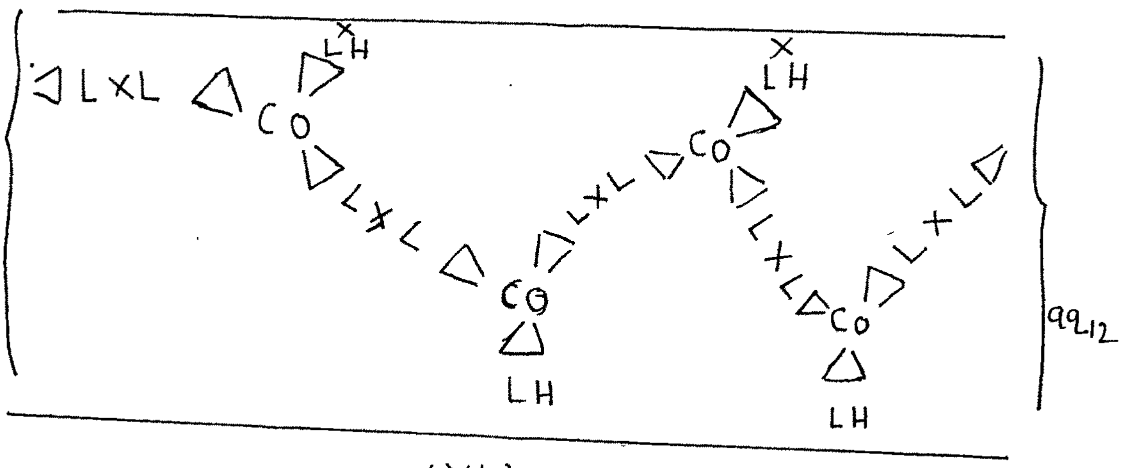
$$\left\{ Co(L\,X\,L)_{aq_3} \right\}_4 \left\{ X(L\,H)_2 \right\}_3$$

(V)

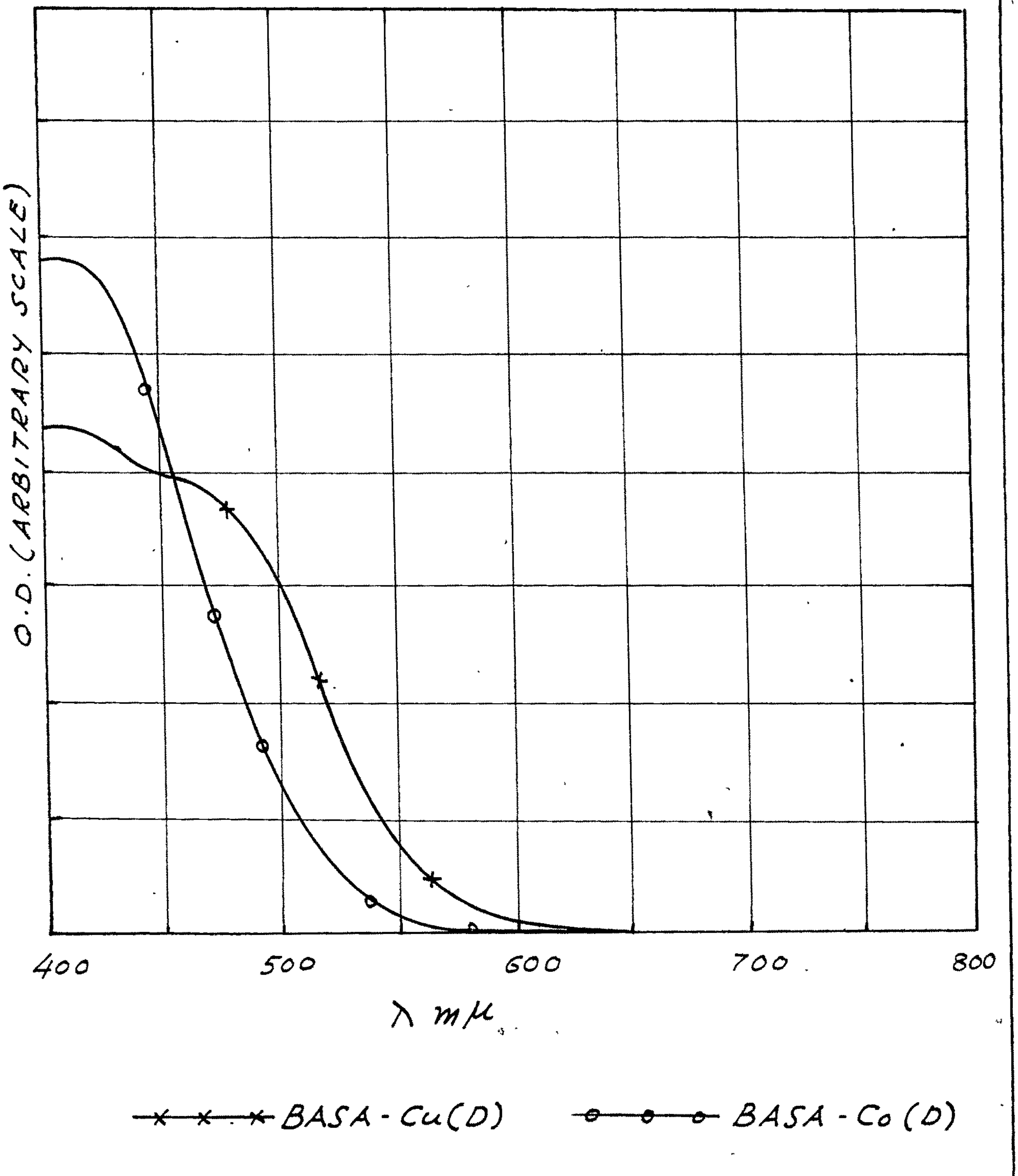
The cobalt chelates of 5-arylazosalicylaldehydes prepared by Ohata, et al. were yellow or reddish yellow in colour. The product obtained by us is coloured reddish yellow. It is sparingly soluble in dimethylformamide and pyridine. The absorption spectrum of the complex in the visible region is presented in fig. R-6. The absorption band is observed at 422 mu and its absorbance is much greater than at 510 mu. It indicates the presence of azo form in the ligand anion.

The magnetic moment of the complex per Co atom is found to be 5.00 B.M. Hence each Co atom may be considered to be in octahedral ligand field.

On the basis of the above observations the product may be considered to contain octahedral units and the polymer may be represented as three dimensional net work (VI) with occluded water



(VI)

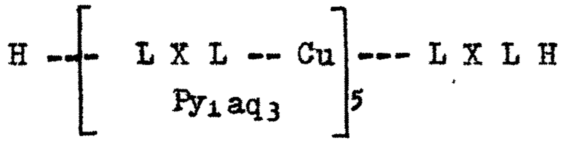


VISIBLE ABSORPTION SPECTRA OF BASA - Cu(D) AND BASA - Co(D)

FIG. R-6

(d) Coordination polymer of copper with BASA in pyridine : BASA-Cu (P) :

The copper complex, prepared in presence of pyridine gave, on analysis, the ratio of metal to nitrogen as 1:5.7. Hence it is formulated as a linear chain (VII) with the association of water and pyridine molecules.



$$H - \left[\underset{Py_1aq_3}{L\,X\,L - Cu} \right]_5 - L\,X\,L\,H$$

(VII)

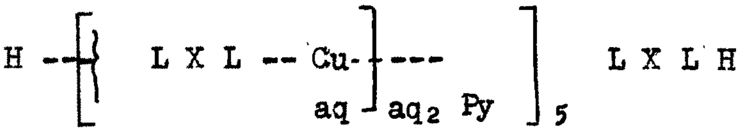
The polymer is sparingly soluble in pyridine and dimethylformamide. A qualitative test was carried out to detect the presence of acetate ; it was found absent. Further copper was not precipitated from its solution by hydrogen sulphide nor was iodine liberated on the addition of potassium iodide to the solution.

The absorption spectra of the polymer in the ultra-violet and visible regions are presented in figs. R-1 and R-3. The bands observed at 510 mμ and 418 mμ in the spectrum of the ligand are absent in the spectrum of the polymer. However, the band at 418 mμ appears to have shifted to a lower value (< 400 mμ). It would indicate that coplanarity of the ligand molecule is affected.

Some important IR bands of the polymer are given in table R-2. The band at 1650 cm^{-1} observed in the spectrum of the ligand and attributed to the chelated carbonyl is observed as a shoulder to the band shifted to 1605 cm^{-1}. Hence it is considered that the ligand is present as an end-molecule in the polymer chain. Further the band for pyridine is found at 1430 cm^{-1} and indicates non-coordinated nature of pyridine in the polymer, the band for water is observed at 3470 cm^{-1} and the band for azo group is observed unshifted at 1005 cm^{-1}.

The thermogram (T.G.A.) of the polymer is presented in fig.R-7. It is suggested from the wt.loss that (i) the polymer losses one water molecule per monomeric unit over a temperature range of 100-130°C, (ii) it losses another molecule of water and a molecule of pyridine over a temperature range of 270-340°C and (iii) it decomposes at higher temperature.

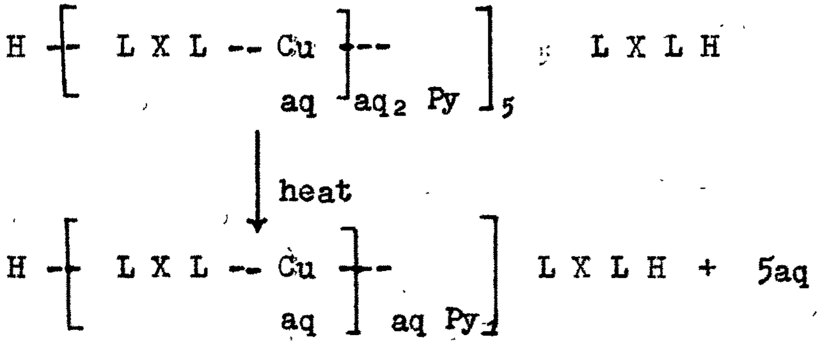
On the basis of the above observations, the polymer may be represented as (VIII).



$$H - \Big[LXL - \underset{aq}{Cu} \Big] \underset{aq_2}{---}\ Py \Big]_5\ LXLH$$

(VIII)

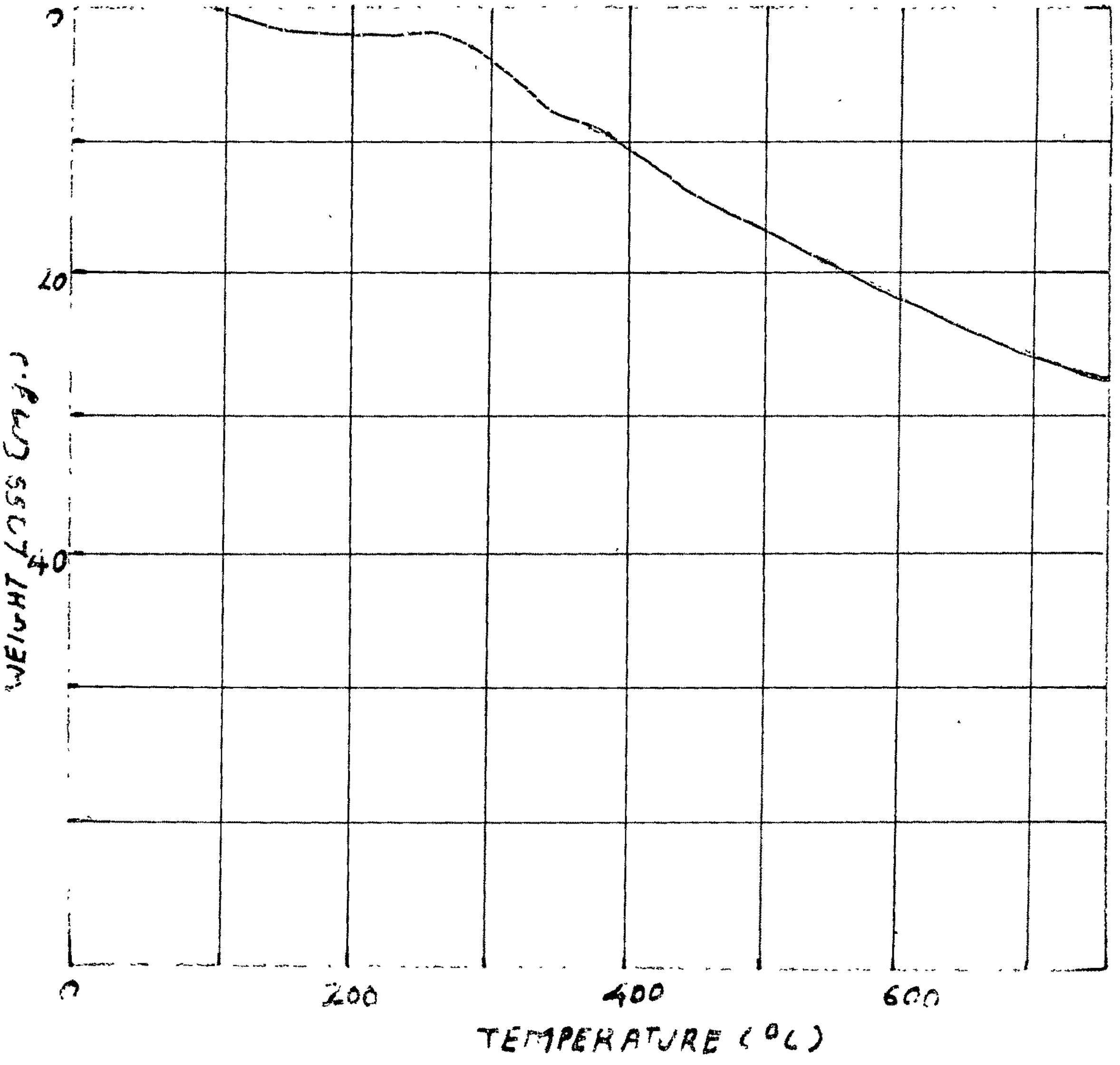
The results indicate relatively low thermal stability of the polymer. The thermal decomposition reactions may be represented as follows :



$$H - \Big[LXL - \underset{aq}{Cu} \Big] \underset{aq_2}{--}\ Py \Big]_5\ LXLH$$

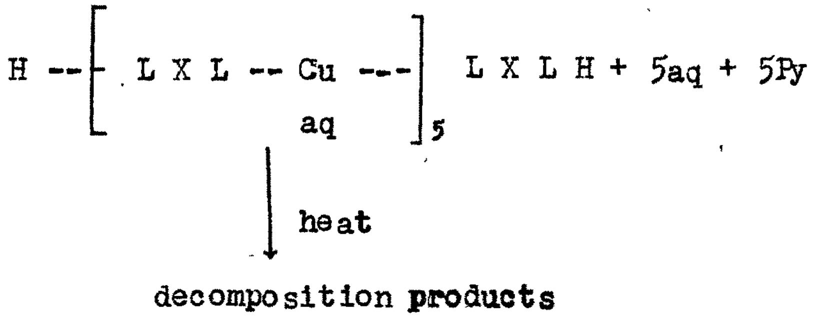
$$\Big\downarrow \text{heat}$$

$$H - \Big[LXL - \underset{aq}{Cu} \Big] \underset{aq}{--}\ Py \Big]\ LXLH + 5aq$$



THERMOGRAMOF BASA-Cu (I)

FIG. R-7



$$H\text{--}\left[\,L\,X\,L\text{--}\underset{aq}{Cu}\text{---}\right]_{5} L\,X\,L\,H + 5aq + 5Py$$

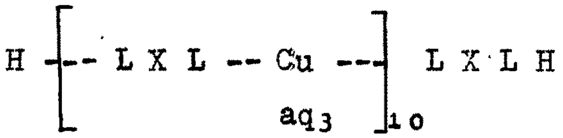
$$\Big\downarrow\ \text{heat}$$

$$\text{decomposition products}$$

The magnetic moment of the polymer per copper atom is calculated as 2.2 B.M.

(e) Coordination polymer of copper with BASA (without pyridine) - BASA-Cu (D):

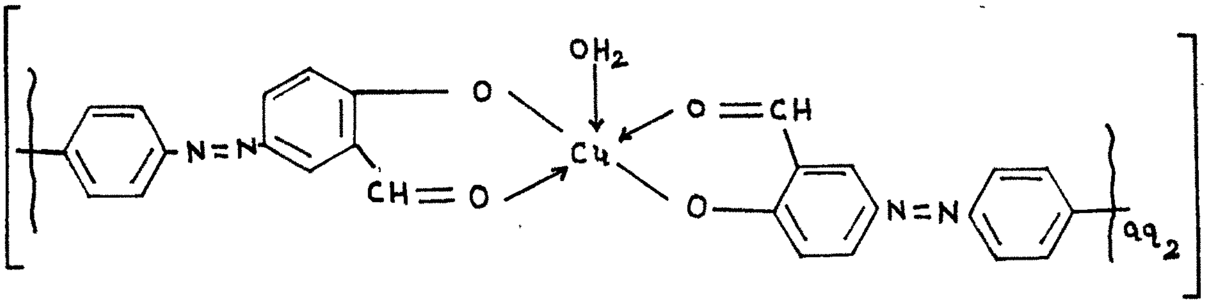
The copper complex prepared without pyridine gave on analysis, the ratio of metal to ligand as 1:1.1. Hence it is formulated as a linear chain (IX) with association of water molecules.



$$H\text{--}\left[\text{--}\,L\,X\,L\text{--}\underset{aq_3}{Cu}\text{---}\right]_{10} L\,X\,L\,H$$

(IX)

It is sparingly soluble in dimethylformamide and pyridine. Its magnetic moment per copper atom has been calculated as 2.44 B.M. It is considered to have square pyramidal nature and be represented as (X)



(X)

(f) Coordination complex of nickel with BASA (in pyridine) BASA - Ni(P) :

The nickel complex prepared in pyridine, gave on analysis the ratio of metal to nitrogen as 1:9. Hence it is formulated as a nickel complex (XI) with association of water and pyridine molecules.

$$\left[\mathrm{H\ L\ X\ L} -\!- \mathrm{Ni} -\!- \mathrm{L\ X\ L\ H}\right]_{\mathrm{Py},\ \mathrm{aq}_4}$$

(XI)

The precipitation of the complex was very slow and the precipitates were obtained in the collodial state. The formation of linear chain may be considered but could not be established from various investigations.

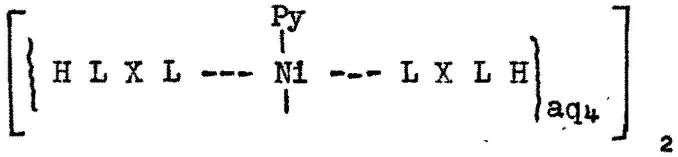
The complex is sparingly soluble in pyridine and dimethylformamide. A qualitative test was carried out to detect acetate; it was found absent. Further nickel was not precipitated from its solution by hydrogen sulphide.

6 The absorption spectra of the complex in the visible and ultra violet regions are presented in figs. R-1 and R-2. The absorption bands are observed at 510 mu and 410 mu. As in the spectrum of the ligand, the absorption band at 410 mu is weaker than that at 510 mu.

Some important IR bands of the complex are given in table R-2. The band at 1650 cm^{-1} observed in the spectrum of the ligand is observed as a shoulder to the band shifted at 1610 cm^{-1}. It would indicate the presence of the chelating groups of the ligand molecules in the coordinated and non-coordinated form in the complex. Further the band for pyridine found as shoulder at 1450 cm^{-1} indicates the presence of coordinated pyridine; a band for chelated hydroxyl is observed at 3100 cm^{-1}, a broad band for water is observed at 3450 cm^{-1}, and the band for azo group is observed at 1000 cm^{-1}.

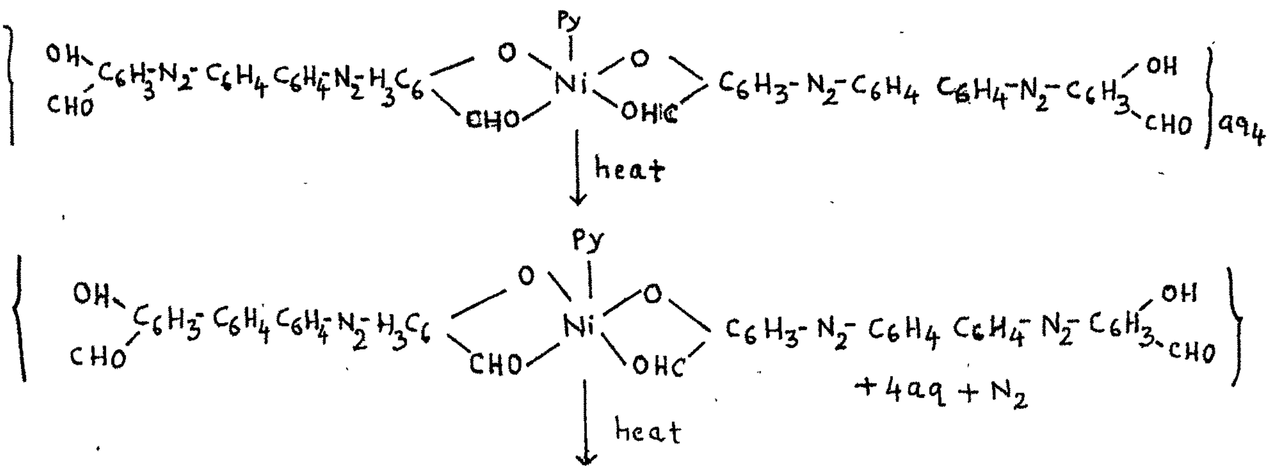
The thermogram (T.G.A.) of the complex is presented in fig. R-8. It is suggested from the wt.loss that (i) the complex loses water and nitrogen over a temperature range of 70-150°C and (ii) undergoes decomposition sharply at 475-85°C. losing further amount of nitrogen. The results indicate low thermal stability of the complex.

Its magnetic moment per nickel atom is calculated at 2.86 B.M. The value is smaller than the one observed for the usual octahedral nickel complexes and can be related to the binuclear octahedral nickel complexes.



$$\left[\left\{ H\,L\,X\,L --- \overset{Py}{\underset{|}{Ni}} --- L\,X\,L\,H \right\}_{aq_4}\right]_2$$

The products of thermal decomposition for the mononuclear species may be represented as follows :



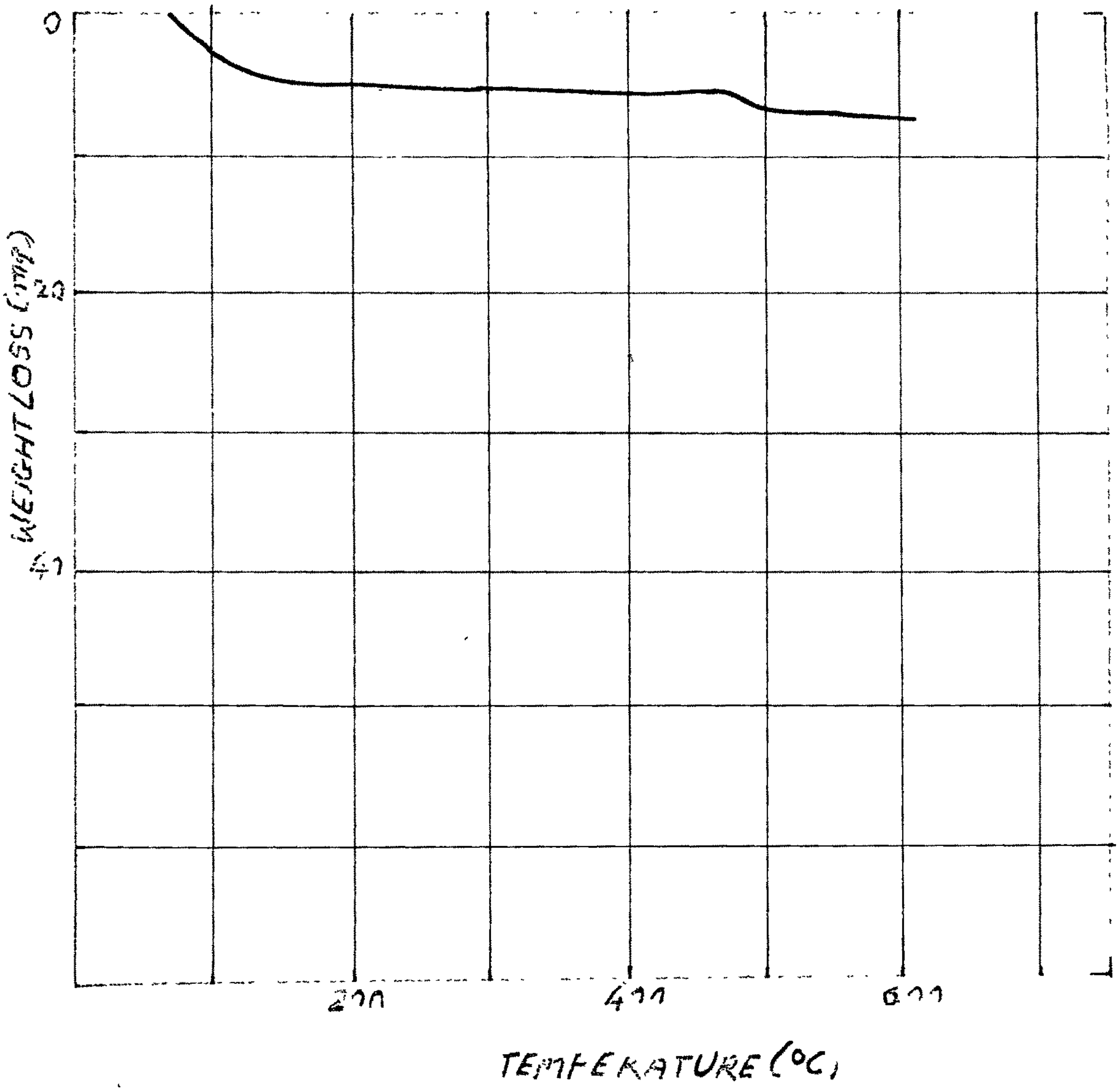
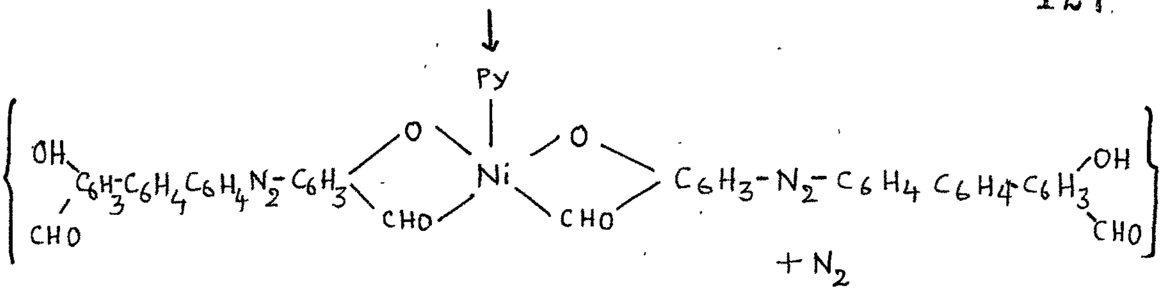


FIG. R-8 THERMOGRAM OF BASA - Ni (P)



The free radicals formed as intermediates during thermal decomposition may combine as shown above or may form other products of decomposition.

The results suggest that the stability of the ligand is much reduced by coordination with nickel.

General :

(i) IR frequency shift:

In the phenoxide ion of salicylaldehyde the carbonyl group must retain essentially carbonyl character; consequently more significance can be attached to correlations between the shifts in this frequency and chelate stability. In fact Bellamy and Branch [154] have found ramarkable correlation between the two for Mg, Zn, Ni, Cu and Pd chelates, in agreement with the stability order suggested by Mellor and Maley[155] (Mg < Zn < Co < Ni < Cu < Pd). We find that frequency shifts are in order Co ~ Ni < Cu and is in fair agreement with earlier observations.

(ii) Thermal fission:

The radical decomposition of azo compounds has been known for a long time. Thus in 1896, Thile and Heuser[156] described the quantitative evoluation of N_2 according to the

$$R - N = N - R' \rightarrow R + R' + N_2$$

as well as the formation of products by the combination of radicals, by the transfer of hydrogen atom from the solvent to the radicals or by the reaction with other particles (X) present in the system as shown by the equation,

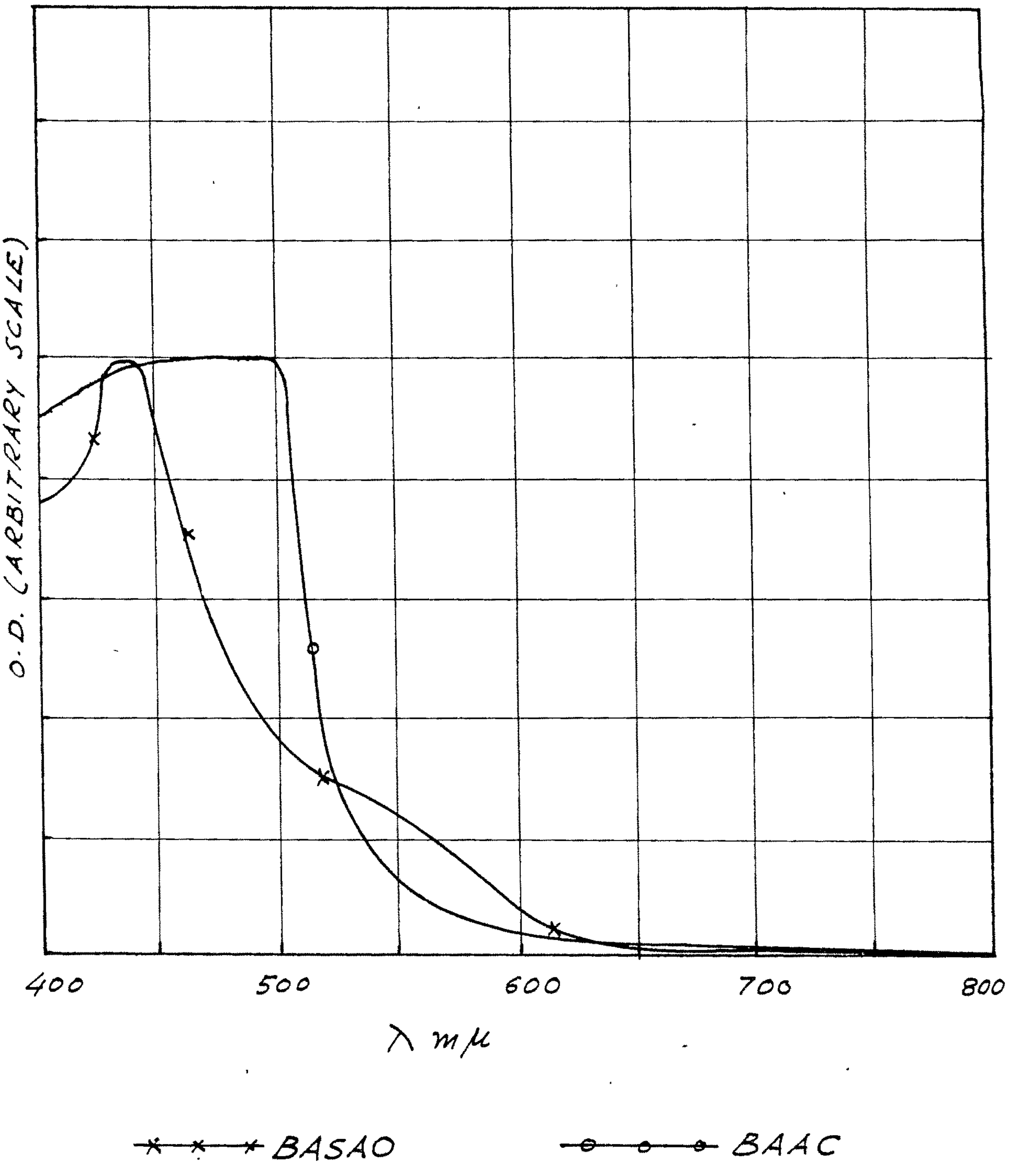
$$R. + R' \longrightarrow R - R'$$
$$R. + H \longrightarrow R - H. \longrightarrow \text{products}$$
$$R'. + H \longrightarrow R'{-}{-}H. \longrightarrow \text{products}$$
$$R. + X \longrightarrow R - X. \longrightarrow \text{products}$$
$$R'. + X \longrightarrow R' - X. \longrightarrow \text{products}$$

On the basis of thermal studies we suggest that the thermal fission involving the evoluation of nitrogen is catalysed by the metal ion chelated to the salicylaldehyde group. Such a reaction is facilitated by nickel, is facilitated by copper with the formation of some other volatile products and is inhibited by cobalt. Thus chelated metal appears to have relatively unusual and varied action on the stability of the azo compound.

III 2. Bis-azo disalicylaldoxime and its nickel (II) complex :

(a) Dioxime of 4,4'-bis(m-formyl-p-hydroxyphenyl azo) biphenyl : (BASAO)

The above ligand was prepared by the action of hydroxylamine on bis-azo disalicylaldehyde (BASA) in pyridine. Its spectrum in the visible region is given in fig. R-9. It shows a broad absorption band at 430-40 mu and shoulders at 500 and 605 mu. Thus the compound appears



VISIBLE ABSORPTION SPECTRA OF BASAO AND BAAC

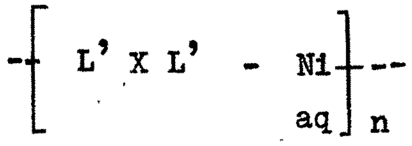
FIG. R-9

to exist mainly in the azo form. Its absorption spectrun in dimethylformamide solution in the ultraviolet region is presented in fig.R-10. The absorption band appears to be near 270 mu.

Some important IR bands are given in table R-3. It shows the absorption bands for (a) OH (oxime) group at 3450 cm^{-1} and (b) C=N at 1630 cm^{-1}.

(b) Coordination polymer of nickel (II) with BASAO : BASAO-Ni)

The nickel complex gave on analysis, the ratio of metal to ligand as 1:1 ; hence it is formulated as a linear chain (XII)

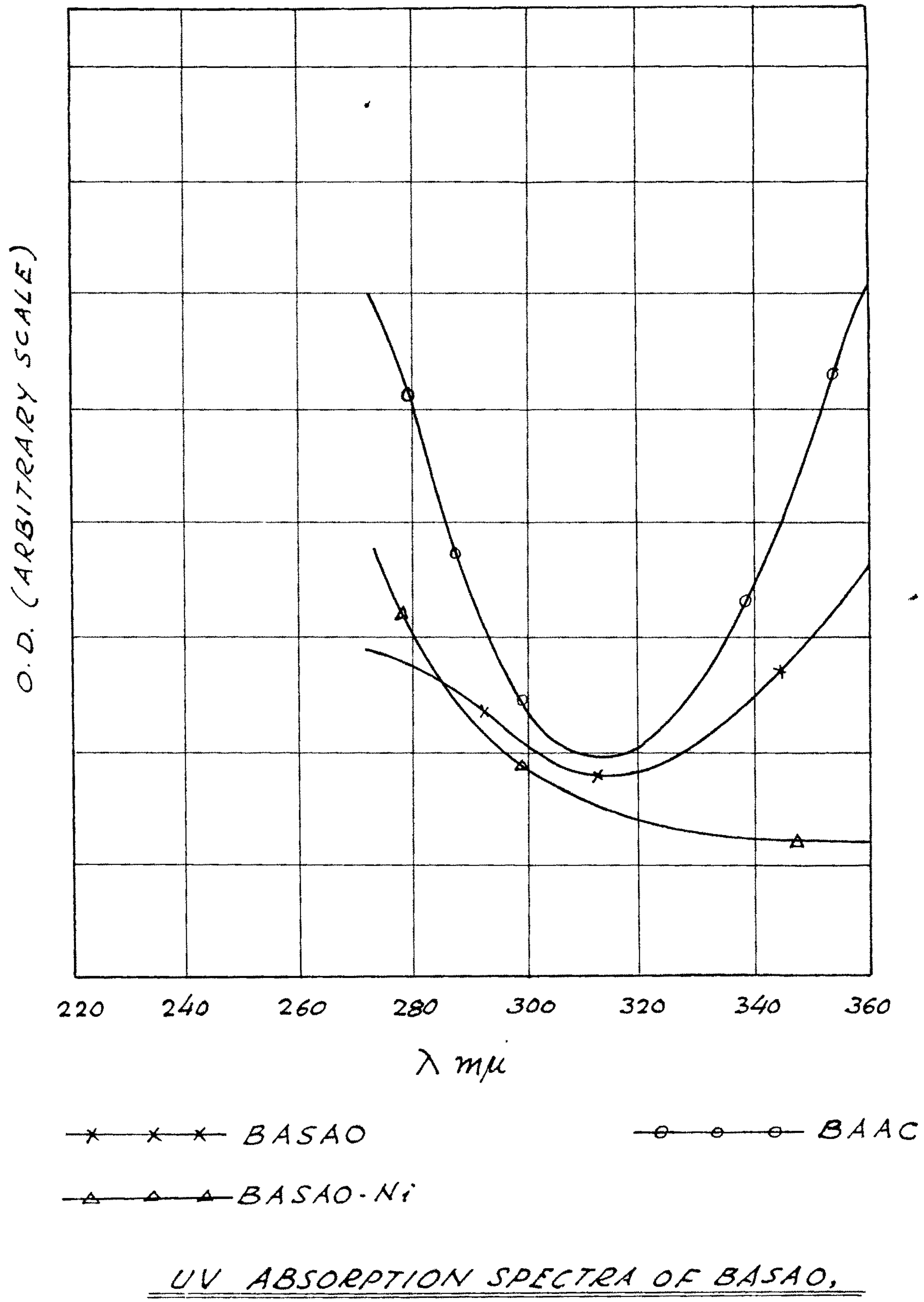


$$-\left[\ L'\ X\ L'\ -\ \underset{aq}{Ni}\ \right]_n--$$

(XII)

where X $(L'H)_2$ represents the ligand BASAO. The polymer is slightly soluble in pyridine and dimethylformamide. A qualitative test was carried out to detect the presence of acetate, it was found absent. Further nickel sulphide was not precipitated from the solution of the polymer by hydrogen sulphide.

The absorption spectrum of the polymer in the visible region is presented in fig. R-11. The absorption band appears to have shifted to the ultraviolet region and the shoulders are observed at 410 and 550 mu. Thus when the spectrum of the coordination polymer is compared with that of its ligand, a blue shift of the band and shoulders is observed. The



UV ABSORPTION SPECTRA OF BASAO, BASAO-Ni AND BAAC

FIG. R-10

Table R - 3

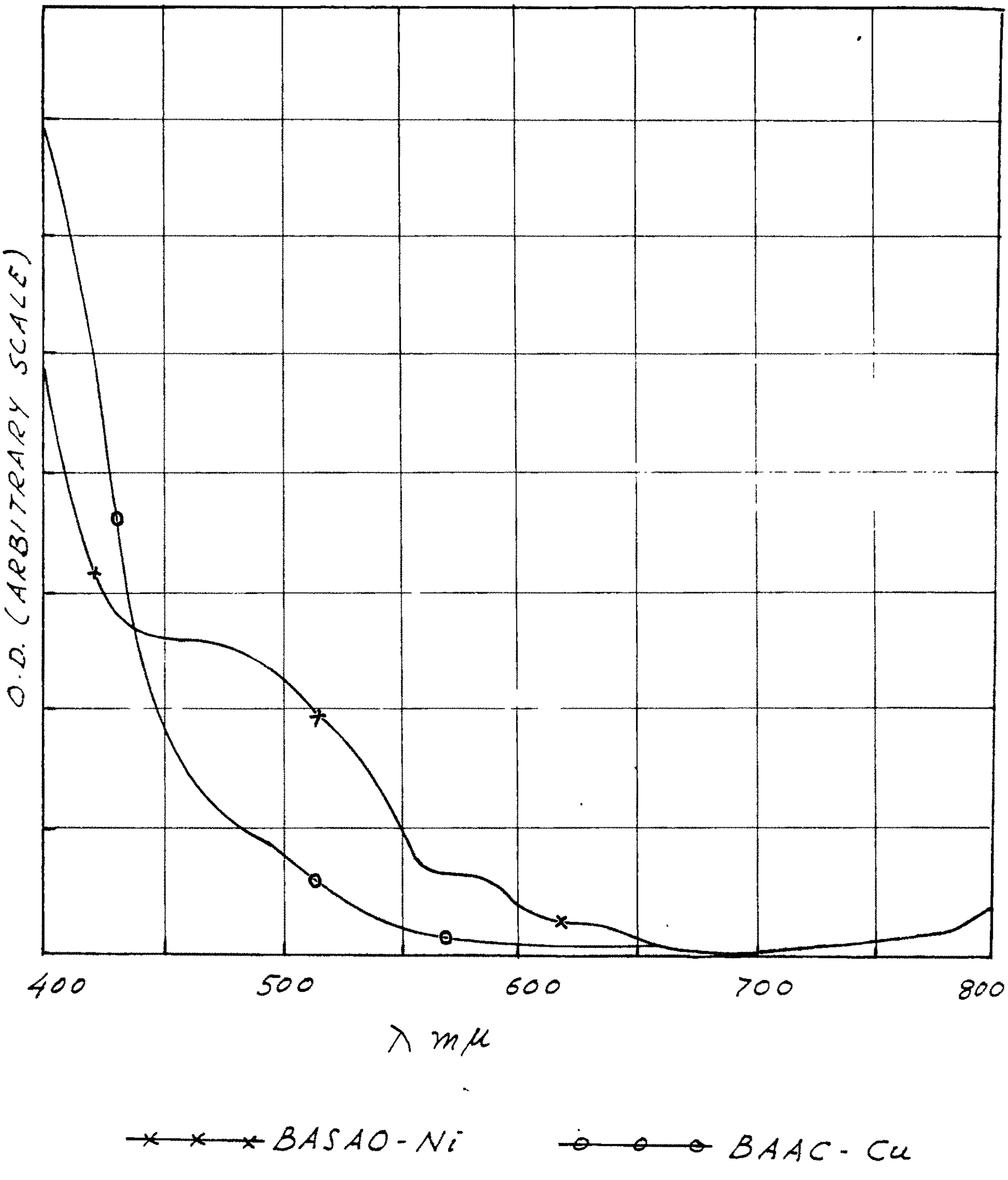
Some characteristic IR frequencies (cm^{-1}) of BASAOand BASAO-Ni (p)

(a) BASAO

3450 (s)
1630 (m)
1550 (m)
1500 (s)
1400 (w)
1300 (w)
1260 (s)
1240 (w)
1200 (w)
1160 (w)
1100 (m)
1010 (m)
950 (w)
900 (w)
830 (s)
810 (w)
790 (w)
740 (w)

(b) BASAO-Ni (p)

3280 (w)
3020 (m)
1630 (w)
1585 (s)
1540 (w)
1475 (s)
1440 (m)
1400 (m)
1290 (s)
1210 (w)
1190 (w)
1140 (w)
1100 (m)
1030 (m)
1000 (w)
940 (w)
900 (w)
890 (w)
830 (s)
740 (w)



VISIBLE ABSORPTION SPECTRA OF BASAO-Ni AND BAAC-Cu

FIG.R.11

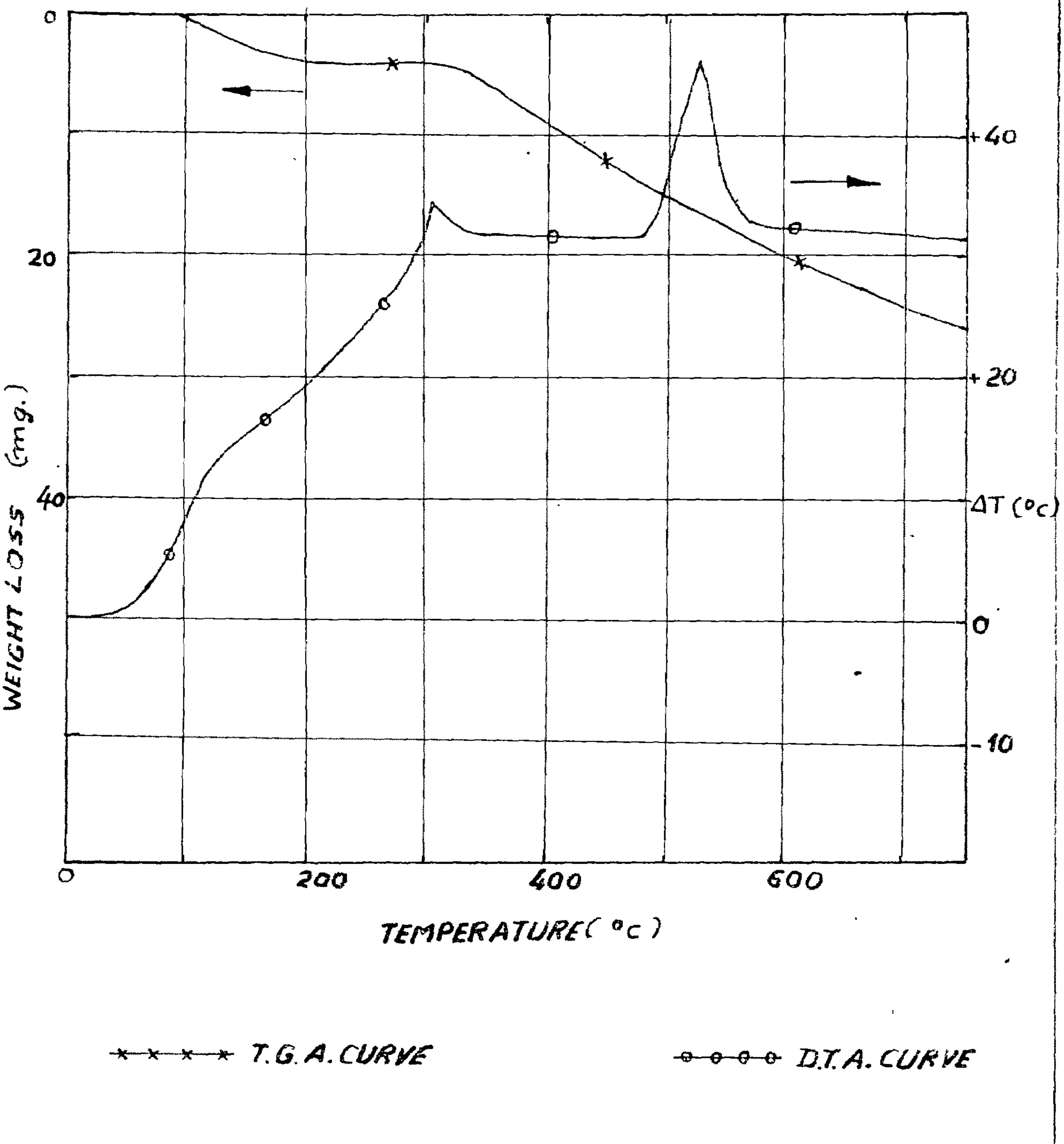
absorption spectrum in the ultraviolet region is shown in fig. R-10. The absorption band near 270 mu in the spectrum of the ligand also appears to have undergone a blue shift in the spectrum of the polymer.

Some important IR bands of the polymer are given in table R-3. The band observed at 3280 cm^{-1} suggests the presence of OH (oxime) group. Further the band for C=N observed at 1630 cm^{-1} in the spectrum of the ligand appears to have shifted to 1585 cm^{-1} with weak band at 1630 cm^{-1} in the spectrum of the polymer. The results indicate coordinated nature of the group and also the presence of the ligand as end molecule in the polymeric chain.

The thermograms (T.G.A. and D.T.A.) are presented in fig.R-12. It may be concluded from the results that there is (i) loss of water at low temperature 90-170°C associated with the decomposition of the ligand and (ii) drastic decomposition above 300°C. The decomposition appears to involve the loss of nitrogen and may take place in two steps.

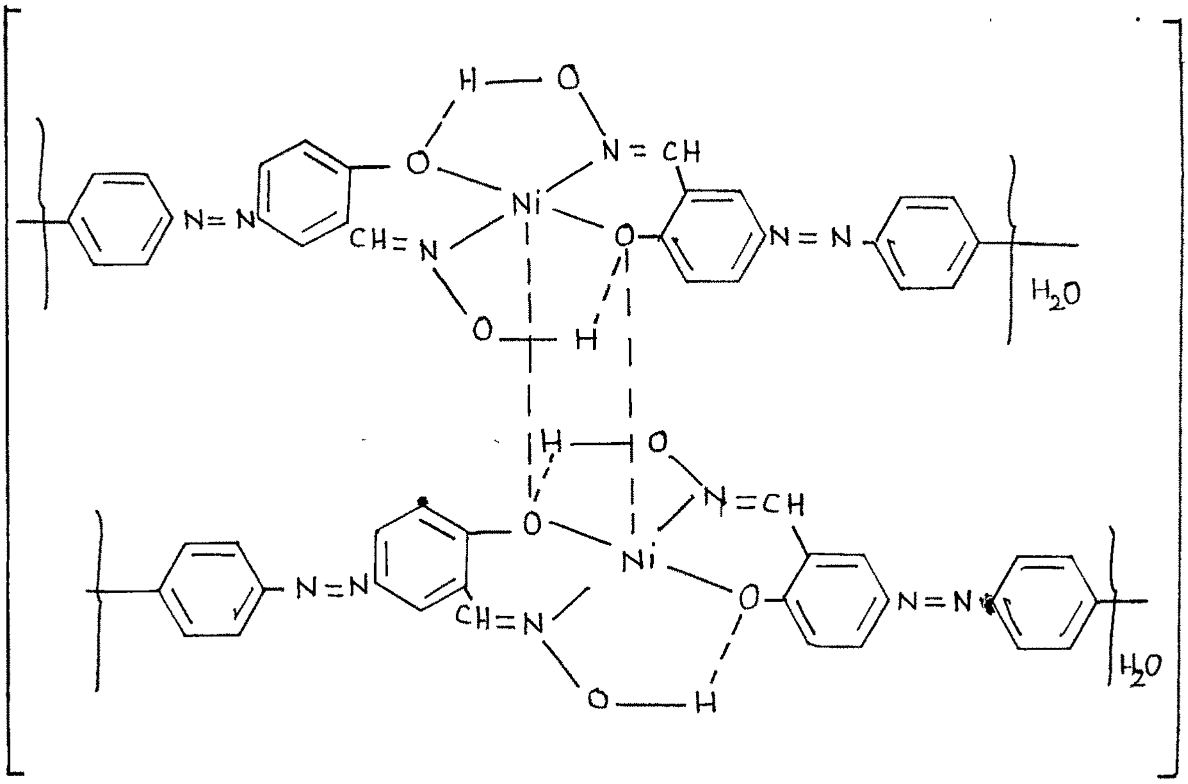
The magnetic moment of the polymer per nickel atom is calculated as 2.75 B.M. The low value may be attributed to 5-coordinate binuclear Ni in the polymer.

On the basis of the above observations the most likely structure of nickel coordination polymer BASAO-Ni would involve the square planar distribution of coordinated groups of the ligand and metal and the bonding of nickel atom with the phenolic oxygen of the adjoining complex forming binuclear complexes. Hence it may be represented as follows:



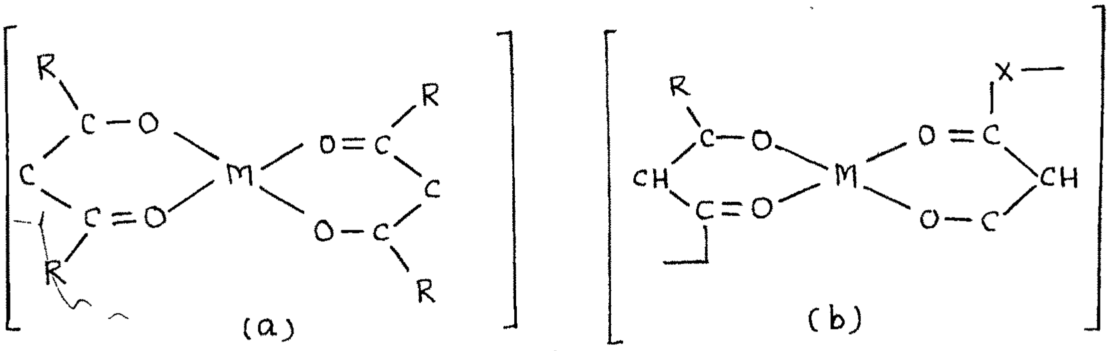
THERMOGRAMS OF BASAO-Ni

FIG. R-12



III 3. Azo-diacetylacetones and their transition metal complexes :

Polymeric metal complexes (XV) of bis-(β-diketones) or tetraketones have been prepared by various methods.



(a) (b)

(XV)

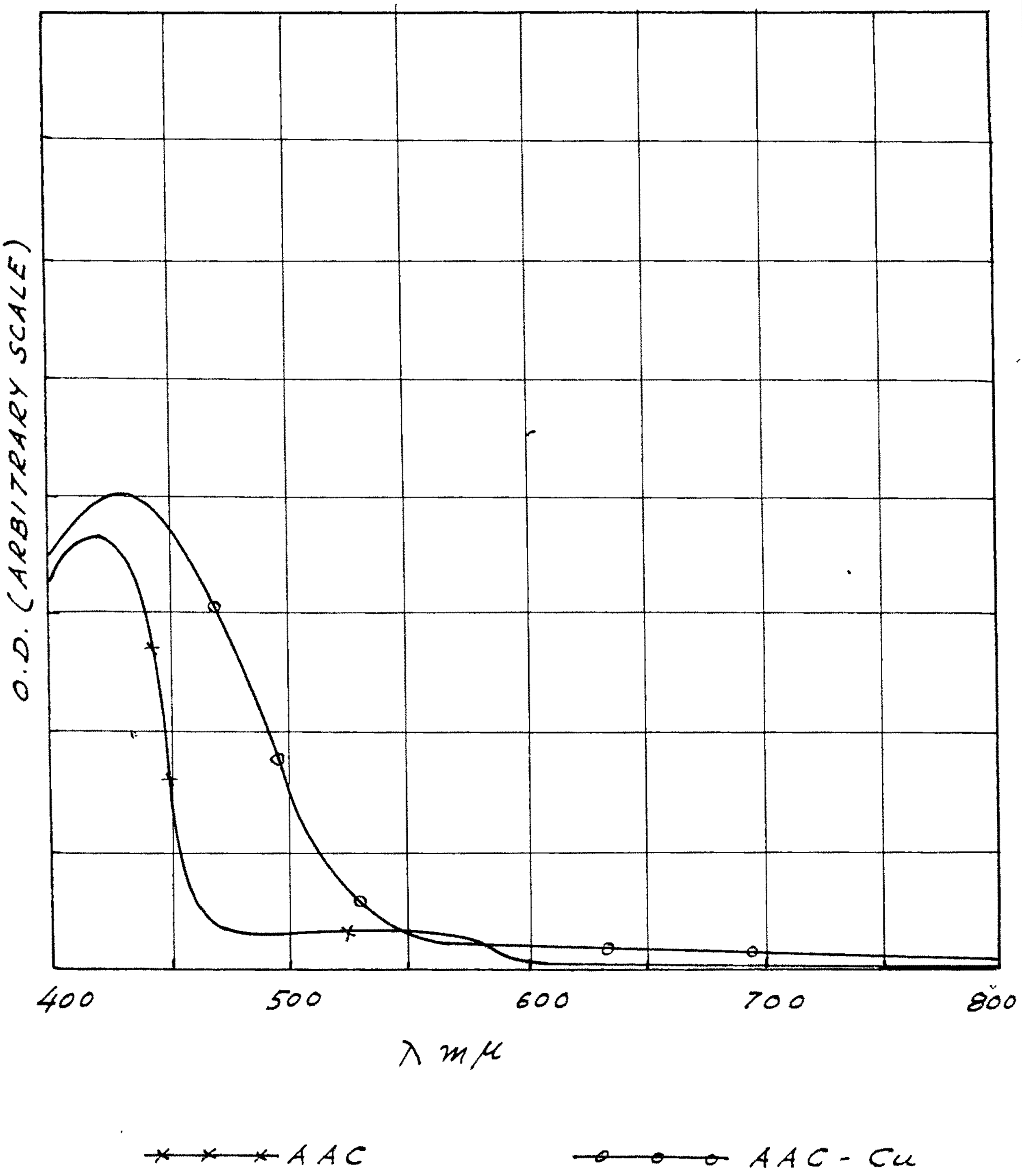
Thus Fernelius and co-workers[34,35] synthesised bis-(β-diketones) of the type  $\begin{matrix}R\,C\,O\\R'C\,O\end{matrix}\!>CH - Y - CH<\!\begin{matrix}C\,O\,R'\\C\,O\,R\end{matrix}$ and have studied the coordination chemistry of bis-(β-diketones), especially the effect of substituents in the ligand and the nature of the metal ion on the thermal stability and molecular weight of resulting polymers. Charles[41,42] prepared Cu, Ni, Co, Zn, Cd and Mg metal chelates from tetraacetylethane and studied their thermal stability and decomposition temperature. Korshak and co-workers[37,39,40] synthesised various bis-(β-diketones) of the types $(RCO)_2CH-Y-CH(COR)_2$ and $(RCOCH_2CO)_2-X$ and their Be, Cu, Cd, Co, Zn, Mn and Ni chelate polymers and studied their thermomech. properties etc. Knobloch and Rauscher[69] prepared Zn, Cu, Ni, Co, Mn, and Cd chelate polymers of $(RCO)_2CH-CH(COR)_2$ and studied their IR spectra. Kluiber and Lewis[43] prepared chelate polymers of $(RCO)_2$-$CH-Y-CH(COR)_2$.

We prepared 3,3'(4,4'-biphenylene bis azo) di(2,4-pentanedione) and its copper complex and for the purpose of comparison prepared 3(phenylazo) 2,4-pentanedione and its copper complex. Ni(II) and Co(II) complexes of the bis-azo ligand could not be prepared.

(a) <u>Azo-ligands</u>:

The bis-azo ligand (BAAC) was prepared by coupling acetylacetone with tetrazotised benzidine and the monoazo ligand (AAC) was obtained by coupling acetylacetone with diazotised aniline.

Their spectra in the visible region are presented in figs. R-9 and R-13. AAC has λ max at 420 mμ and 530 mμ. The relative intensities of the two bands indicate the existance of the compound mainly in the azo form in solution BAAC has λ max at 430 mμ and 490-500 mμ. The relative



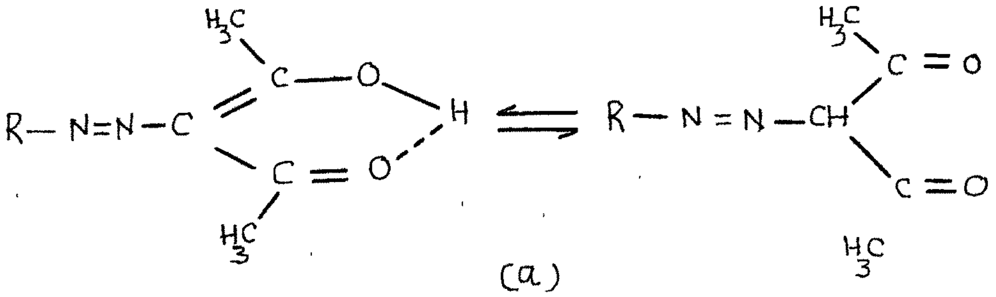
VISIBLE ABSORPTION SPECTRA OF AAC AND AAC-Cu

FIG. R-13

intensities of the two bands suggest the existence of equilibrium between the azo and hydrazone structures of the compound in solution.

Their spectra in the ultraviolet region are presented in figs. R-10 and R-14. BAAC appears to have an absorption band near 270 mμ, which is probably shifted to lower value and is not boserved in the case of AAC.

Some of the important IR bands of AAC and BAAC are presented in table R-4. AAC has an absorption band at 3020 cm^{-1} which may be attributed to chelated enol group. An absorption band for dicarbonyl group is presented at 1665 cm^{-1} and for chelated carbonyl group is at 1620 cm^{-1}. BAAC has absorption bands for dicarbonyl group at 1680 cm^{-1} and for chelated carbonyl group at 1620 cm^{-1}. The band at 3050 cm^{-1} may be attributed to the chelated enol group. Hence these compounds may be considered to exist in the keto-enol tautomeric forms (XVI) .



(XVI)

where R = C_6H_5 or p- C_6H_4

Further, BAAC has an absorption band at 3130 cm^{-1} which may be attributed to the hydrazone NH group. It may indicate the azo-hydrazone tautomeric form (XVII) for BAAC.

Table R - 4

Some characteristic IR frequencies (cm^{-1}) of azoacetylacetones and their copper complexes

(a) AAC

3020 (m)
1665 (vs)
1620 (s)
1600 (m)
1500 (vs)
1450 (m)
1410 (m)
1350 (vs)
1290 (vs)
1275 (s)
1170 (vs)
1140 (s)
1075 (w)
1050 (m)
1020 (m)
980 (m)
935 (s)
910 (m)
780 (m)
750 (vs)
740 (vs)

(b) BAAC

3130 (m)
3050 (m)
1680 (s)
1620 (m)
1590 (w)
1500 (vs)
1400 (m)
1375 (m)
1350 (m)
1340 (m)
1300 (s)
1260 (m)
1200 (s)
1180 (s)
1160 (s)
1050 (w)
1020 (w)
980 (m)
930 (m)
850 (w)
780 (m)
740 (m)

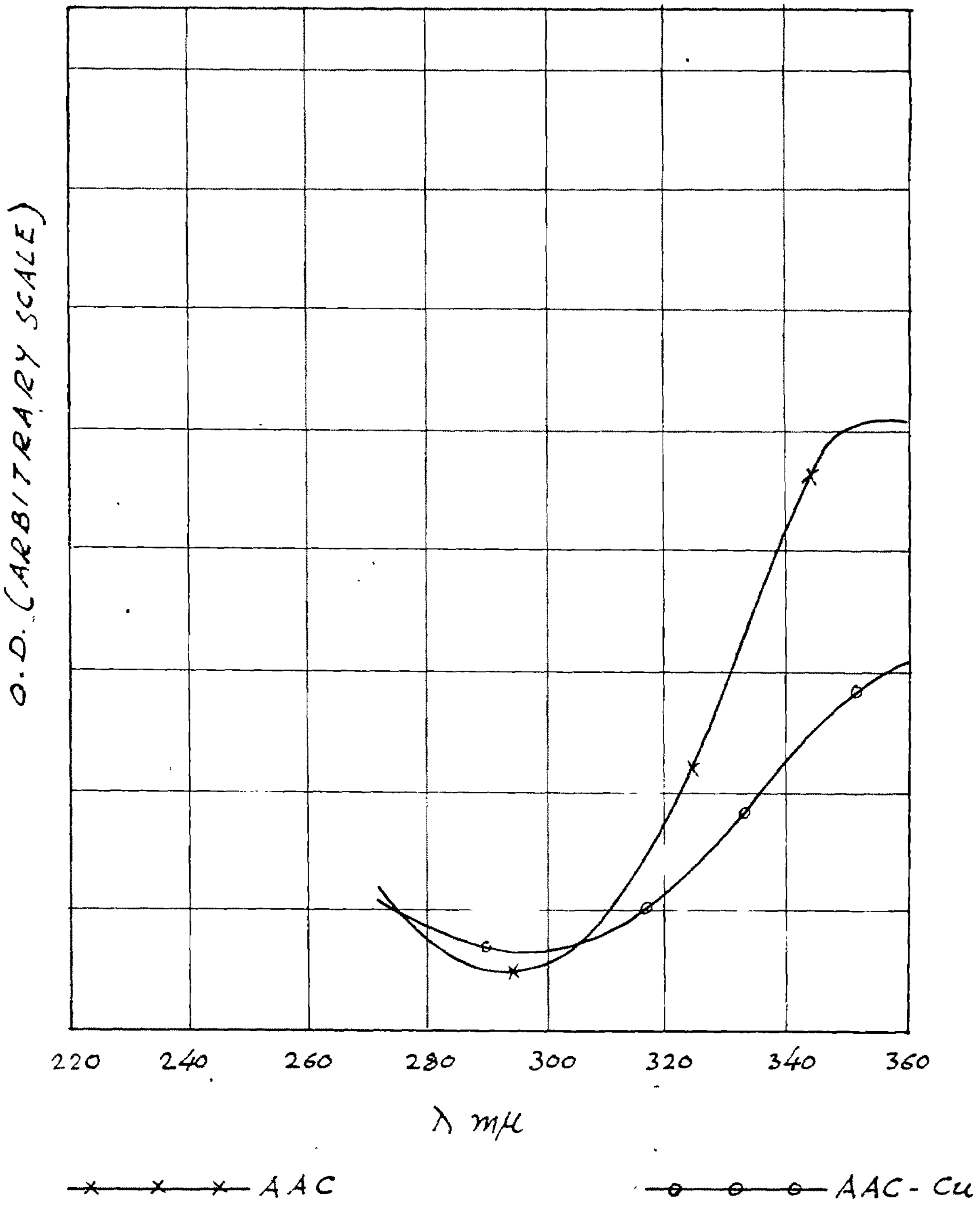
Table R-4 (contd).

(c) AAC-Cu

3450 (w)
3000 (w)
1650 (sh)
1620 (s)
1520 (s)
1350 (s)
1290 (m)
1200 (m)
1060 (w)
1030 (w)
990 (w)
950 (w)
910 (w)
780 (w)
750 (w)

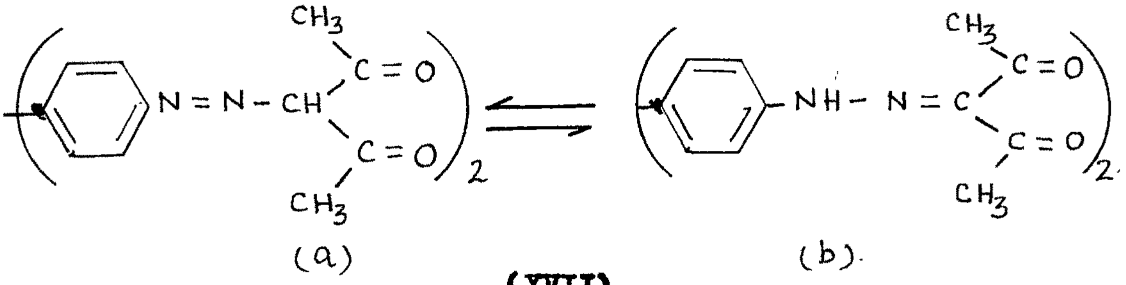
(d) BAAC-Cu

3400 (m) b
1660 (m)
1620 (sh)
1600 (s)
1500 (m)
1390 (s)
1350 (s)
1325 (s)
1210 (m)
1175 (w)
1090 (w)
1050 (w)
1000 (w)
950 (m)
820 (m)
760 (w)



UV ABSORPTION SPECTRA OF AAC AND AAC-Cu

FIG. R-14



(XVII)

(b) Cu-complex with AAC :

On the basis of analysis the complex of Cu with AAC shows the ratio of metal to ligand as 1:2; hence it may be represented as (XVIII).

$$CuL_2^*$$

(XVIII)

where LH* represents the ligand AAC. It is soluble in alcohol, acetone, benzene, petroleum ether etc. and gives greenish yellow solution with alcohol.

The absorption spectra of the complex in the visible and ultraviolet regions are presented in figs. R-13 and R-14. It has an absorption band at 430 mμ with a shoulder at 558 mμ.

Its magnetic moment has been calculated as 2.16 B.M. It is suggested from the colour and magnetic moment observations that copper forms square planar complex with the two ligand anions and can be 5-coordinate by linking to the adjoining molecule.

Some of the IR bands of the complex are presented in table R-4. The absorption band for chelated carbonyl group observed at 1620 cm^{-1} in the spectrum of the ligand appears intensified in the spectrum of the complex.

The thermogram (T.G.A.) of the complex is presented in fig. R-15. It can be suggested from wt. loss that the complex undergoes decomposition on heating and that the decomposition takes place in two steps. The results suggest that the stability of azoacetylacetone is much reduced by its coordination with copper.

(c) Cu-complex with BAAC :

On the basis of analysis, the complex of copper with BAAC shows the ration of copper to ligand as 3:1; hence it appears to possess a complicated structure. It gave a positive test for acetate; it may, therefore, be represented as (XIX).

$$\left[\left\{ \mathrm{Cu - R} \right\}\right] \left[\left\{ \mathrm{Cu\ Ac_2} \right\}\right]_2 \quad \mathrm{aq_2}$$

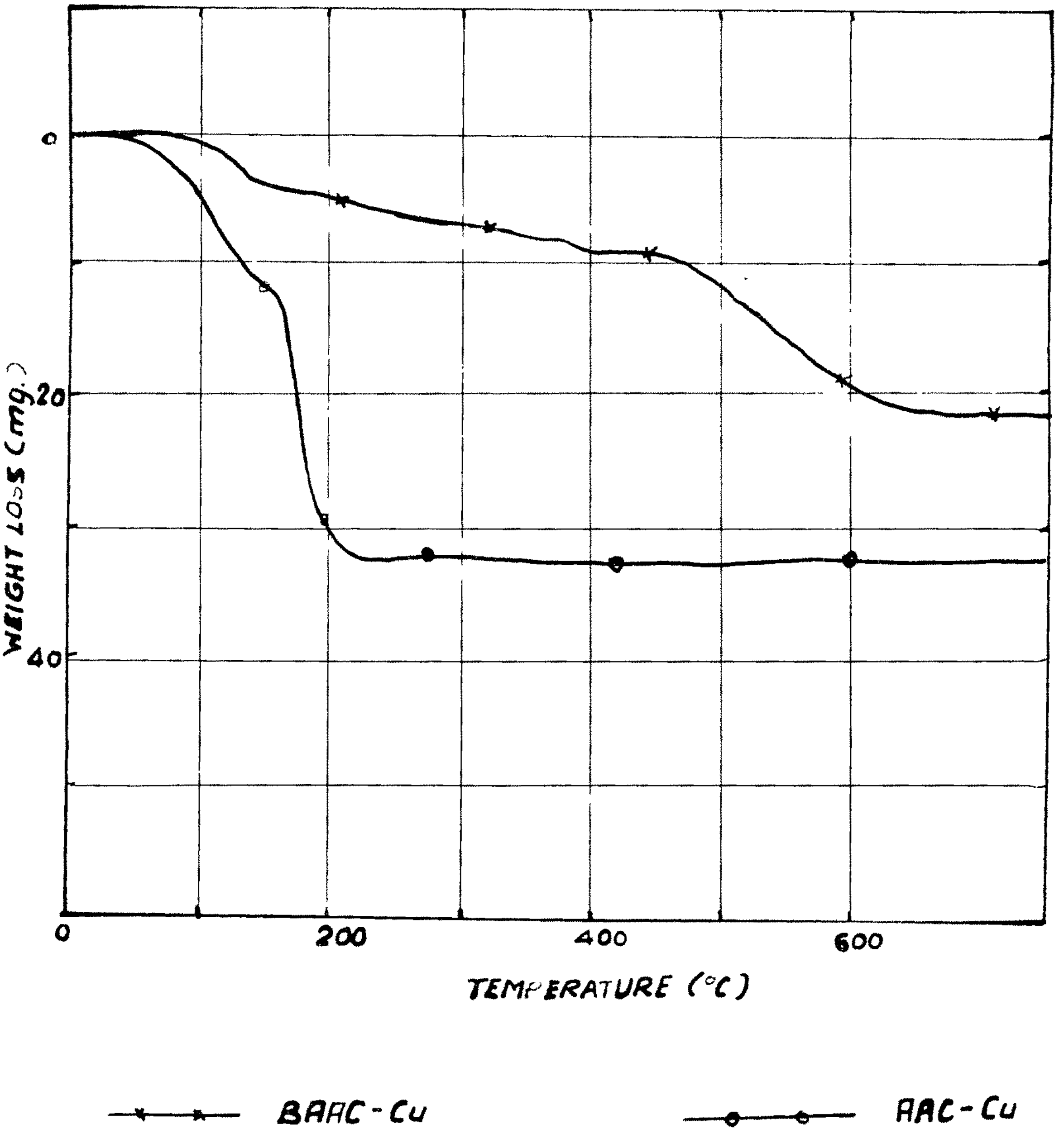
(XIX)

where RH_2 represents BAAC and AcH acetic acid.

It is sparingly soluble in dimethylformamide and possesses considerable mechanical strength. The crystals are hard to grind ; and can be obtained in powdered form with great difficulty.

The absorption spectrum in the visible region of the complex in dimethylformamide is presented in fig. R-11. It has a shoulder at 480 mμ.

Some of the IR bands of the complex are presented in table R-4. The bands at 3400 cm^{-1} and 3280 cm^{-1} indicate



THERMOGRAM OF AAC-Cu AND BAAC-Cu

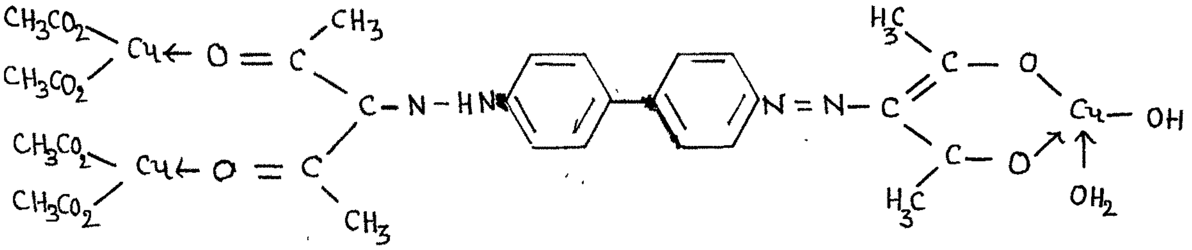
FIG. R-15

the presence of water and hydrazone NH in the molecule. Further the bands observed at 1660 cm^{-1}, 1620 cm^{-1} and 1600 cm^{-1} may be attributed to the acetate, coordinated dicarbonyl and chelated enolic ketone groups present in the complex.

The thermogram (T.G.A.) of the complex is presented in fig. R-15. It is suggested from the wt. loss that (i) it decomposes losing water and acetate and (ii) the decomposition continues at higher temperature.

The magnetic moment of the complex has been determined as 2.43 B.M.

On the basis of the above observations the complex may be represented as (XX).



(XX)

The results show that the thermal stability of BAAC-Cu is greater than that of AAC-Cu.

III 4. Schiff bases of salicylaldehyde and their transition metal complexes and coordination polymers :

Pfeiffer and coworkers[142,157] prepared copper salicylaldiminates wherein aromatic diamines such as o, m and p-phenylenediamines, benzidine, 1,4-naphthalenediamine etc. were used.

Terent'ev and coworkers[158] obtained slimy precipitates of Cu and Ni chelates of Schiff bases of salicylaldehyde with diamines such as benzidine, m- and p-phenylenediamine etc. Later they[72,104] investigated the formation of Fe, Co, Ni, and Cu chelates of the Schiff bases of 5,5'-methylene bis-(salicylaldehyde) with mono- and diamines.

Marvel and coworkers[101,102] prepared the coordination polymers of Fe, Co, Ni and Cu with Schiff bases of 5,5'-methylene bis-(salicylaldehyde) and Goodwin and Bailer (jr)[100] studied the coordination polymers of Fe, Co, Ni and Cu with the Schiff bases of 5,5'-methylene (or sulphonyl) bis-(salicylaldehyde) with triamines and tetramines. Belskii and Tsiknov[74] also investigated the coordination polymers of Fe, Co, Ni and Cu with Schiff bases of 5,5'-methylene bis(salicylaldehyde) with mono- and diamines. In recent years Lewis and Walton[159] investigated the Cu chelates of Schiff bases of salicylaldehyde with numerous diamines and studied their various properties.

We have prepared the chelates of Cu, Ni and Co with the Schiff bases of salicylaldehyde and diamines such as benzidine and p-phenylenediamine. Their magnetic moments calculated from their magnetic susceptibilities and diamagnetic corrections are presented in Table R-5.

(a) Schiff bases :

Schiff bases of salicylaldehyde with benzidine and p-phenylenediamine were prepared by the known methods.[142,158] Attempts were made to prepare the complexes of Cu, Ni and Co with these Schiff bases but they were unsuccessful. Similarly when metal acetates, salicylaldehyde and diamine were mixed together, the product separated was insoluble Schiff base and it did not contain any metal. Further, when metal amine was mixed with salicylaldehyde, the precipitates of the Schiff base were obtained. Hence it can be concluded that (i) the solubility of Schiff base is much less than that of the chelated Schiff base, (ii) metal-amine bond is very weak and would readily break in presence of salicylaldehyde with the formation of Schiff base and (iii) salicylaldehyde preferentially couples with amine rather than with metal. We found, however, that when bis-(salicylaldehyde) metal is treated with amine the Schiff base of the metal chelate is formed. Excess of amine was used as it was considered that some of it might be used up in coordination with the metal.

(b) Cu-complex with the Schiff base of salicylaldehyde and benzidine : (SAB-Cu)

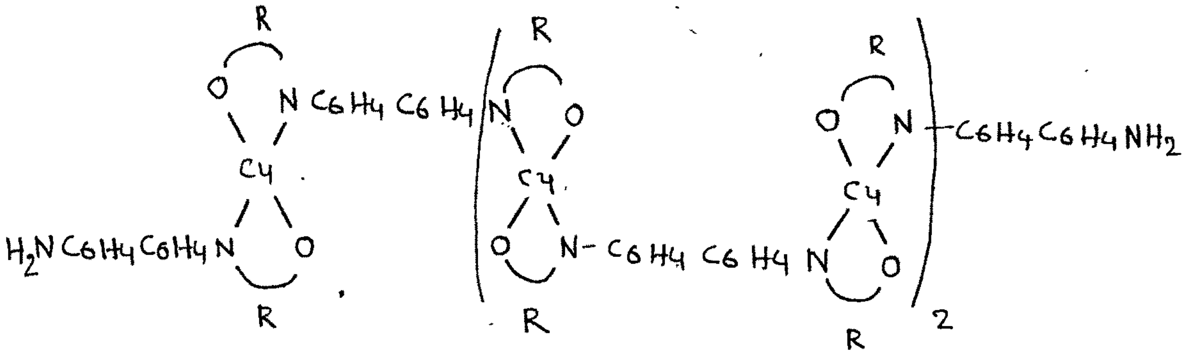
It was prepared from bis-(salicylaldehyde) copper and benzidine.

On the basis of analysis, it is formulated as a linear chain (XXI).

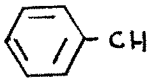
Table R-5

Magnetic moments of the complexes

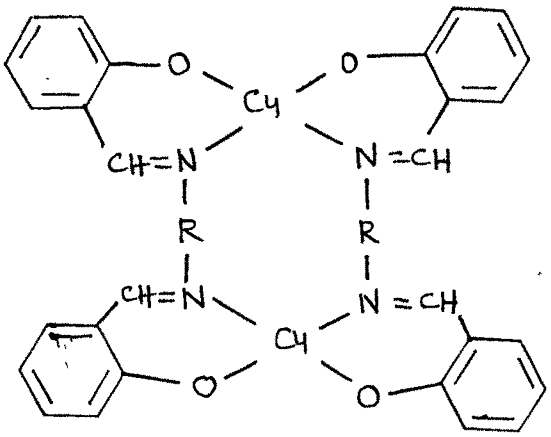
No.	Compound	Molar Magnetic susceptibility (per metal atom) $X_m \times 10^6$	Corrected Molar Magnetic susceptibility (per metal atom) $X_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1	SAB-Cu	1442	1689	2.00
2	SAB-Co	8181	8483	4.56
3	SAB-Ni	3529	3752	3.03
4	SAP-Cu	1486	1712	2.05
5	SAP-Co	10420	10724	5.14
6	SAP-Ni	6792	6957	4.18



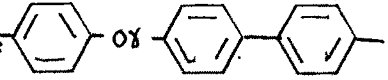
(XXI)

where R represents 

Earlier investigators have represented their products in both the polymeric and nonpolymeric forms. Pfeiffer and coworkers reported first the preparation of monomeric complexes of Cu but later showed, on the basis of cryoscopic measumements, that these were actually dimers and represented them as (XXII)



(XXII)

where R = 

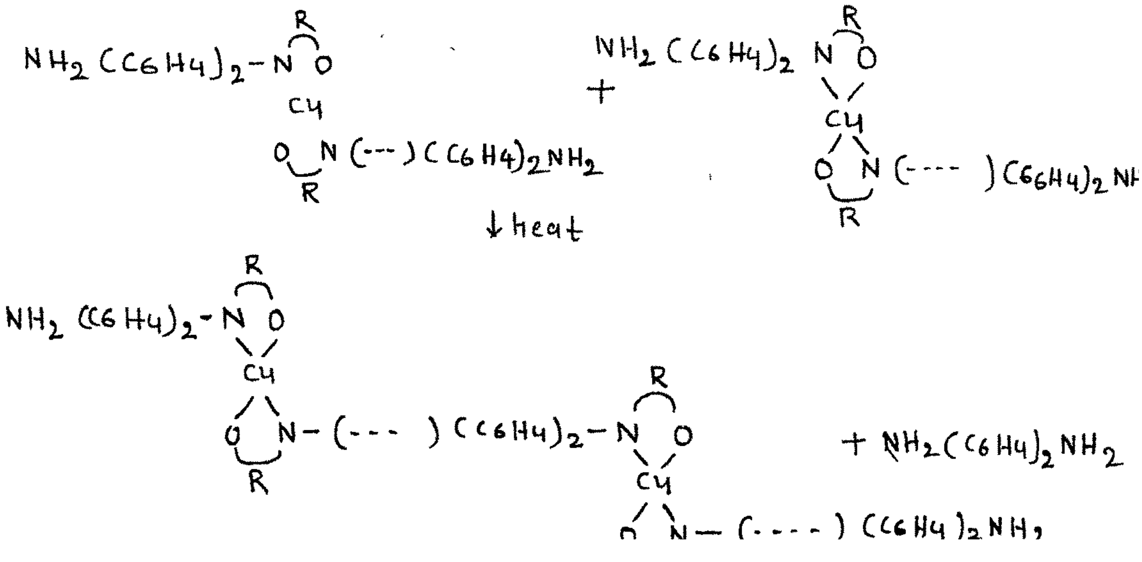
No iodine is liberated from its dilute solution by potassium iodide.

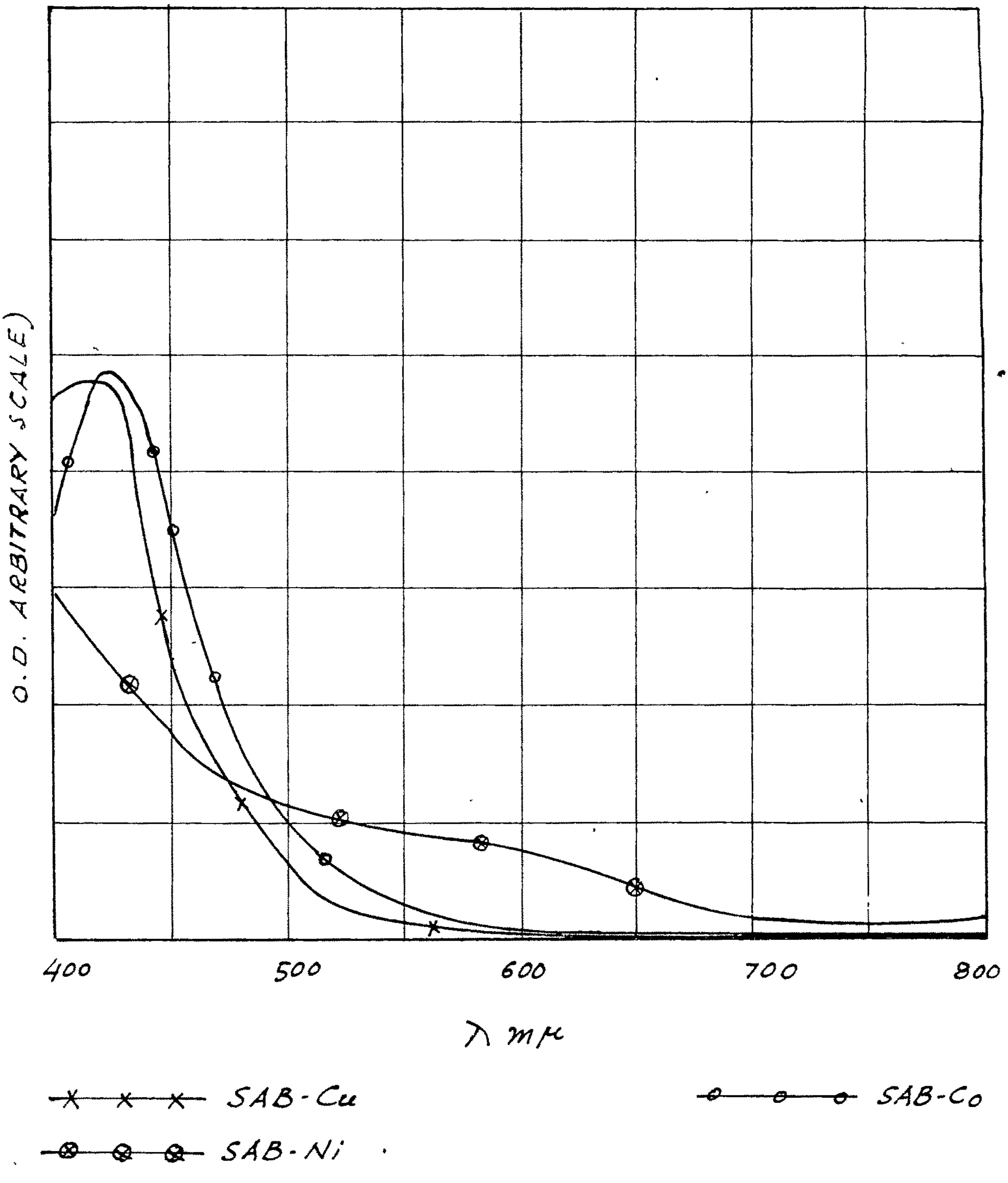
The magnetic moment of the complex is calculated as 2.0 B.M.

The absorption spectrum of the complex in the visible region is presented in fig. R-16. A band at 410-20 mμ is observed.

Some important IR bands of the complex are presented in Table R-6. The band at 3410 cm^{-1} is attributed to the free NH_2 group. Capella and Fedeli[160] found that C=N bond is split for the copper complex and may be due to the nonplanar nature (SP^3) while no split is observed for Co and Ni complexes (dsp^2 or d^2sp^3). In the present case the band is observed at 1615 cm^{-1} without splitting and may be attributed to dsp^2 or dsp^3 nature of bonding.

The thermogram of the complex (T.G.A.) is presented in fig. R-17. The results indicate that heating leads to further polymerisation through anil formation by exchange reaction with the loss of excess benzidine molecules of the linear chains. The results suggests that the product obtained has relatively low degree of polymerisation which can be increased by thermal treatment. The above observations are in agreement with the structure (XXI) proposed earlier. The thermal polymerisation reaction may be represented as follows:





VISIBLE ABSORPTION SPECTRA

OF SAB-M

FIG. R-16

Table R-5

Some characteristic IR frequencies (cm^{-1}) of the chelates of Schiff's bases :

(a) SAB-Cu

3410 (w) b
1630 (vs)
1540 (s)
1505 (m)
1495 (s)
1450 (s)
1380 (m)
1350 (w)
1340 (m)
1180 (s)
1150 (s)
1120 (w)
1025 (w)
1000 (w)
980 (w) b
920 (w)
860 (w)
830 (m)
755 (m)

(b) SAB-Co

3330 (m)
3220 (w)
3020 (w)
1600 (s)
1575 (s)
1525 (s)
1480 (s)
1450 (m)
1430 (s)
1380 (m)
1340 (w)
1300 (m)
1170 (s)
1150 (s)
1130 (w)
1030 (w)
1005 (w)
970 (w)
860 (w)
825 (m)
760 (m)

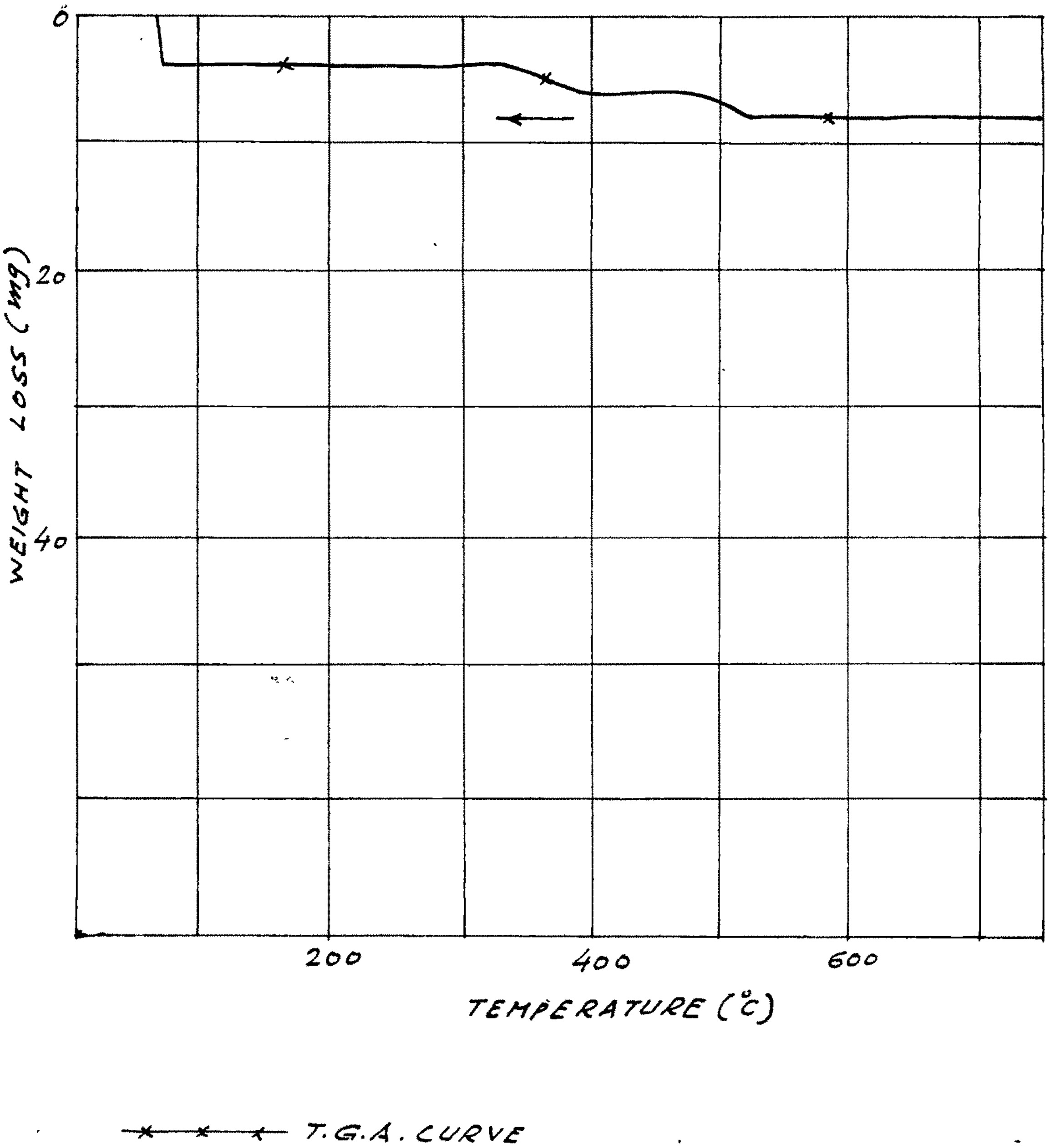
Table R-6 (contd.)

(c) SAP-Cu

3300 (m)
1600 (vs)
1500 (s)
1460 (m)
1420 (m)
1400 (w)
1320 (w)
1170 (w)
1140 (m)
1110 (w)
1015 (w)
900 (w)
835 (w)
765 (w)

(d) SAP-Co

3300 (s)
1600 (s)
1460 (s)
1300 (m)
1170 (m)
1150 (m)
900 (w)
835 (w)
760 (m)



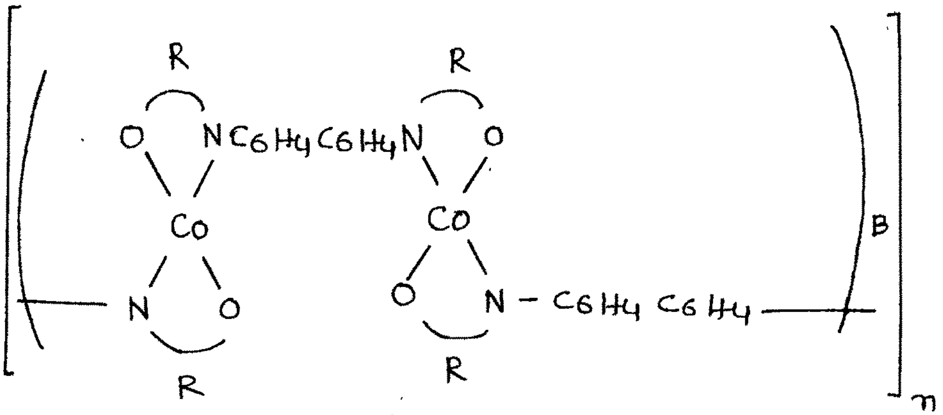
THERMOGRAM OF SAB-Cu

FIG. R.-17

(c) Cobalt complex of the Schiff base of salicylaldehyde with benzidine (SAB-Co):

It was prepared from bis-(salicylaldehydo) cobalt and benzidine.

On the basis of analysis, it is formulated as (XXIII).



(XXIII)

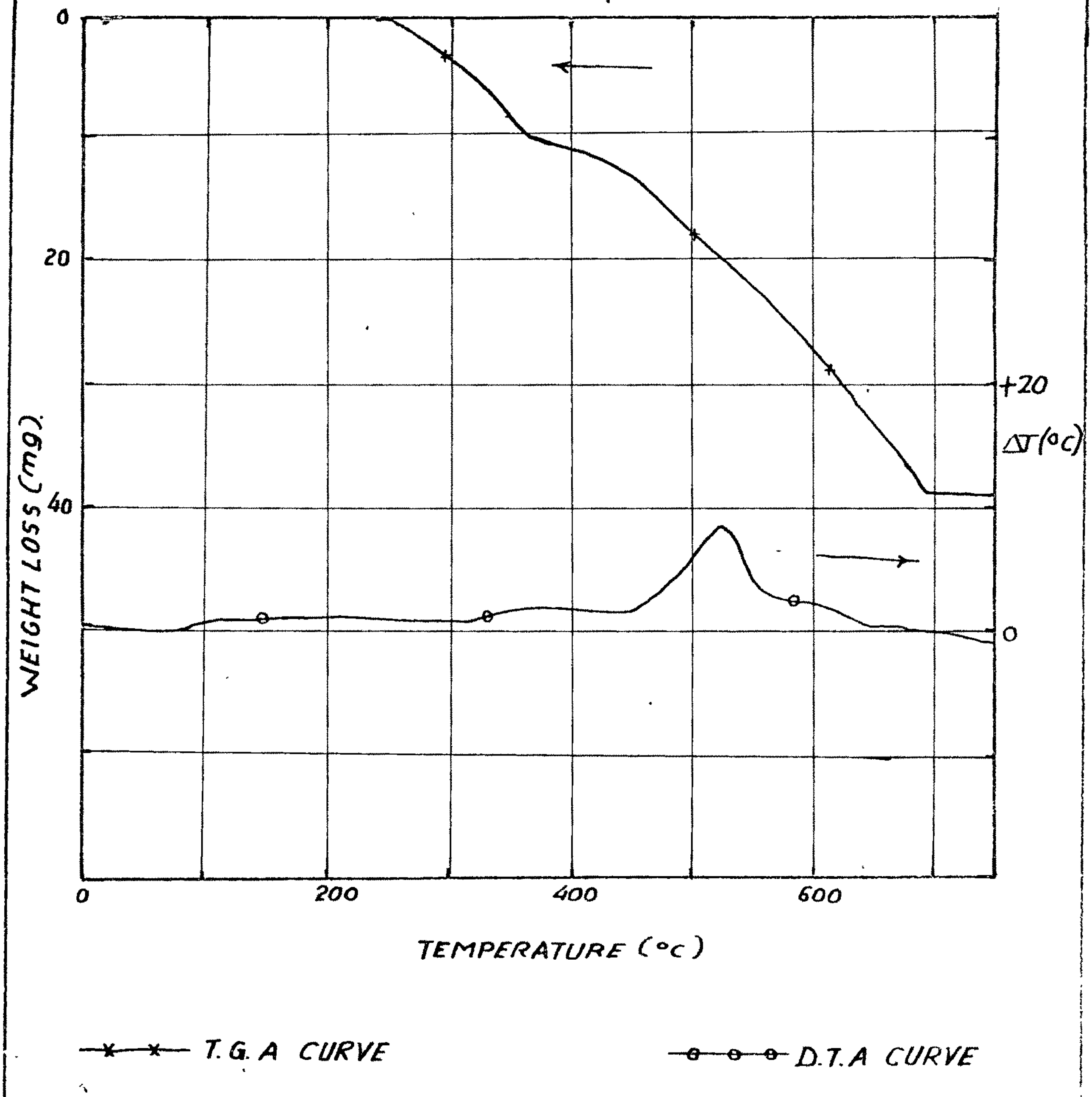
Where B represents benzidine. It was possible to isolate both the Schiff base and benzidine from the complex.

The absorption spectrum of the complex in the visible region is presented in fir. R-16. It has an absorption band at 430 mμ.

Some important IR bands of the complex are presented in Table R-6. A band for free (weakly coordinated) NH_2 group is observed at 3350 cm^{-1}.

The magnetic moment of the complex is 4.56 B.M. It suggests tetrahedral nature of the monomeric unit.

The thermograms (T.G.A. and D.T.A.) of the complex are presented in fig. R-18. The results indicate that (i) it loses benzidine over a temperature range of 260-360°C. and (ii) decomposis at higher temperature. The results suggest that the complex SAB-Co is thermally much less stable than SAB-Cu.



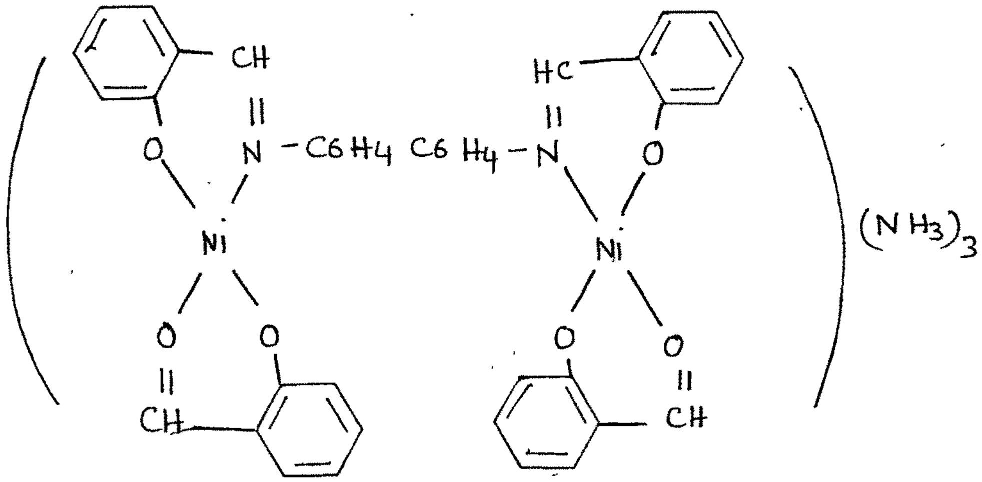
THERMOGRAMS OF SAB-Co.

FIG. R-18

The above observation do not clearly indicate whether benzidine is weakly coordinated to metal atom or not. Hence structure (XXIII) or its modification with benzidine weakly coordinated to Co-atom may be considered possible.

(d) Ni-complex of the Schiff base from salicylaldehyde and benzidine (SAB-Ni) :

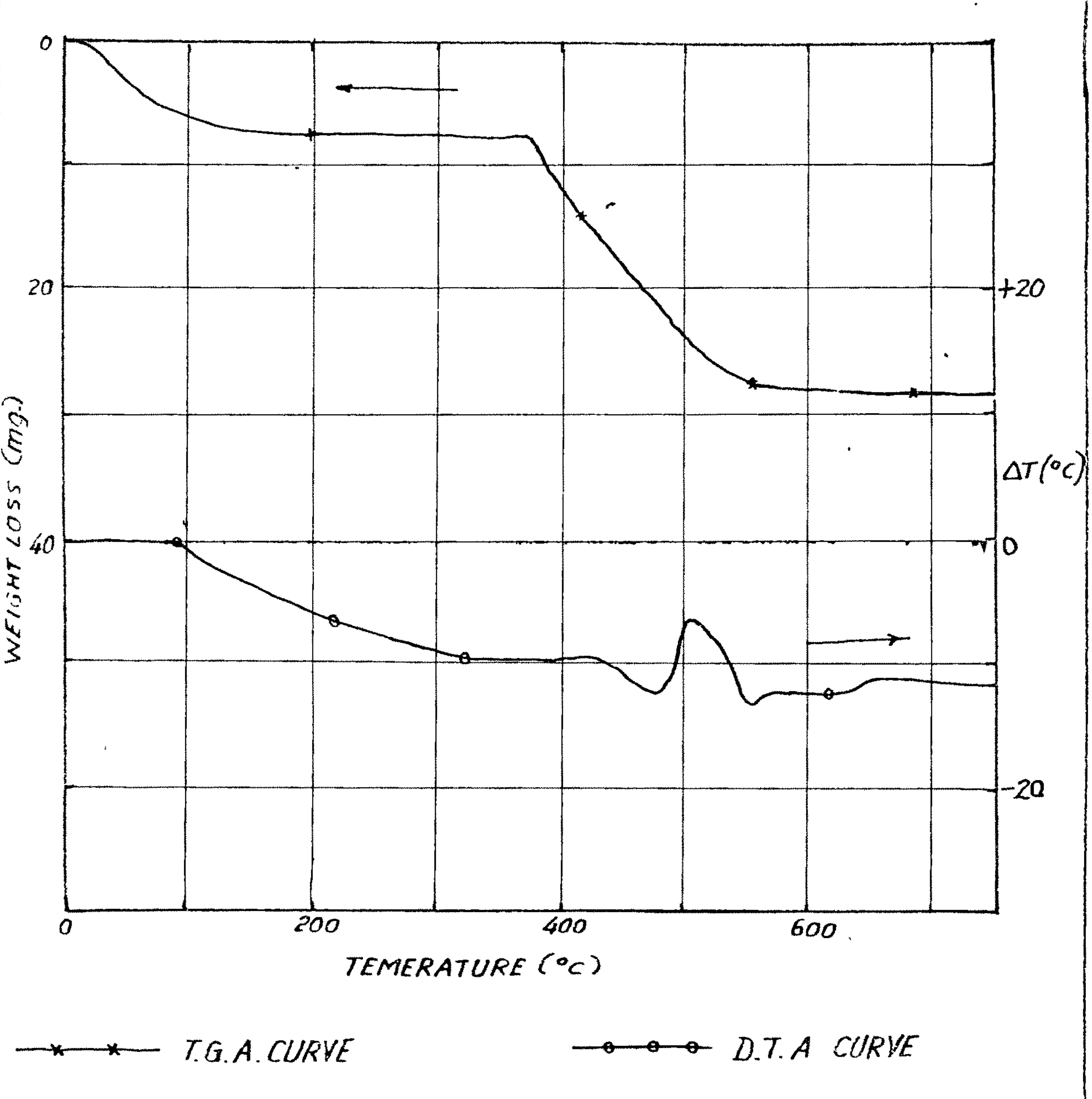
It was prepared from bis-(salicylaldehydo) nickel and benzidine. The ratio of metal to nitrogen is found from analysis as 1:2.5. Hence it is formulated as (XXIV).



(XXIV)

The absorption spectrum of the complex in the visible region is presented in fig. R-16. It has a shoulder at 460 mμ.

The thermograms (T.G.A. and D.T.A.) of the complex are presented in fig. R-19. The results indicate that (i) it loses absorbed water and ammonia upto 100°C. and (ii) decomposes at higher temperature.



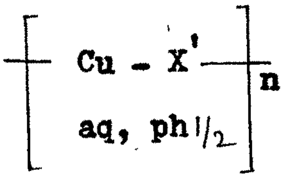
THERMOGRAMS OF SAB - Ni

FIG. R-19

Its magnetic moment per nickel atom is calculated as 3.03 B.M. The monomer is considered to have tetrahedral configuration, although the magnetic moment is lower than anticipated.

(e) Copper complex of the Schiff base of salicylaldehyde with p-phenylenediamine (SAP-Cu) :

It was prepared from bis-(salicylaldehydo) copper and p-phenylelediamine. On the basis of analysis, it is formulated as (XXV)



$$\left[\begin{matrix} \text{Cu} - X' \\ \text{aq}, \ \text{ph}\,1/2 \end{matrix} \right]_n$$

(XXV)

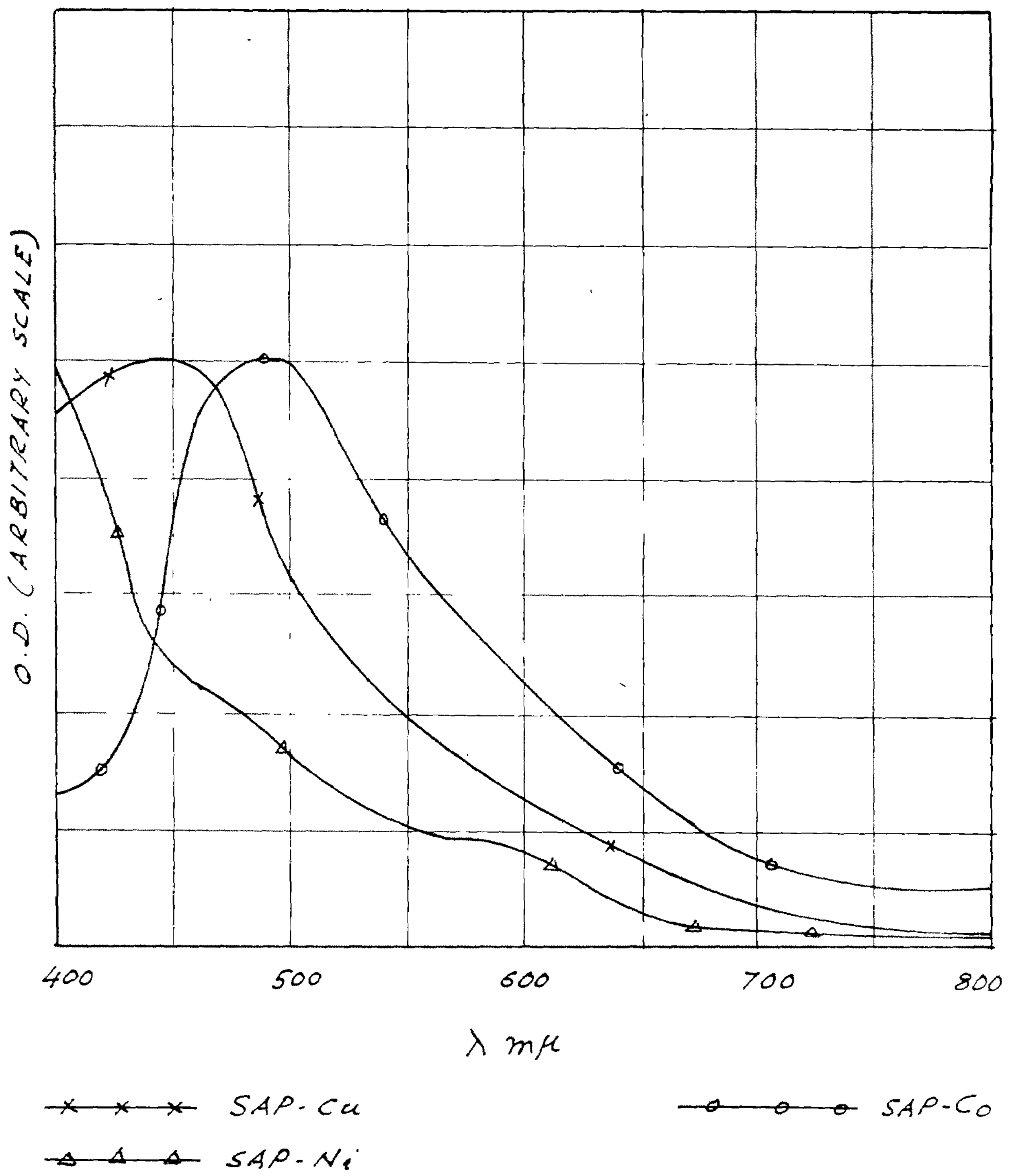
where $X'H_2$ represents the Schiff base and ph represents p-phenylenediamine.

It was possible to isolate p-phenylenediamine and Schiff base from the complex.

Its absorption spectrum in the visible region is presented in fig. R-20. The absorption band is observed at 440 mμ.

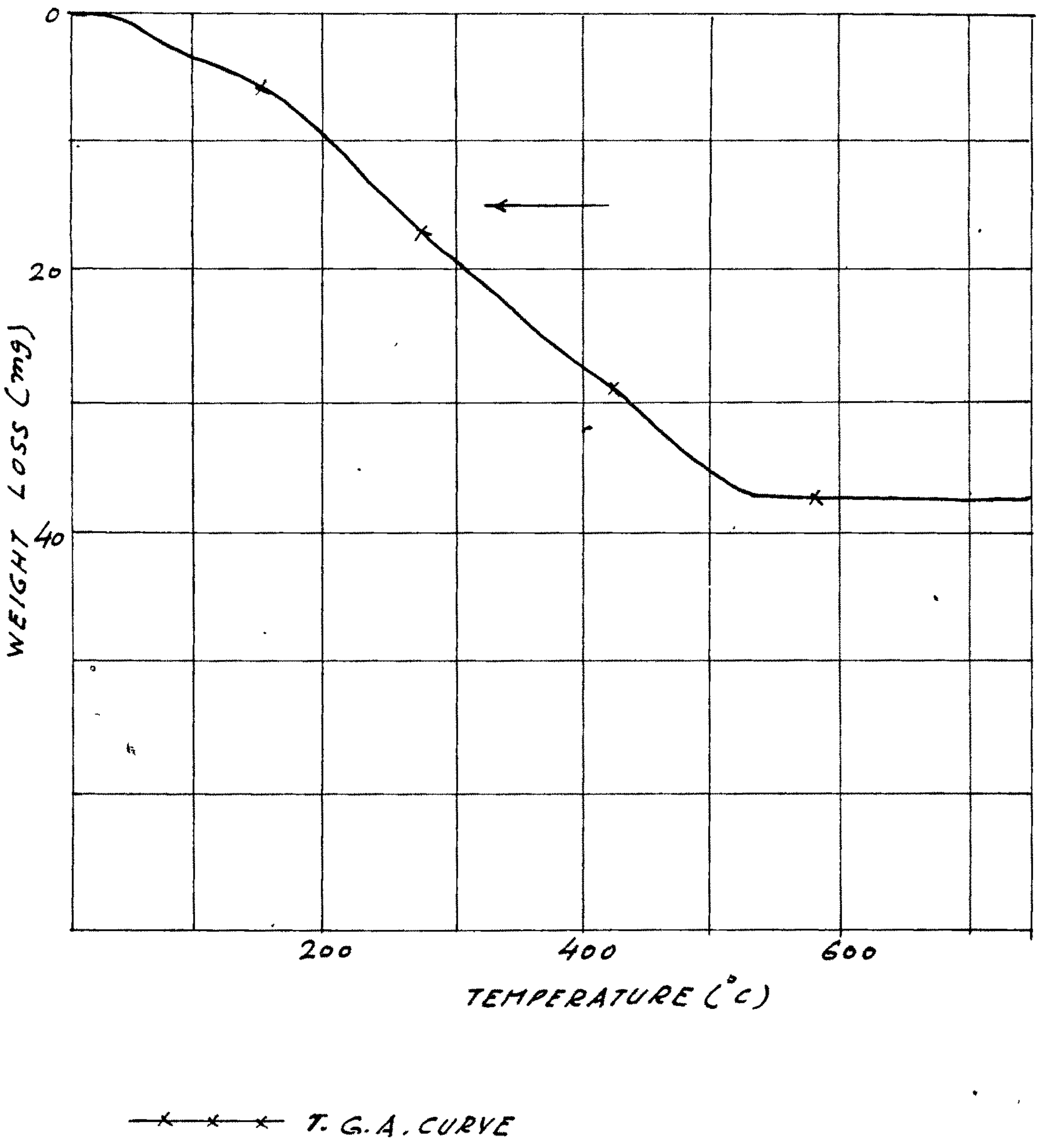
Some important IR bands are given in Table R-6. A band observed at 3300 cm^{-1} may be attributed to coordinated NH_2 group.

The thermogram of the complex is presented in fig. R-21. It shows that the complex loses water and p-phenylenediamine and the loss is accompained by the decomposition of the complex.



VISIBLE ABSORPTION SPECTRA OF SAP-M

FIG. R-20

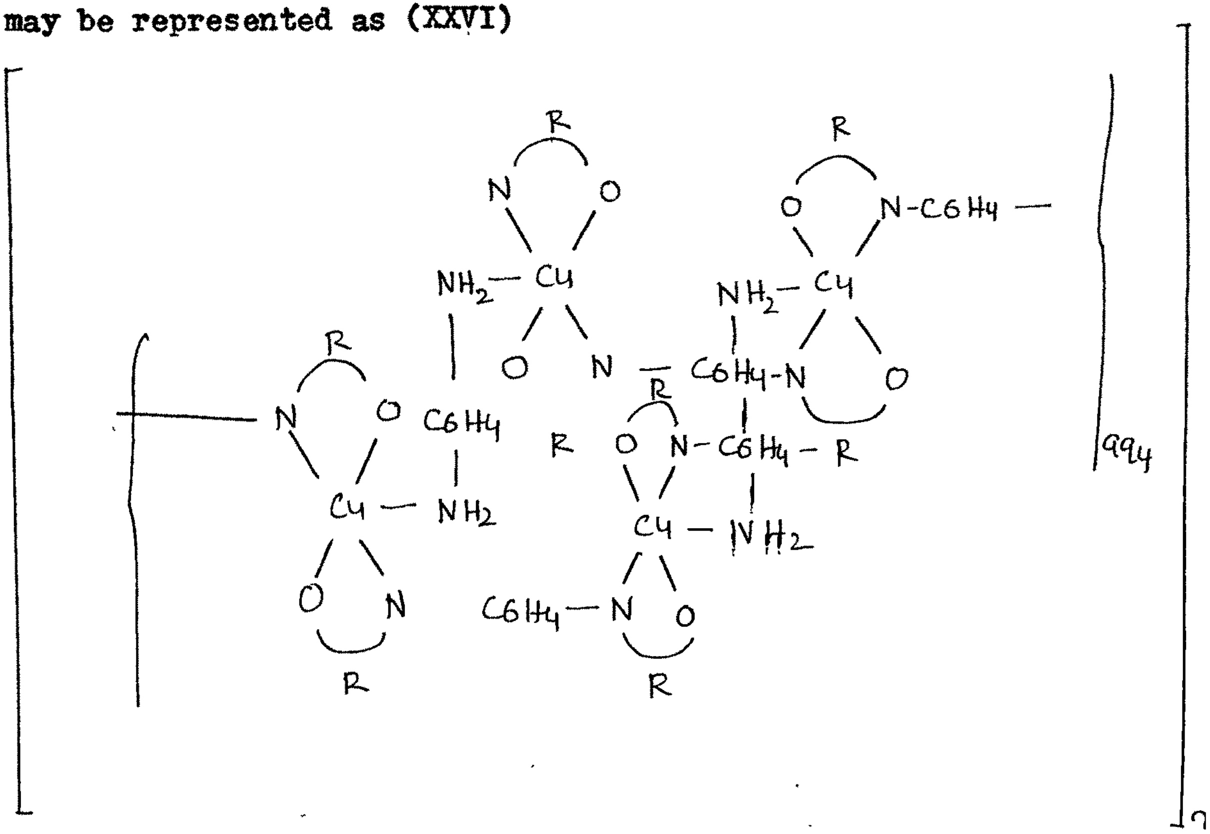


THERMOGRAM OF SAP - Cu

FIG. R-21

Its magnetic moment per Cu-atom is calculated as 2.05 B.M.

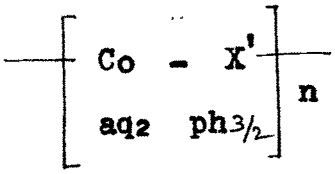
On the basis of the above observations Cu in the complex is considered to be 5-coordinated and the complex may be represented as (XXVI)



(XXVI)

(f) <u>Cobalt complex of the Schiff base of salicylaldehyde with p-phenylenediamine (SAP-Co)</u> :

It was prepared from bis-(salicylaldehydo) cobalt and p-phenylelediamine. On the basis of analysis, it is formulated as (XXVII).



$$-\left[\begin{array}{cc} \mathrm{Co} & -\ \mathrm{X'} \\ \mathrm{aq_2} & \mathrm{ph_{3/2}} \end{array}\right]_n-$$

(XXVII)

It was possible to isolate p-phenylenediamine and Schiff base from the complex.

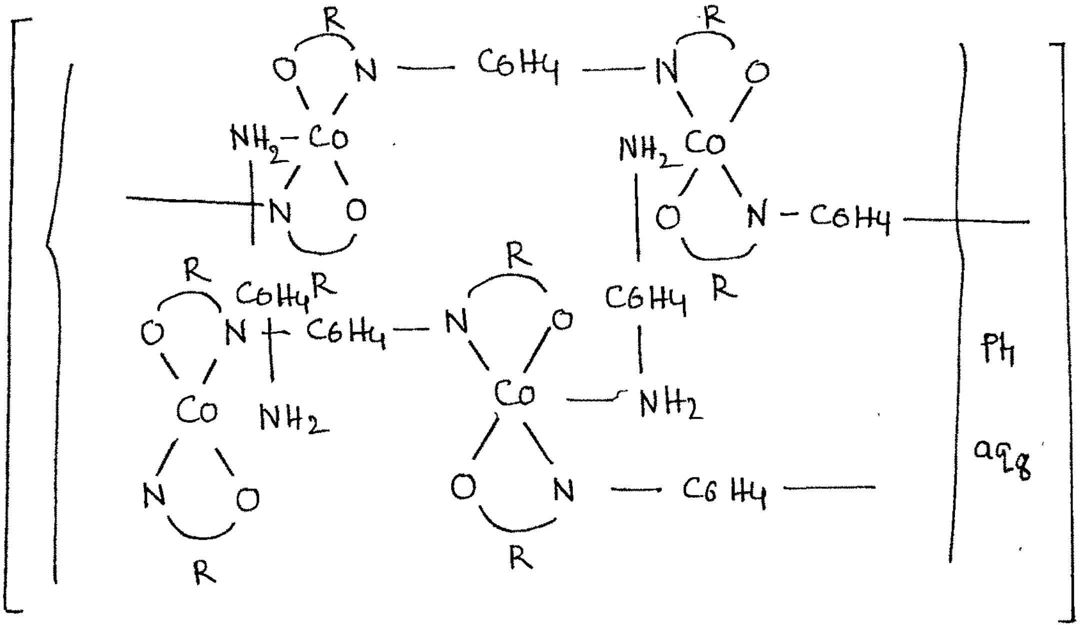
Its absorption spectrum in the visible region is presented in fig. R-20. It has an absorption band at 490 mμ.

Some important IR bands are given in Table R-6. A band observed at 3300 cm^{-1} may be attributed to coordinated NH_2 group.

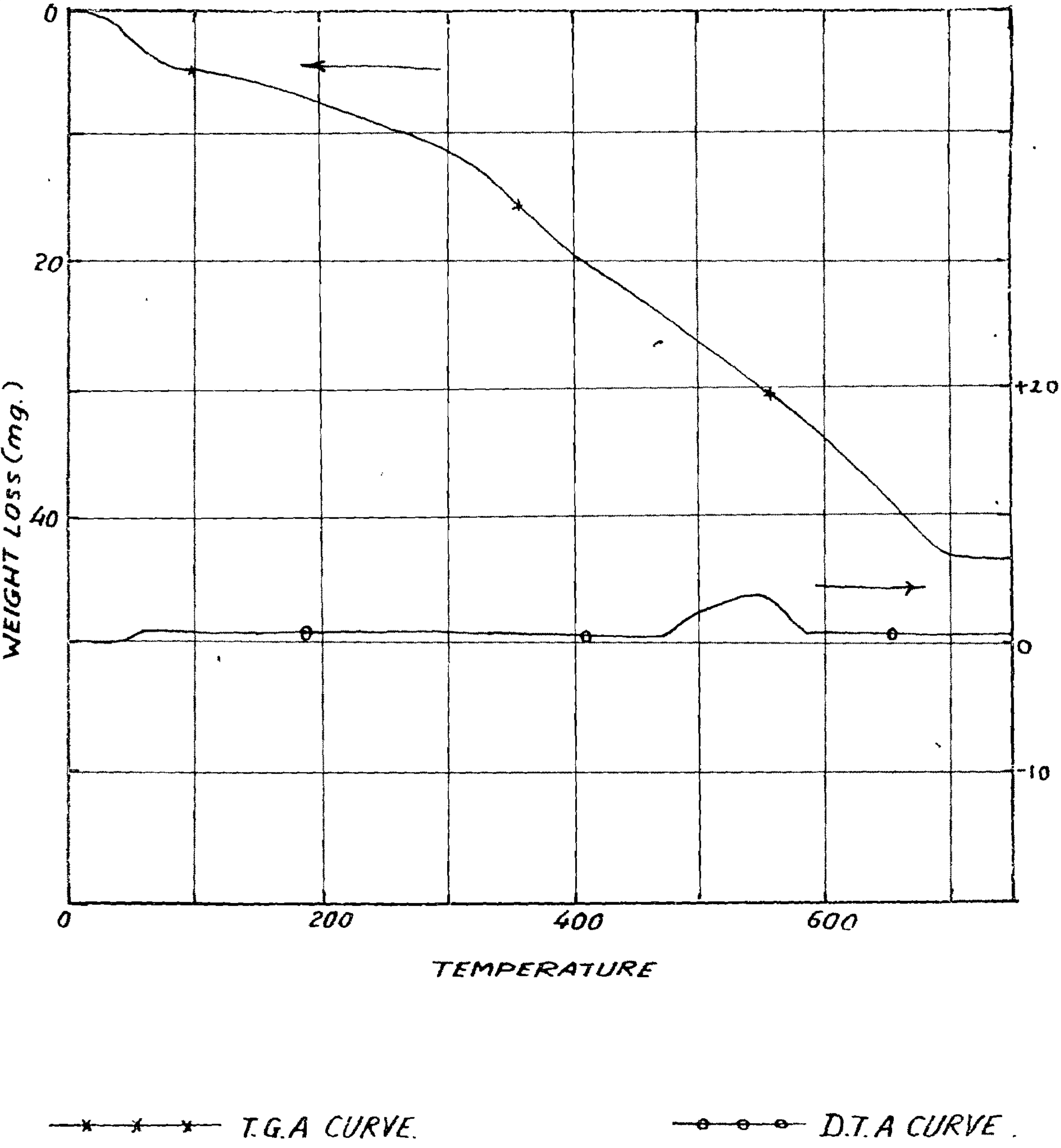
The thermograms (T.G.A. and D.T.A.) of the complex are presented in fig. R-22. The results indicate that (i) at low temperature water is readily removed (ii) on further heating it loses p-phenylenediamine without evolution or absorption of heat and (iii) it decomposes at higher temperature, with the evolution of heat and probably leaving the residue of cobalt.

Its magnetic moment per Co-atom is calculated as 5.14 B.M. Hence the monomer is considered to have an octahedral structure.

On the basis of the above observations the complex is considered to be polymeric and represented as (XXVIII).



(XXVIII)

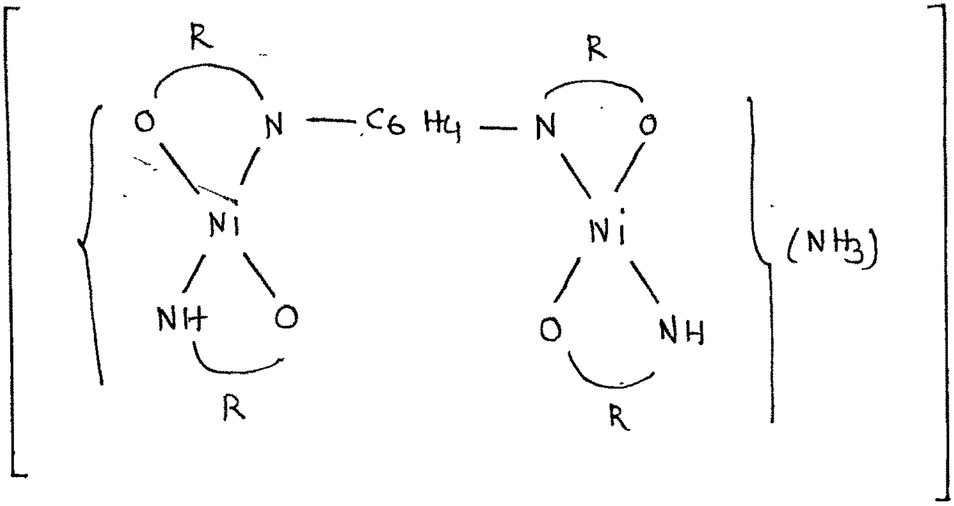


THERMOGRAMS OF SAP-Co.

FIG. R-22(a)

(g) Nickel complex of the Schiff base of salicylaldehyde with p-phenylenediamine (SAP-Ni) :

It was prepared from bis-(salicylaldehydo) nickel and p-phenylenediamine. On the basis of analysis it is formulated as (XXIX).

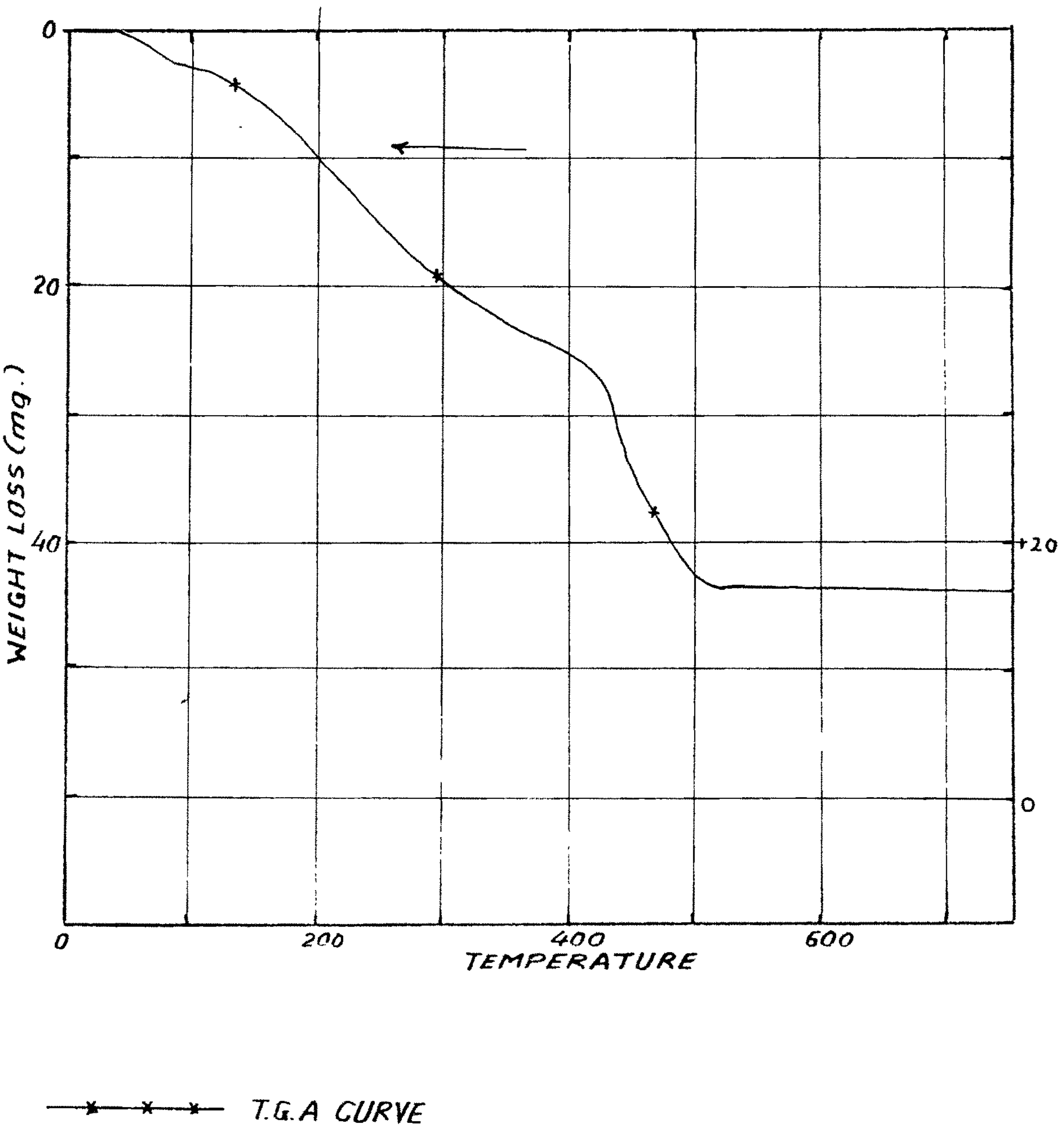


(XXIX)

Its absorption spectrum in the visible region is presented in fig. R-20. It has shoulders at 440 mμ and 560 mμ.

Its magnetic moment for Ni-atom is calculated as 4.18 B.M. Hence it is considered to possess tetrahedral structure.

The thermogram of the complex is presented in fig. R-23. It indicates that the complex (i) loses absorbed water and ammonia at low temperature and (ii) undergoes decomposition in two steps leaving the residue of nickel. The results indicate that SAP-Ni is much less thermally stable than SAB-Ni.



THERMOGRAM OF SAP – Ni

FIG R·22(b)

General :

We may have some generalisations regarding the nature of these complexes :

(i) These complexes do not appear to be monomeric . They are dimeric (e.g. Ni complexes) or polymeric (e.g. Cu and Co complexes). However, dimeric structures for the polymeric complexes suggested cannot be ruled out on the basis of the present observations alone.

(ii) The role of additional diamine molecules present in the case of copper and nickel complexes is not quite clear from the present investigations.

(iii) Ni complexes differ from Cu and Co complexes with respect to the Schiff base formation also. Only one of the two aldehyde groups of bis-(salicylaldehydo) nickel get transformed into anil with benzidine or p-phenylenediamine and the other group remains unattacked by benzidine (and ammonia) or gets converted into simple aldimine with p-phenylenediamine (and ammonia), whereas both groups get converted into anils in case of copper and cobalt complexes.

(iv) The thermal unstability, measured in terms of % loss in weight on heating is greater for the complexes of Schiff bases with p-phenylenediamine, than those of Schiff bases with benzidine.

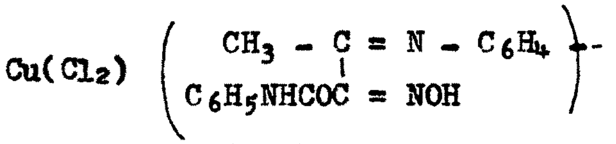
III 5. Schiff bases of vic-oxime ketones with diamine and their transition metal complexes :

Pfeiffer[161] and Masuda[162] studied the transition metal complexes of Schiff bases of 2,3-butanedione-2-oxime. Mathur and Narang[163] investigated such Schiff bases as gravimetric reagents for Ni and Pd.

Schiff bases of 2,3-dioxobutyranilide-2-oxime with aromatic and aliphatic monoamines have been prepared earlier[143,144] and their transition metal complexes have been studied. However, attempts to prepare the Schiff bases of the above oxime-ketone with aromatic diamines were unsuccessful. Hence transition metal complexes of such Schiff bases were prepared by treating (i) metal chlorides (ii) metal acetates or (iii) metal sulphates, with oxime-ketone and the diamine. Their magnetic moments calculated from magnetic susceptibilities and diamagnetic corrections are presented in Table R-7.

(i) Chloride method :

(a) The copper complex (OB-CuCl) prepared from copper chloride, oxime-ketone and benzidine, gave on analysis, the ratio of copper to nitrogen as 1:3 and it contained chlorine. Hence it is represented as (XXX).



$$Cu(Cl_2)\left(\begin{array}{r} CH_3-\underset{|}{C}=N-C_6H_4- \\ C_6H_5NHCOC=NOH \end{array}\right)$$

(XXX)

It is insoluble in common solvents except pyridine and dimethylformamide and does not melt upto 300°C.

Its magnetic moment per Cu-atom is calculated as 2.23 B.M.

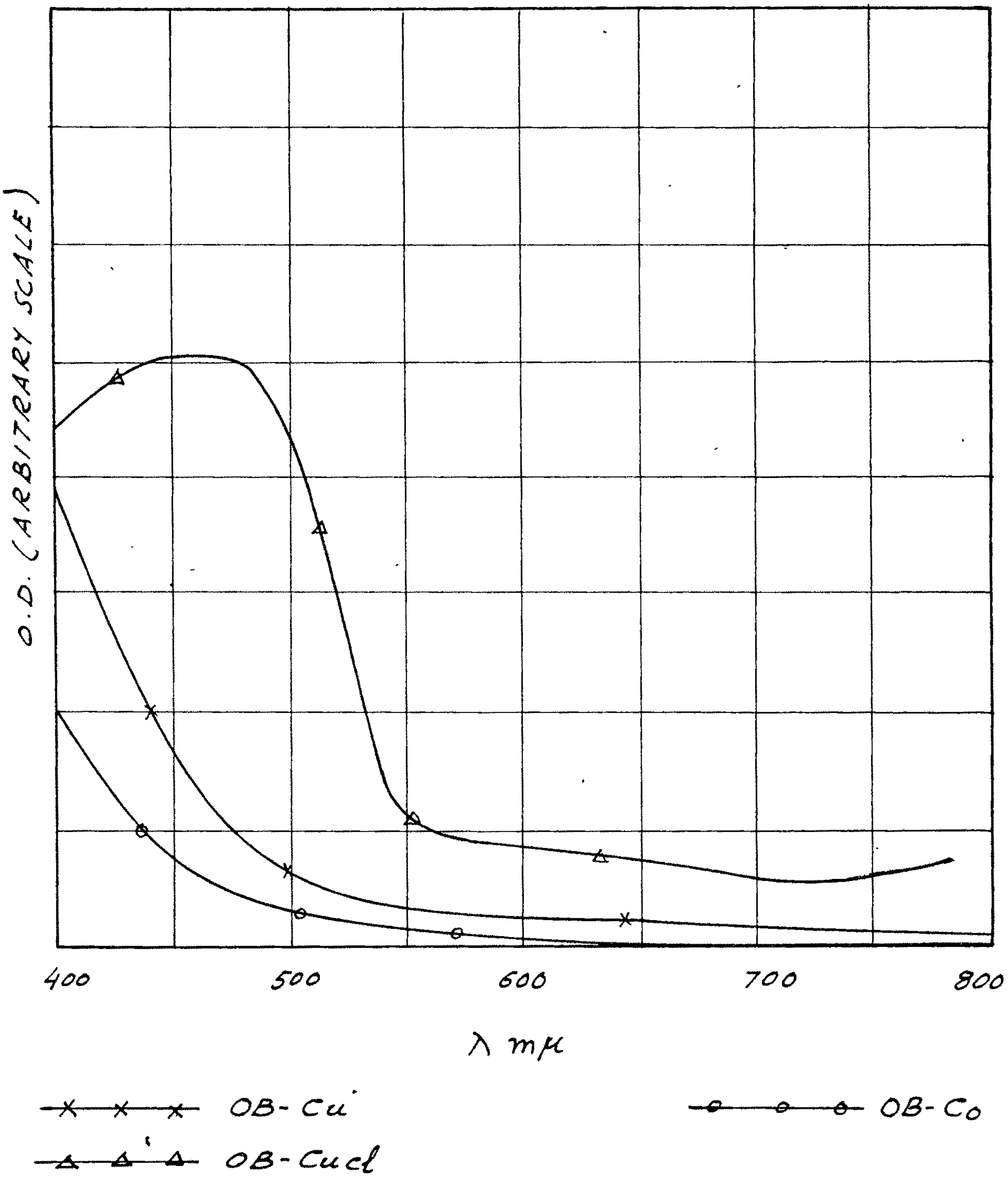
Its absorption spectrum in the visible region is presented in fig. R-23. It has a broad maximum at 440-80 mμ.

The thermogram of the complex is presented in fig.R-24.

Table R-7

Magnetic moments of the complexes

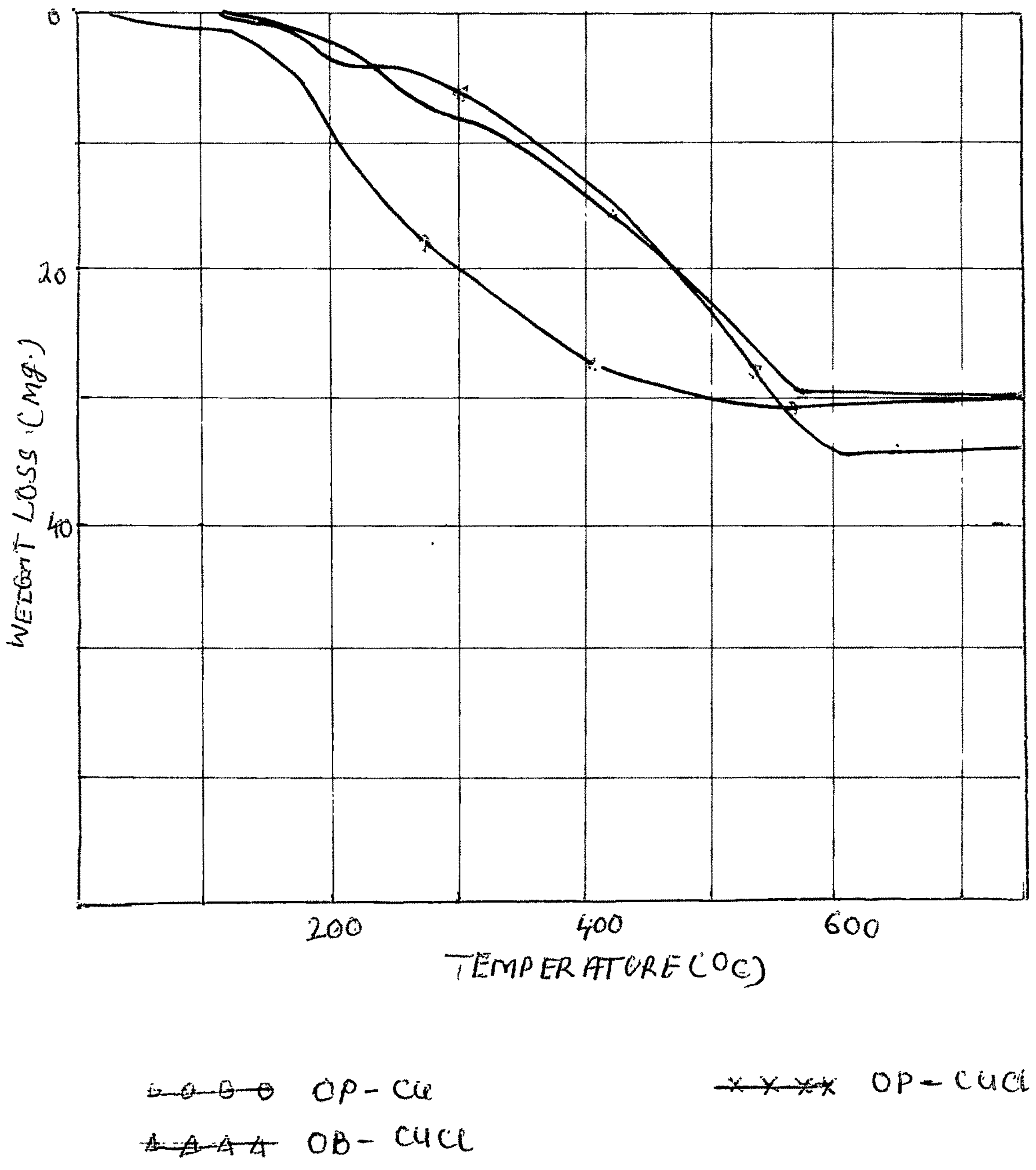
No.	Compound	Molar Magnetic susceptibility (per metal atom)	Corrected Molar magnetic susceptibility (per metal atom)	Magnetic moment (per metal atom)
		X_m x 10^6	X_m x 10^6	(μ) B.M.
(a)	Chloride method			
1	OB-NiCl	4291	4600	3.2
2	OB-CuCl	1853	2051	2.23
3	OP-NiCl	4237	4459	3.3
4	OP-CuCl	4899	5226	3.58
(b)	Acetate method			
5	OB-Cu	8541	8820	1.6
6	OB-CO	2415	2749	2.59
7	OP-Cu	879	1139	1.59
8	OP-Co	2594	2962	2.13
(c)	Sulphate method			
9	OB-Fe	4276	4660	3.36
10	OP-Fe	1120	1322	5.71



VISIBLE ABSORPTION SPECTRA OF

OB-Cu, OB-Cucl AND OB-Co

FIG.R-23

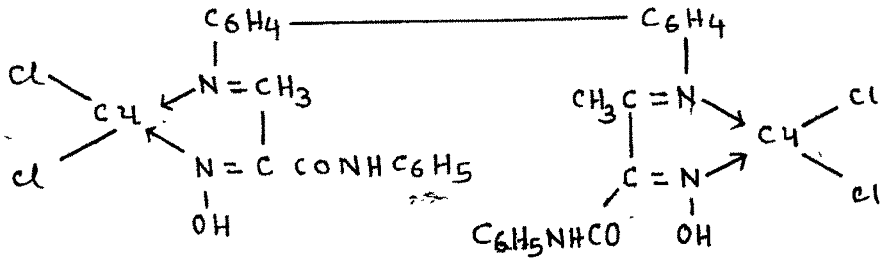


THERMOGRAMS OF OP-CU, OB-CUCl AND OP-CUCl

FIG. R·24

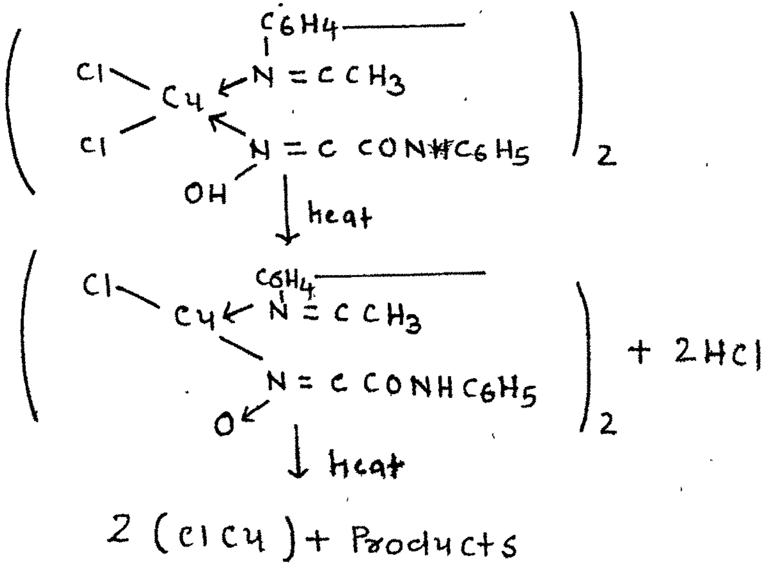
The results indicate that the complex (i) loses hydrochloric acid over a temperature range of 140 to 220°C. and (ii) decomposes at higher temperature, leaving the residue possibly of CuCl.

On the basis of the above observations it is suggested that (i) Cl is not present in the ionic form in the complex and (ii) Cl and ligand form square planar complex with copper. It is considered therefore that because of the bis-(bidentate) nature of the ligand, the complex will be dimeric and may be represented as (XXXI).

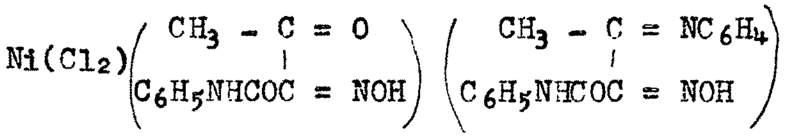


(XXXI)

The thermal decomposition reactions may be represented as follows :



(b) The nickel complex (OB-NiCl) was prepared from nickel chloride, oxime-ketone and benzidine. It was found from analysis that it contained chlorine and that the ratio of metal to nitrogen was 1:5. Hence it may be represented as (XXXII).



$$Ni(Cl_2)\left(\begin{array}{c} CH_3 - C = O \\ | \\ C_6H_5NHCOC = NOH \end{array}\right)\left(\begin{array}{c} CH_3 - C = NC_6H_4 \\ | \\ C_6H_5NHCOC = NOH \end{array}\right)$$

(XXXII)

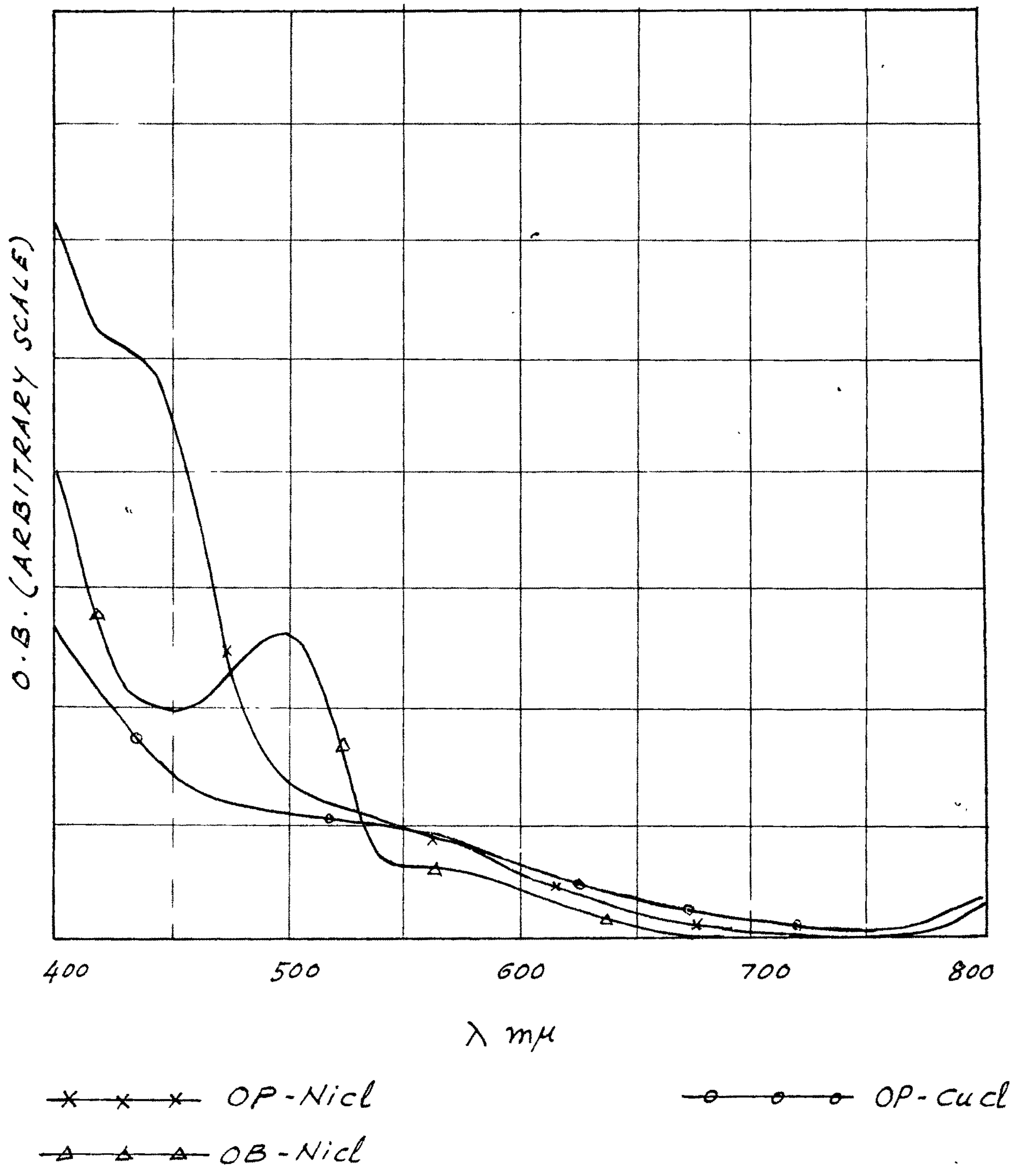
It is insoluble in common solvents except pyridine and dimethylformamide and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-25. It has an absorption band at 490-510 mμ.

Its magnetic moment per Ni-atom is calculated as 3.2 B.M. Hence it is considered to have an octahedral structure.

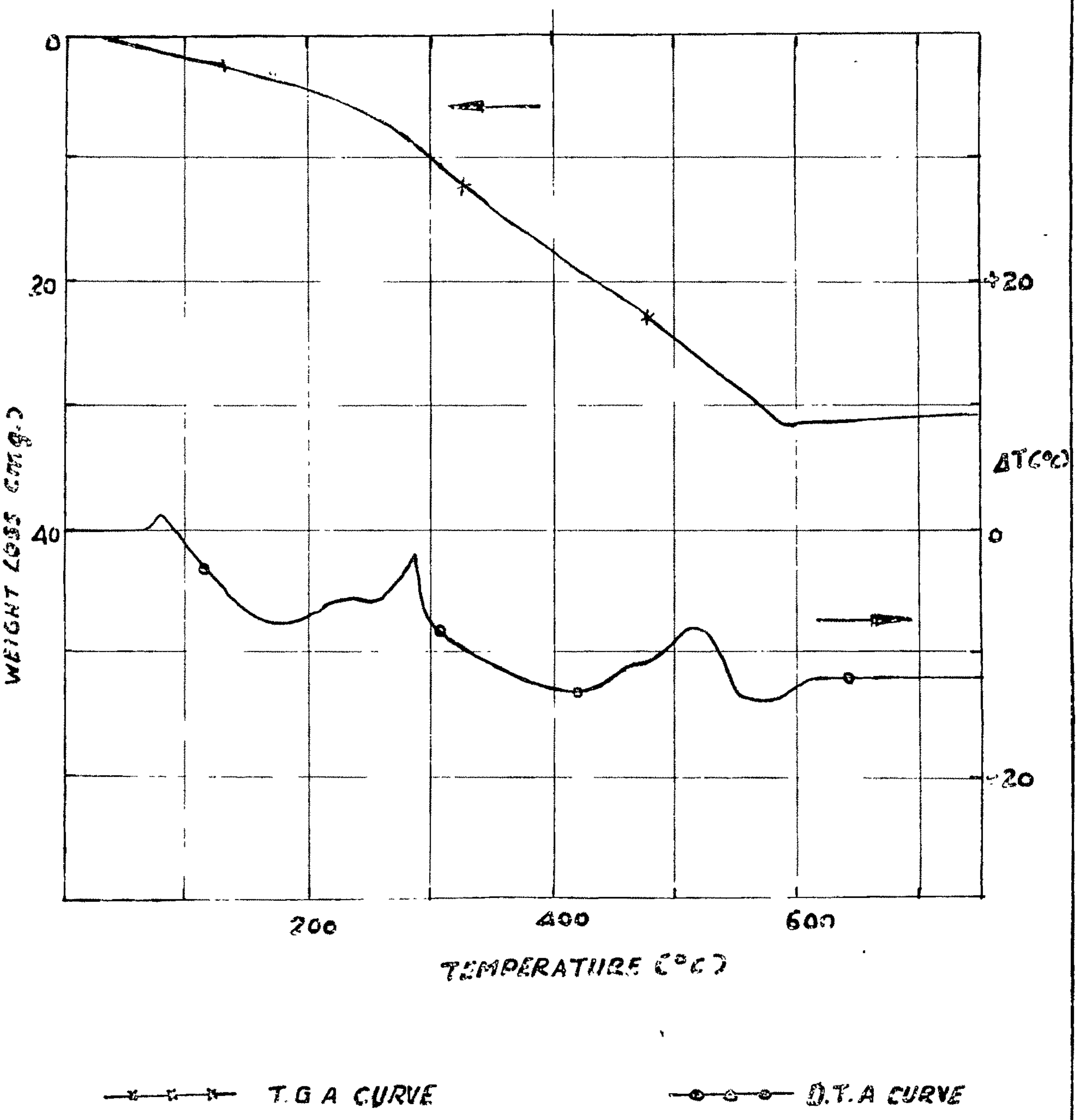
Its thermograms (D.T.A. and T.G.A.) are presented in fig. R-26. The results indicate that the complex (i) loses hydrochloric acid upto a temperature of 270°C. and (ii) decomposes at higher temperature.

On the basis of the above observations, it is suggested that the presence of bis-(bidentate) ligand in the complex leads to the formation of a dimeric complex (XXXIII)



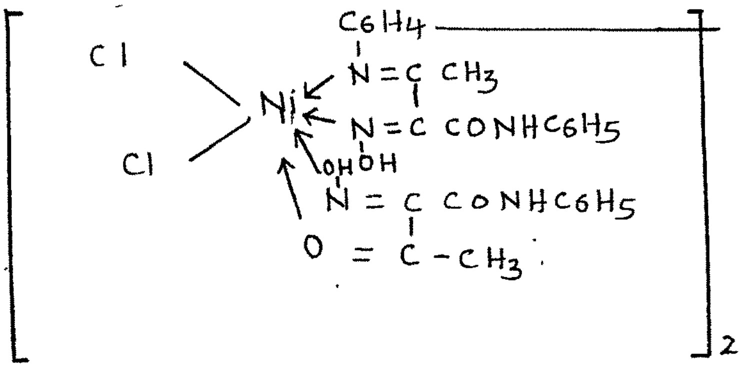
VISIBLE ABSORPTION SPECTRA OF
OB-NiCl, OP-NiCl AND OP-CuCl.

FIG R-25



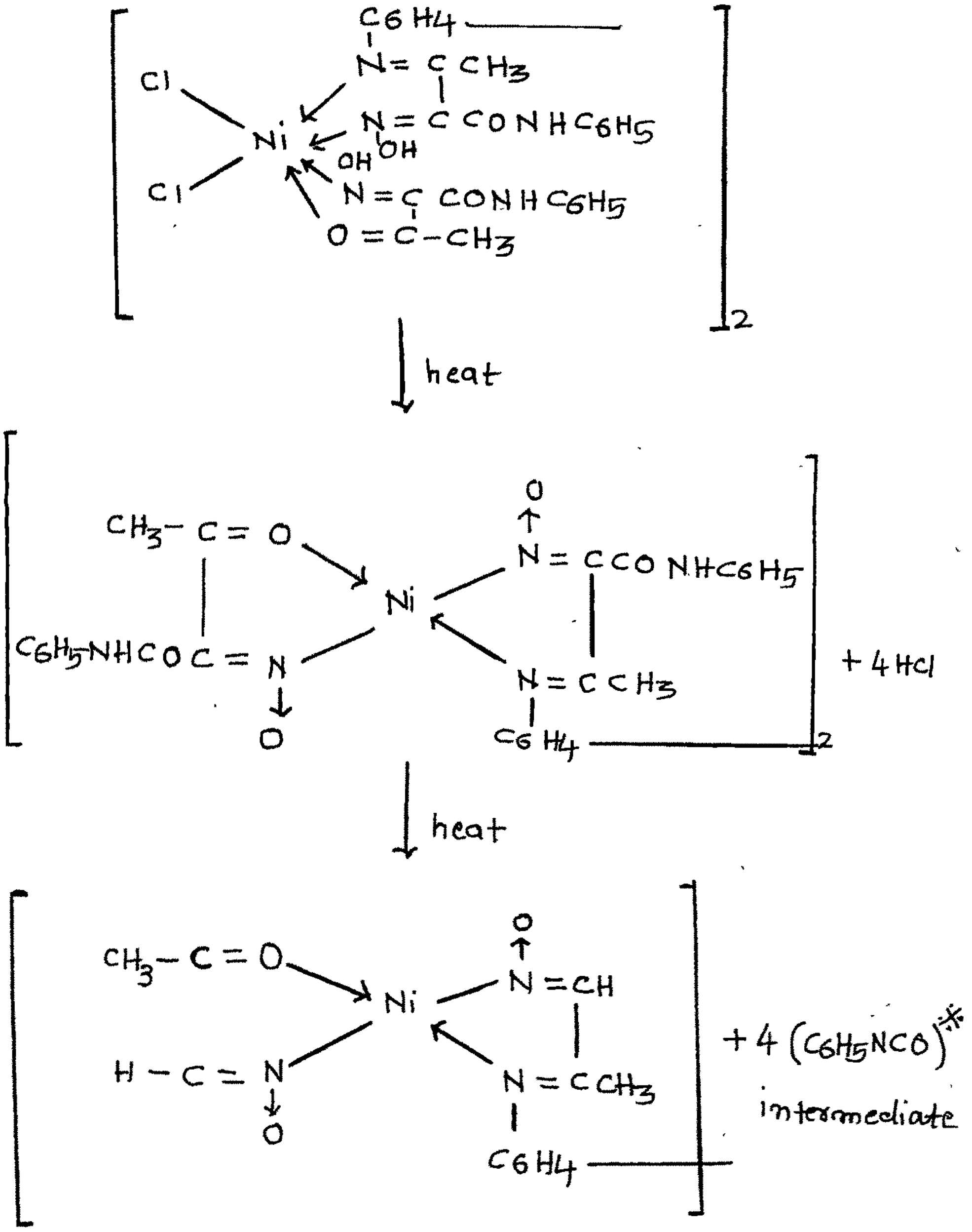
THERMOGRAMS OF OB-NiCl

FIG. R-26

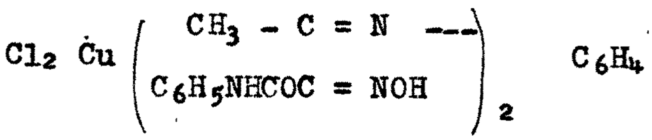


(XXXIII)

The thermal decomposition reactions may be represented as follows :



(c) The copper complex (OP-CuCl) was prepared from copper chloride, oxime-ketone and p-phenylenediamine. It was found from analysis, that it contains chlorine and that the ratio of copper to nitrogen is 1:6, hence it is represented as (XXXIV).



$$Cl_2\,Cu\left(\begin{array}{l} CH_3 - C = N \;--- \\ C_6H_5NHCOC = NOH \end{array}\right)_2 \quad C_6H_4$$

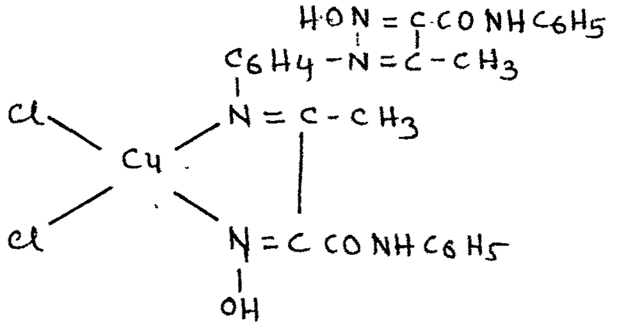
(XXXIV)

It is insoluble in all common solvents except pyridine and dimethylformamide and does not melt upto 300°C. Its absorption spectrum in the visible region is presented in fig. R-25.

Its magnetic moment is calculated as 3.58 B.M. It is a relatively high value for bivalent copper and needs further investigation.

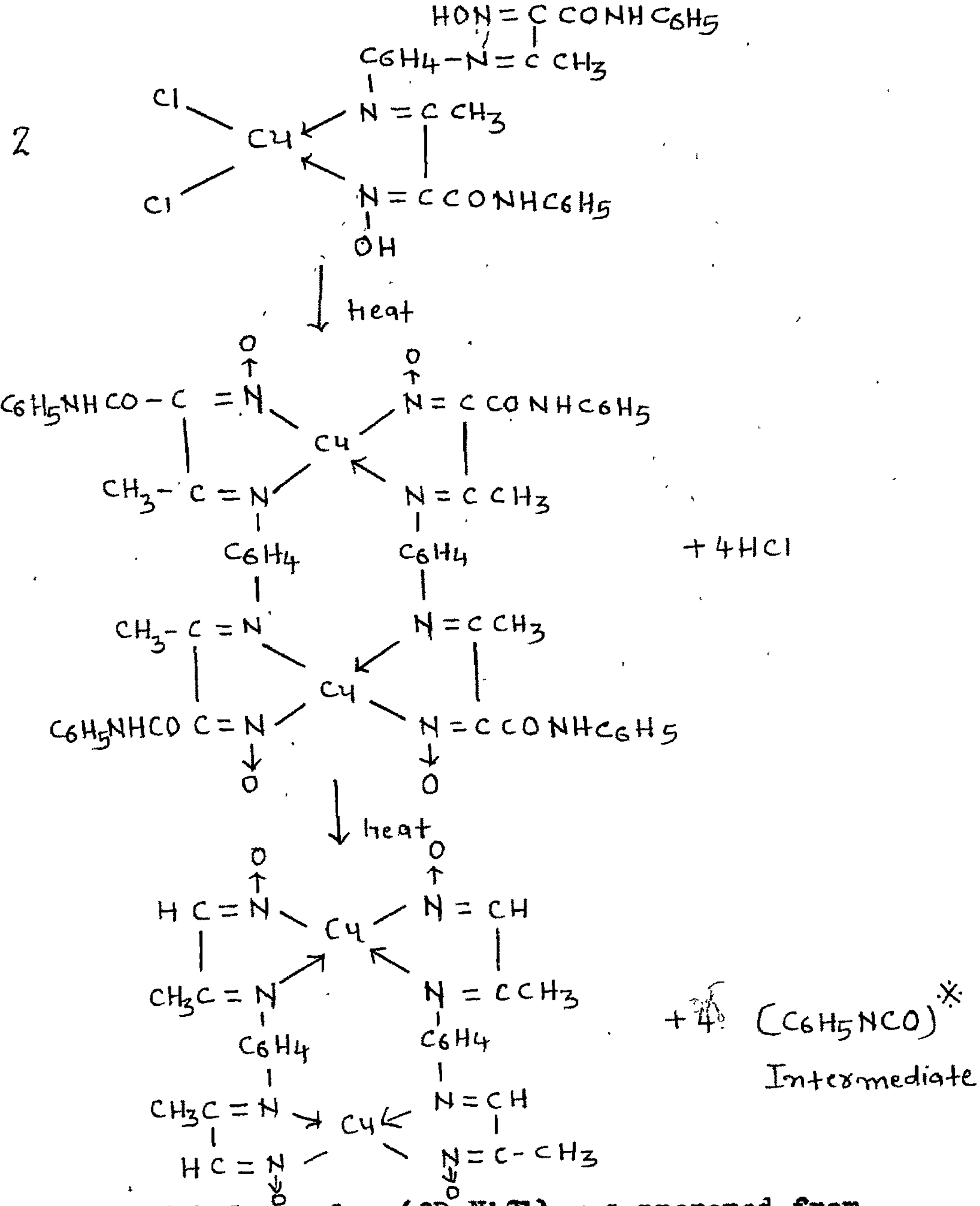
The thermogram of the complex is presented in fig. R-24. The results indicate that the complex (i) loses hydrochloric acid upto a temperature of 300°C. and (ii) decomposes at higher temperature.

On the basis of the above observations, the complex is considered to be square planar and be represented as (XXXV).

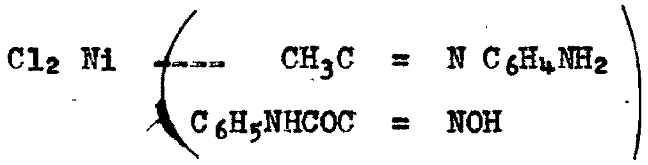


(XXXV)

The thermal decomposition reactions may be represented as follows :



(d) The nickel complex (OP-NiCl) was prepared from nickel chloride, oxime-ketone and p-phenylenediamine. It is found to contain chlorine and, the ratio of nickel to nitrogen is 1:4. Hence it may be represented as (XXXVI).



$$Cl_2\,Ni \left(\begin{array}{lcl} \leftarrow CH_3C & = & N\,C_6H_4NH_2 \\ \swarrow C_6H_5NHCOC & = & NOH \end{array} \right)$$

(XXXVI)

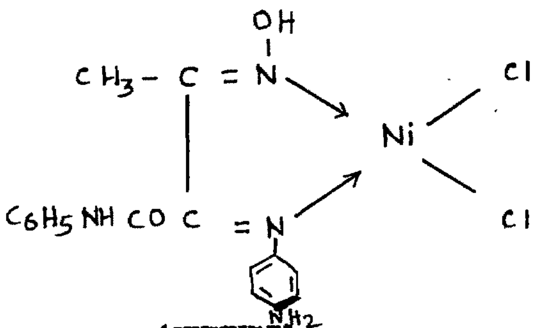
It is insoluble in common solvents except pyridine and dimethylformamide and does not melt upto 300°C.

Its absorption spectrum in the visible region is given in fig. R-25. It has a shoulder at 420 mμ.

Its magnetic moment has been calculated as 3.3 B.M. The results indicate tetrahedral configuration of the complex.

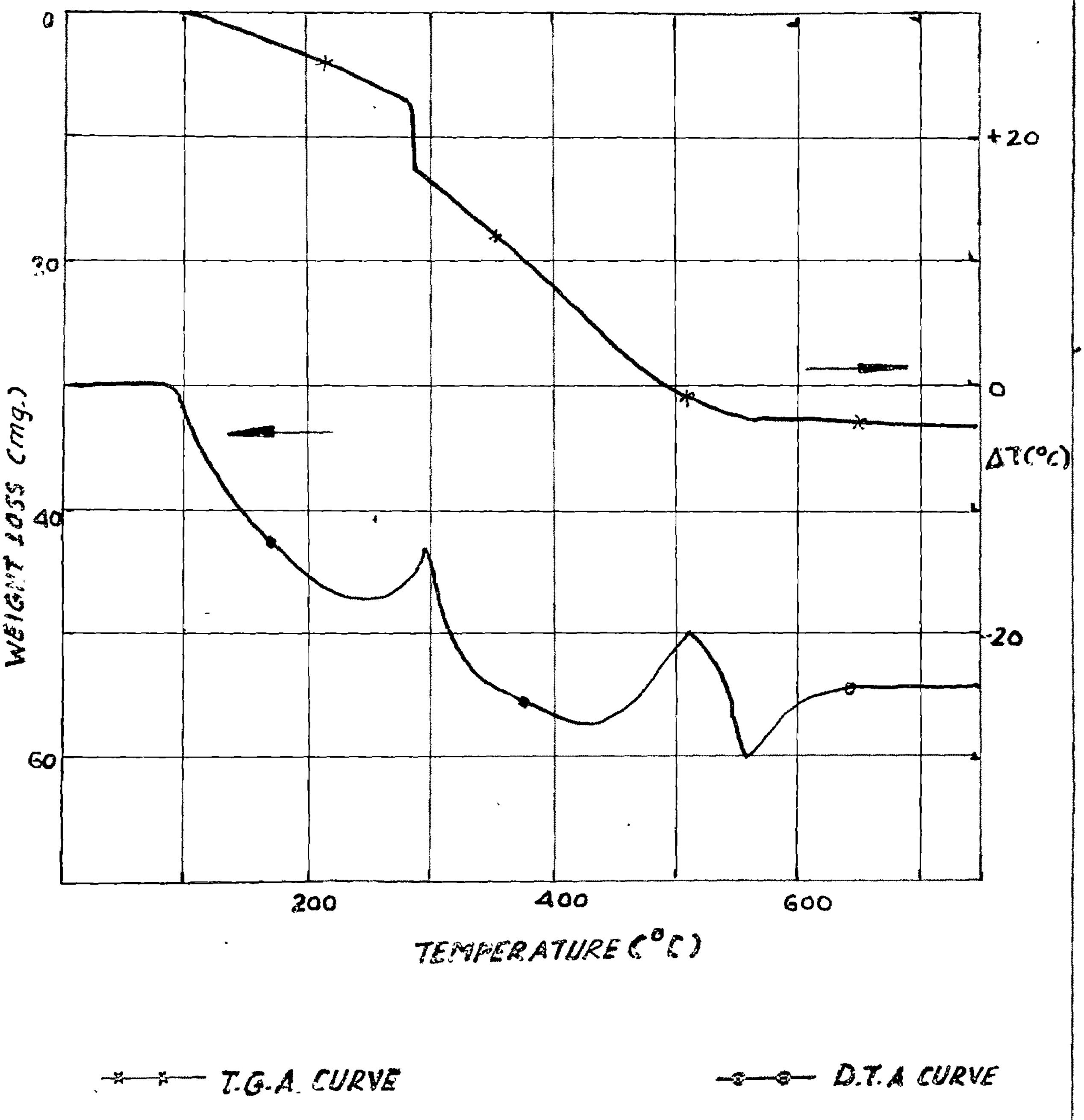
The thermograms (D.T.A. and T.G.A.) of the complex are presented in fig. R-27. The results indicate that the complex (i) loses hydrochloric acid upto a temperature of 300°C. and (ii) decomposes further at higher temperature.

On the basis of the above observations the complex may be represented as (XXXVII).



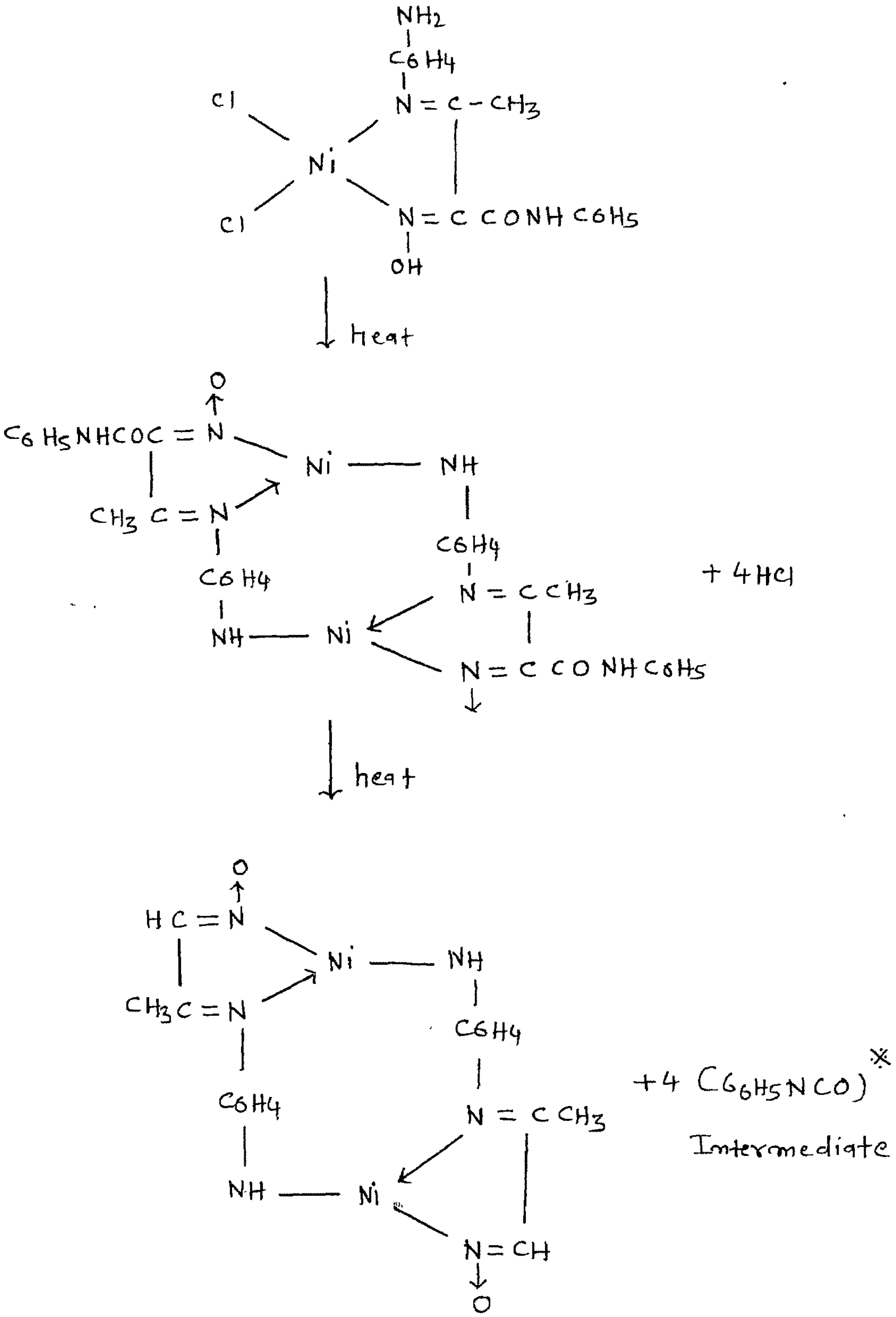
(XXXVII)

The thermal decomposition reactions may possibly be represented as follows :



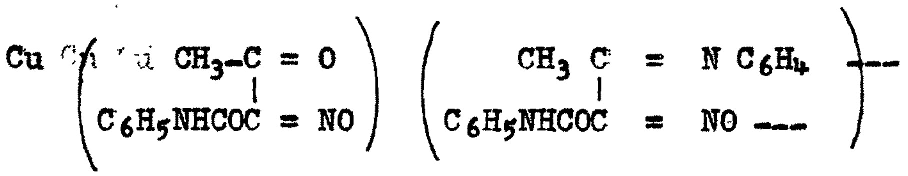
THERMOGRAMS OF OP, NiCl

FIG. R·27


NH2
C6H4
N = C - CH3
Cl
Ni
Cl
N = C CONH C6H5
OH
heat
O
C6H5NHCOC = N
Ni
NH
CH3 C = N
C6H4
C6H4
N = C CH3
+ 4HCl
NH
Ni
N = C CO NH C6H5
heat
O
HC = N
Ni
NH
CH3C = N
C6H4
C6H4
N = C CH3
+4 C6H5NCO)※
Intermediate
NH
Ni
N = CH
O

(ii) <u>Acetate method</u> :

(a) The copper complex (OB-Cu) was prepared from copper acetate, oxime-ketone and benzidine. It was found from analysis that it contains the ratio of copper to nitrogen as 1:5. Hence it is represented as (XXXVIII).



$$Cu\left(\begin{array}{l} CH_3-C = O \\ C_6H_5NHCOC = NO \end{array}\right)\left(\begin{array}{l} CH_3\ C = N\ C_6H_4 - \\ C_6H_5NHCOC = NO - \end{array}\right)$$

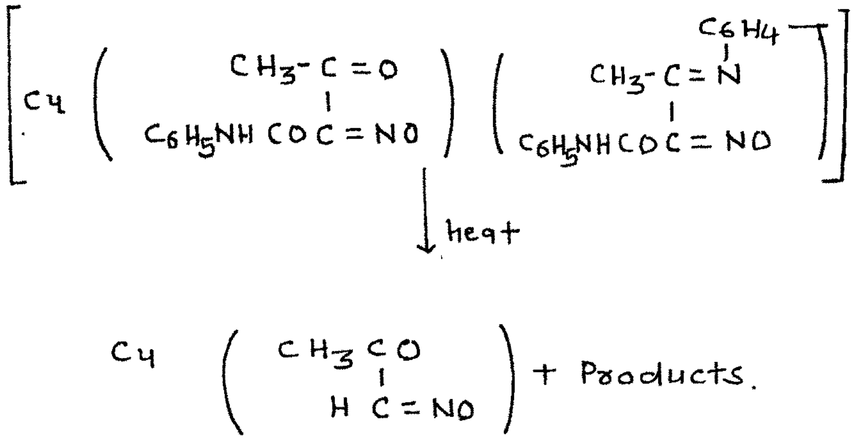
(XXXVIII)

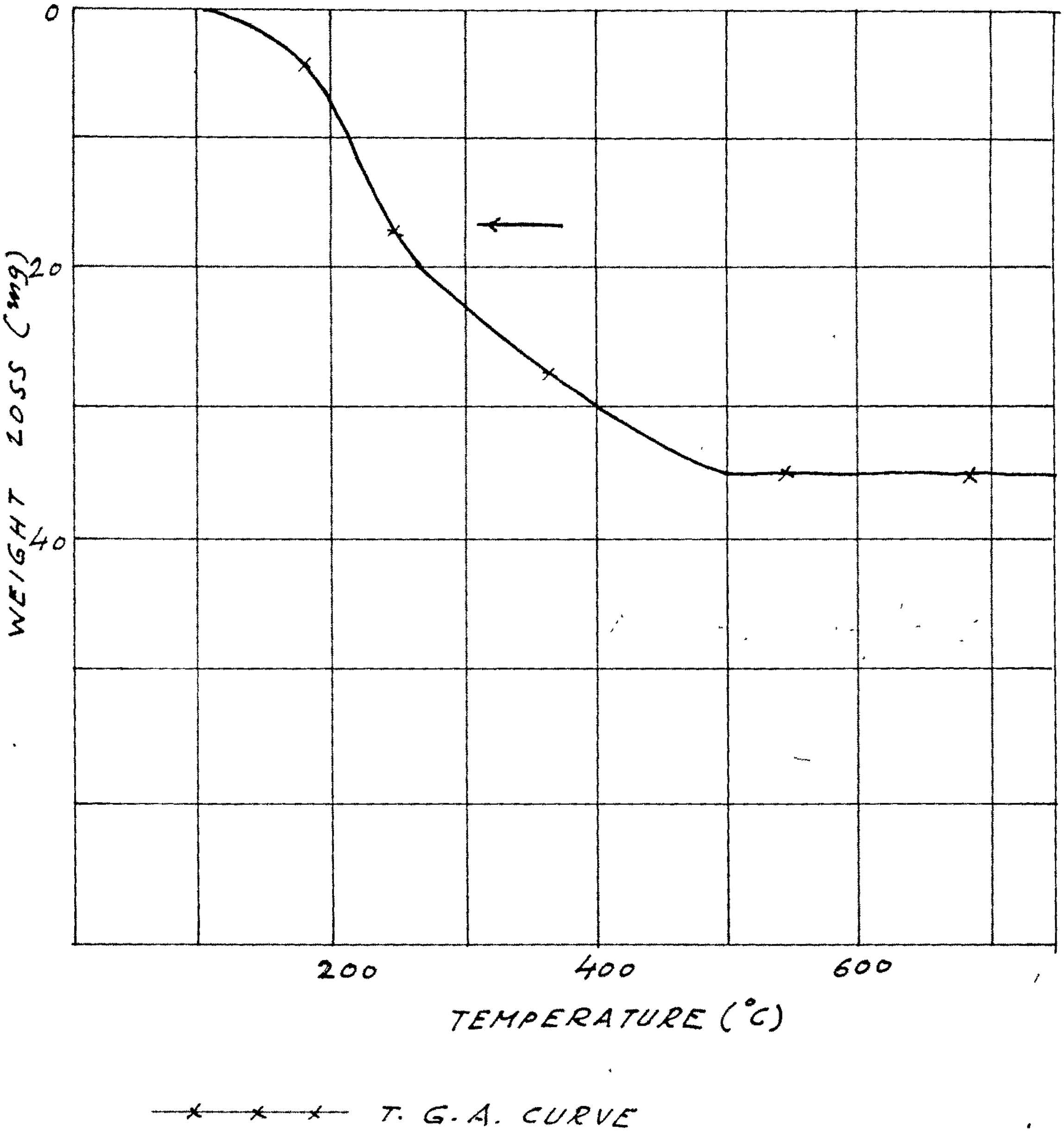
It is insoluble in common solvents and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-23.

Its magnetic moment is found to be 1.6 B.M. The value is some what lower then anticipated.

The thermogram of the complex is presented in fig. R-28. The results indicate that the complex decomposes on heating, The thermal decomposition may be represented as follows:

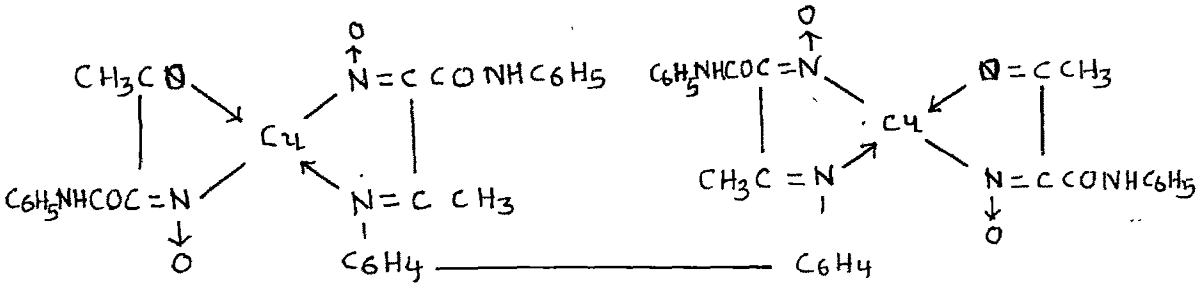




THERMOGRAM OF OB-Cu

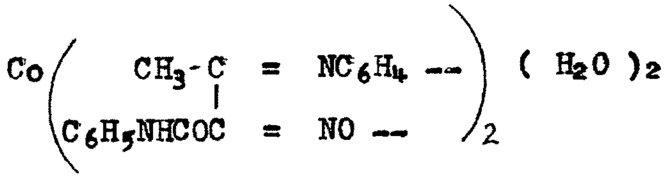
FIG. R-28

On the basis of the above observations the complex is considered to be square planar and to possess dimeric structure due to the bis(bidentate) nature of the Schiff base. Hence it is formulated as (XXXIX).



(XXXIX)

(b) The cobalt complex (OB-Co) was prepared from cobalt acetate, oxime-ketone and benzidine. It was found from analysis that the ratio of metal to nitrogen is 1:6. Hence it is formulated as (XXXX).



$$Co\left(\begin{array}{ccc} CH_3-\underset{|}{C} & = & NC_6H_4 -- \\ C_6H_5NHCOC & = & NO -- \end{array}\right)_2 (H_2O)_2$$

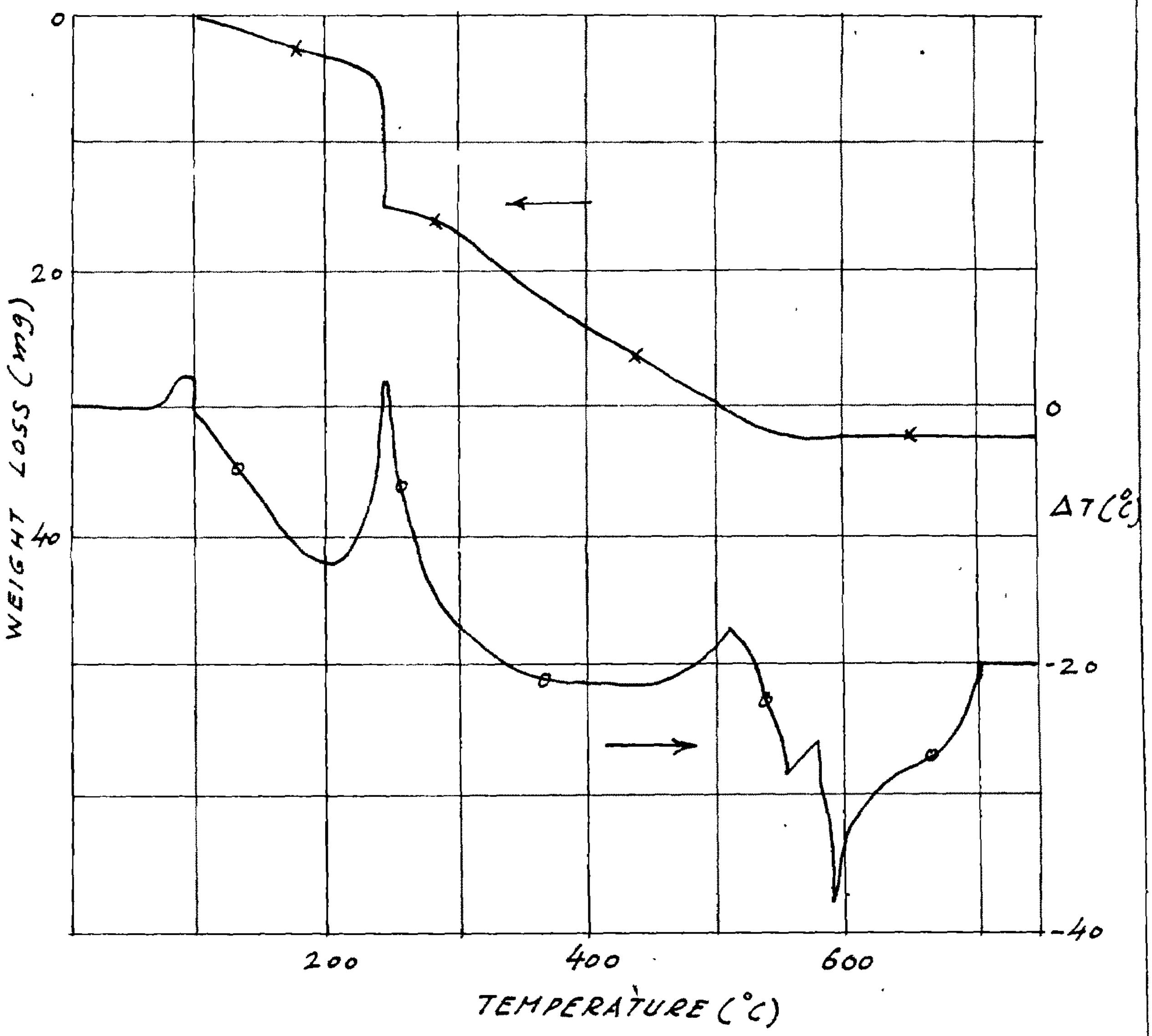
(XXXX)

It is insoluble in common solvents and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-23.

Its magnetic moment is found to be 2.59 B.M. Hence it is considered to be a spin-paired complex, probably with square planar configuration.

The thermogram of the complex is presented in fig. R-29. The results indicate that the complex decomposes



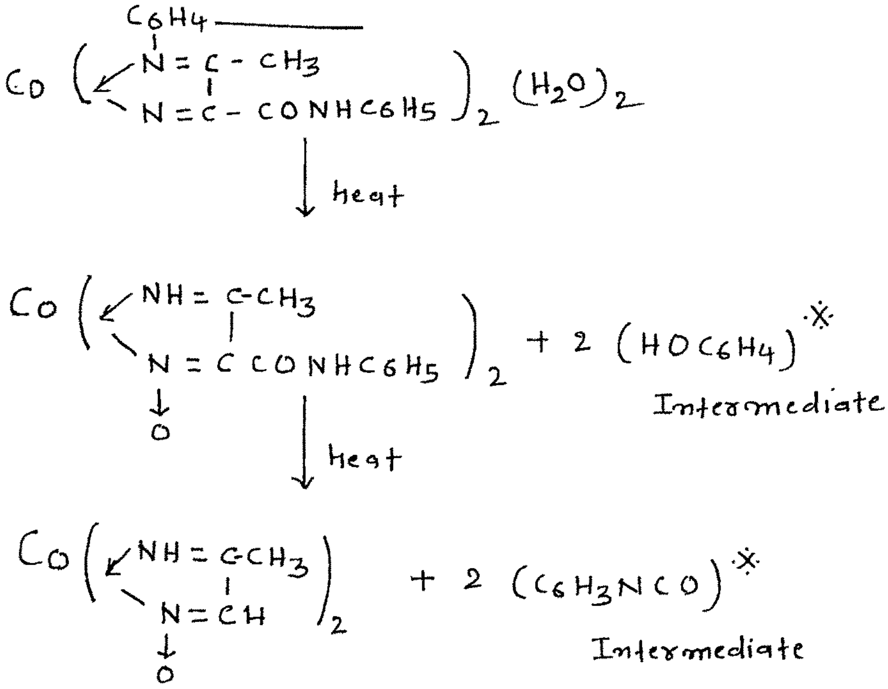
—×—×—×— T.G.A. CURVE —o—o—o— D.T.A. CURVE

THERMOGRAMS OF OB-CO

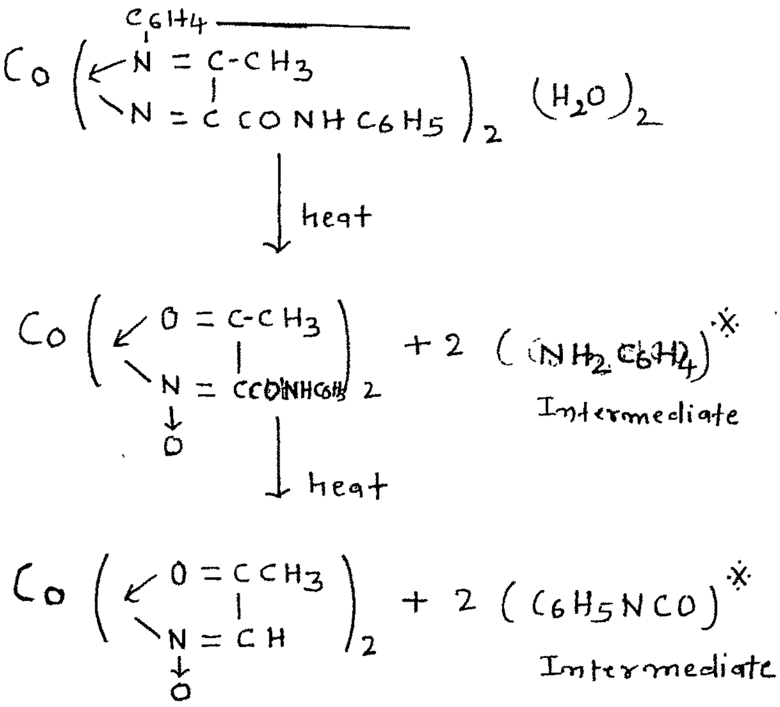
FIG. R-29

in two steps. The decomposition reactions may be represented by (a) or (b) as follows :

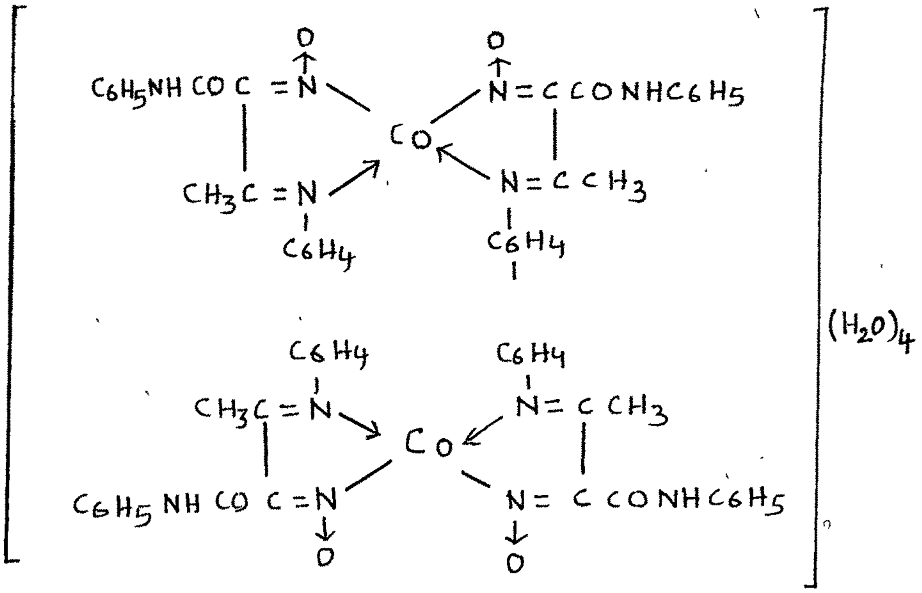
(a)



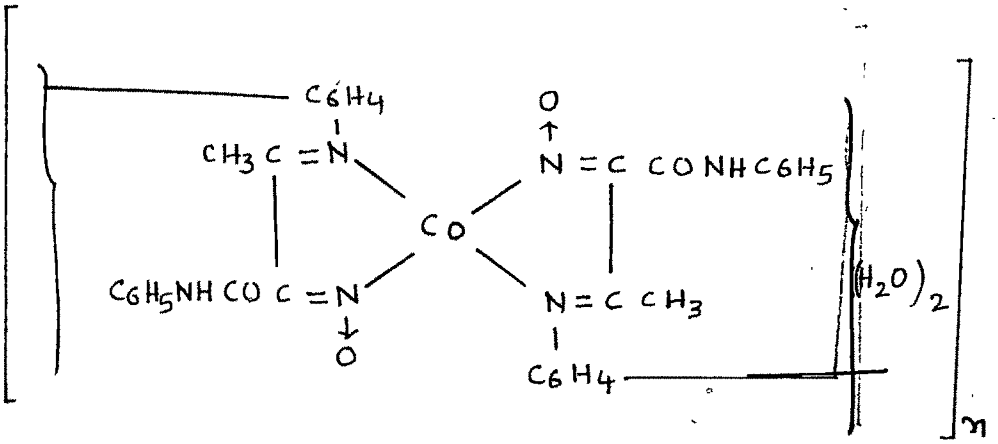
(b)



On the basis of the above observations, the complex may be represented as (a dimer (XXXXI) or a polymer (XXXXII).

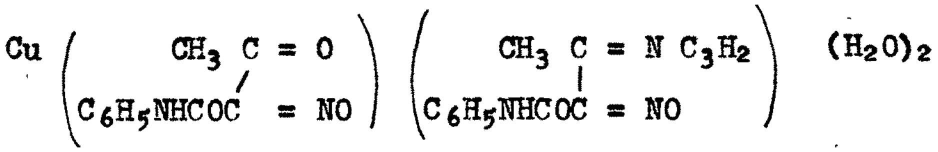


(XXXXI)



(XXXXII)

(c) The copper complex (OP-Cu) was prepared from copper acetate, oxime-ketone and p-phenylenediamine. It is found from analysis that the ratio of copper to nitrogen is 1:5. Hence it is represented as (XXXXIII).



$$Cu\left(\begin{array}{l} CH_3\ C = O \\ C_6H_5NHCOC = NO \end{array}\right)\left(\begin{array}{l} CH_3\ C = N\ C_3H_2 \\ C_6H_5NHCOC = NO \end{array}\right)(H_2O)_2$$

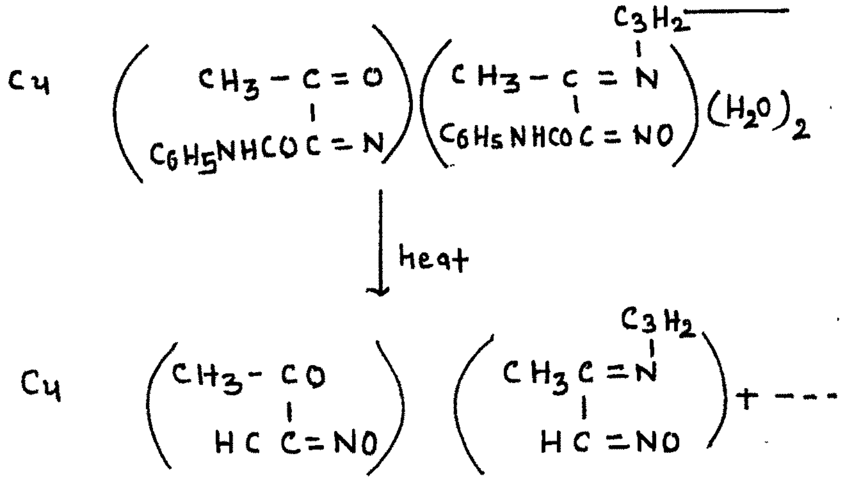
(XXXXIII)

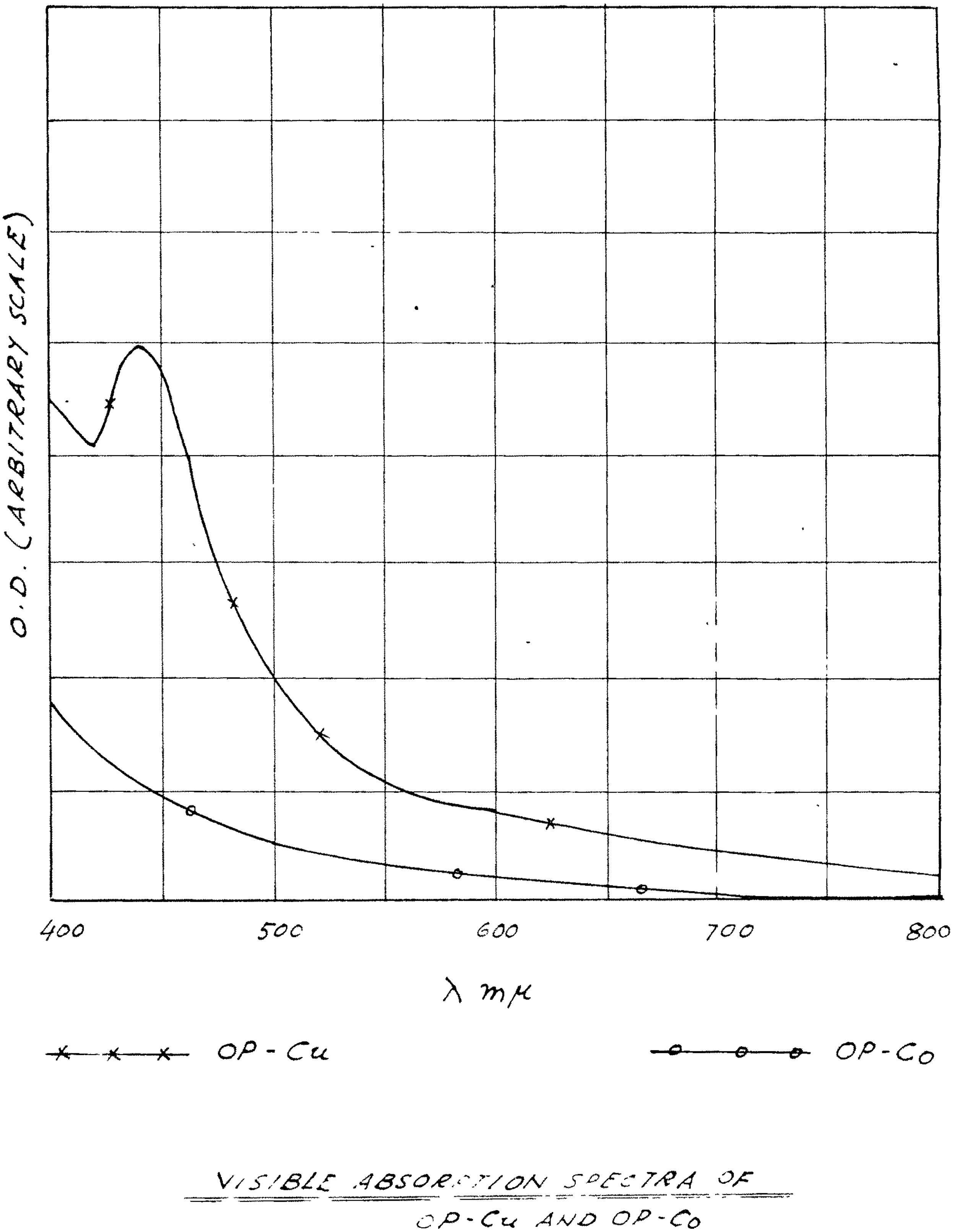
It is insoluble in common solvents and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-30. It has absorption band at 440 mμ.

Its magnetic moment is found as 1.59 B.M. The value is lower than anticipated.

The thermogram of the complex is presented in fig. R-24. The results indicate that the complex decomposes on heating. The decomposition may be represented as follows:

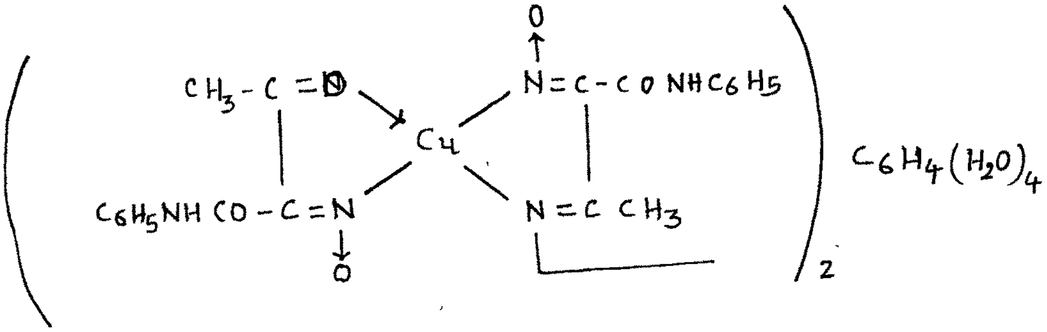




VISIBLE ABSORPTION SPECTRA OF OP-Cu AND OP-Co

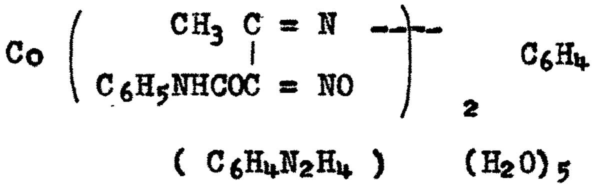
FIG. R-30

On the basis of the above observations the complex is represented as a dimer (XXXXIV).



(XXXXIV)

(d) The complex (OP-Co) was prepared from cobalt acetate, oxime-ketone and p-phenylenediamine. It was found from analysis that the ratio of cobalt to nitrogen is 1:7. Hence it is represented as (XXXXV).



$$\mathrm{Co}\left(\begin{array}{l} \quad CH_3\ \underset{|}{C} = N \\ C_6H_5NHCOC = NO \end{array}\right)_2 C_6H_4 \quad (\ C_6H_4N_2H_4\ )\quad (H_2O)_5$$

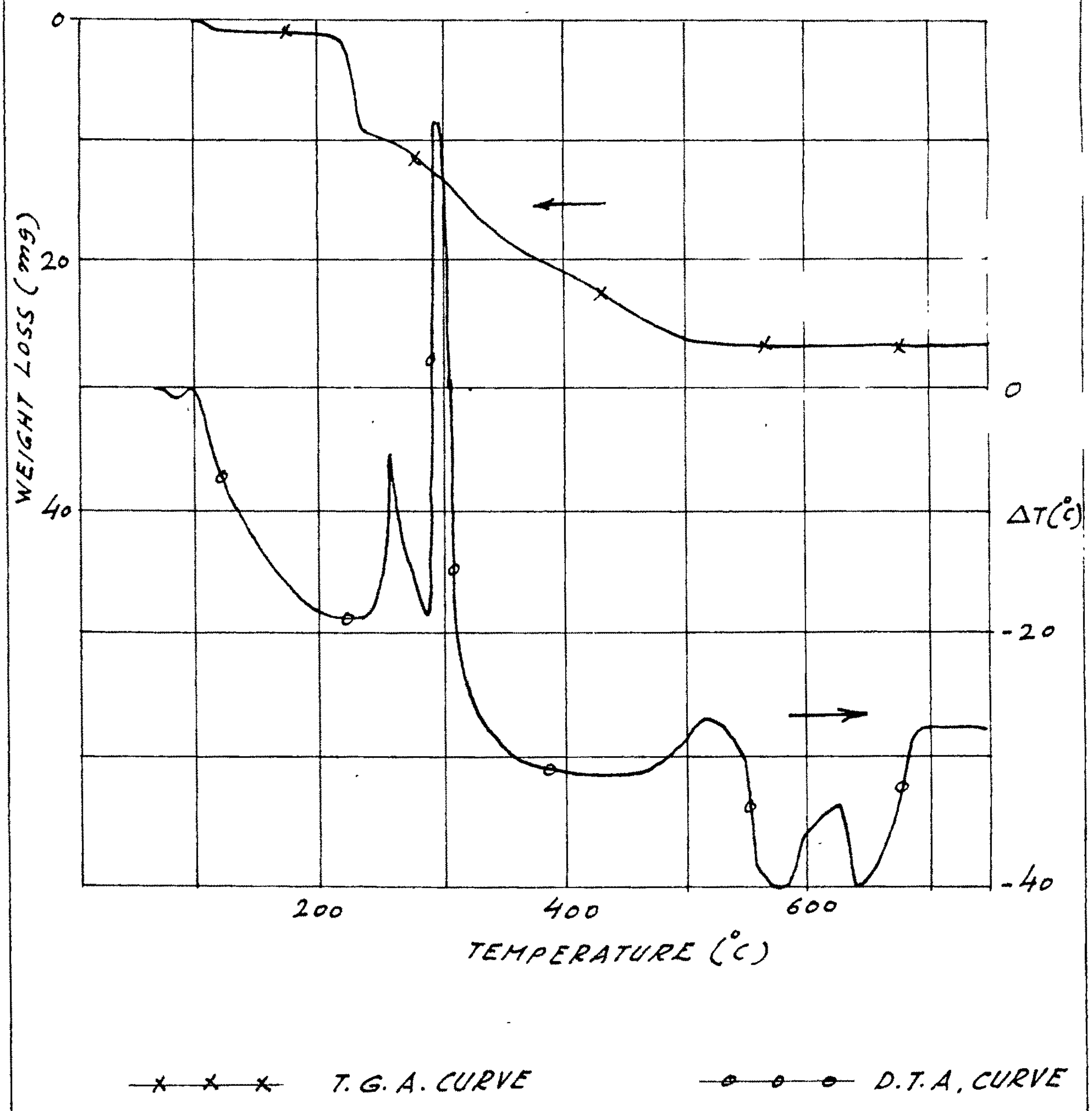
(XXXXV)

It is insoluble in common solvents and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-30.

Its magnetic moment has been calculated as 2.13 B.M. It indicates spin paired 5-coordinate ofnature of Co in the complex.

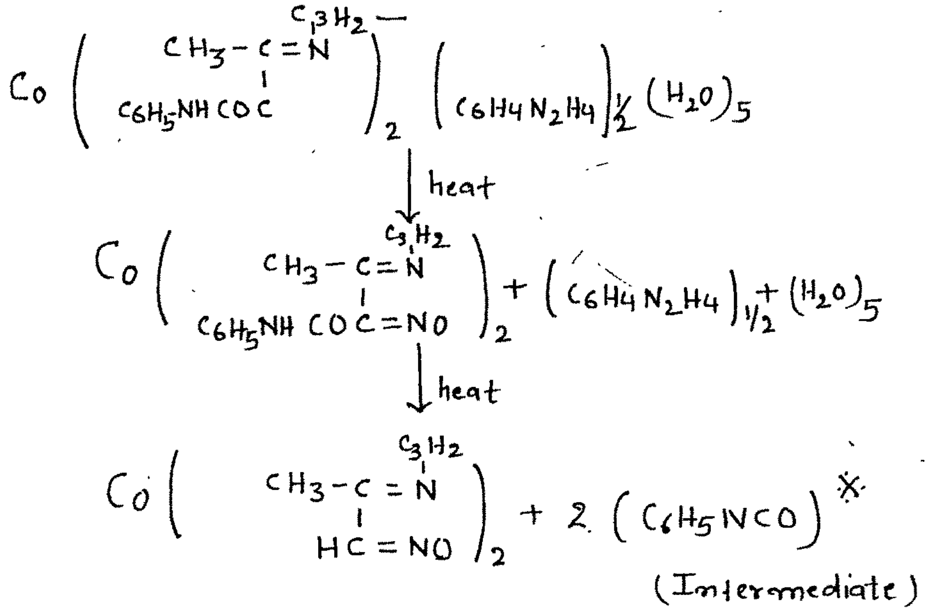
The thermograms (T.G.A. and D.T.A.) of the complex are presented in fig. R-31. The results indicate that the complex (i) loses water and p-phenylenediamine upto 250°C.



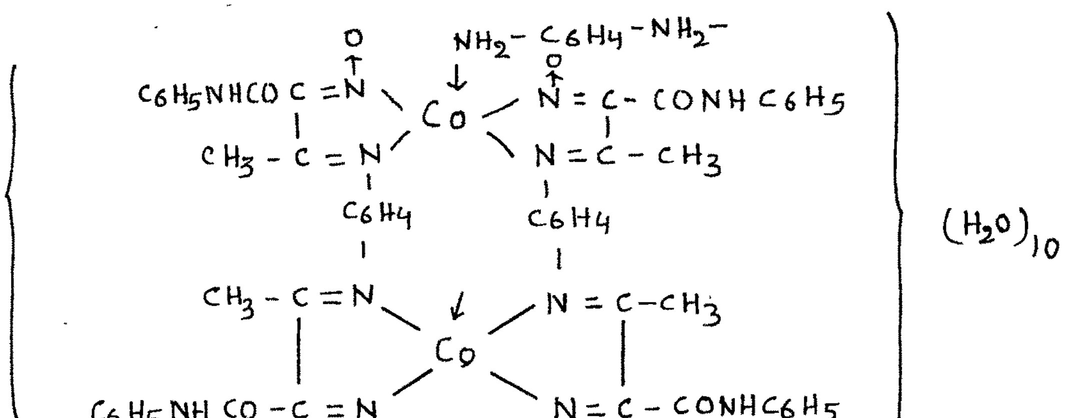
THERMOGRAMS OF OP-CO

FIG. R-31

and (ii) decomposes at high temperature. The thermal decomposition reactions may be represented as follows :



On the basis of the above observations the complex is represented as a dimer (XXXXVI).

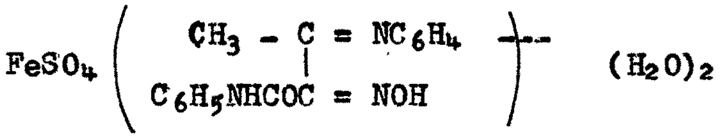


(XXXXVI)

p-Phenylenediamine is considered to coordinate with two Co-atoms of adjacent planes.

(iii) Sulphate method :

(a) The complex (OB-Fe) was prepared from Iron(II) sulphate, oxime-ketone and benzidine. It was found from analysis that it contains sulphate and that the ratio of metal to nitrogen is 1:6. Hence it is formulated as (XXXXVII).



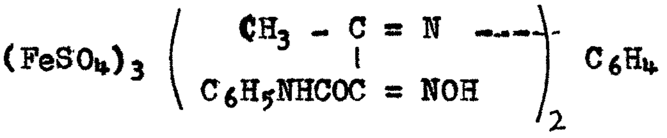
$$FeSO_4\left(\begin{array}{c} CH_3 - C = NC_6H_4 - \\ | \\ C_6H_5NHCOC = NOH \end{array}\right)(H_2O)_2$$

(XXXXVII)

It is a blue coloured product, soluble in various organic solvents. It does not melt upto 300°C.

Its magnetic moment is calculated as 3.36 B.M. It indicate tetrahedral nature of the complex.

(b) The complex (OP-Fe) was prepared from Iron(II) sulphate, oxime-ketone and p-phenylenediamine. It was found from analysis that it contains sulphate and that the ratio of metal to nitrogen is 1:2. Hence it is formulated as (XXXXVIII).



$$(FeSO_4)_3\left(\begin{array}{c} CH_3 - C = N - \\ | \\ C_6H_5NHCOC = NOH \end{array}\right)_2 C_6H_4$$

(XXXXVIII)

It is a blue coloured complex, soluble in various organic solvents. It does not melt upto 300°C.

Its magnetic moment per Fe-atom is calculated as 5.71 B.M.

(iv) General :

(a) When metal acetate are used in the formation of complexes, acetate ions are removed completely and complexes with oximino ligands are formed. However, when metal chlorides are used, chlorine is not displaced; on the other hand, additive complexes with the oximino ligands appear to be formed. Thus the anion appears to a play a part in deciding the nature of the complexes formed.

(b) We find that the formation of Schiff base between the oxime-ketone and diamine is influenced by the nature of the metal ion with which the oxime-ketone may be considered to form the complex. Thus both the ligand molecules are found to form Schiff base in case of cobalt complexes, whereas one of the two ligand molecules undergo Schiff base formation in the case of copper complexes.

(c) Thermal decompositions of copper and cobalt complexes of these Schiff bases show that complexes formed by Schiff bases with benzidine show a different behaviour from the complexes formed by Schiff bases with p-phenylenediamine. Thus the complexes of the first type are considered to decompose with the loss of Schiff base whereas the complexes of the second type appear to retain the Schiff base on heating.

III 6. N-Ligands from vic-oxime ketones and their transition metal complexes :

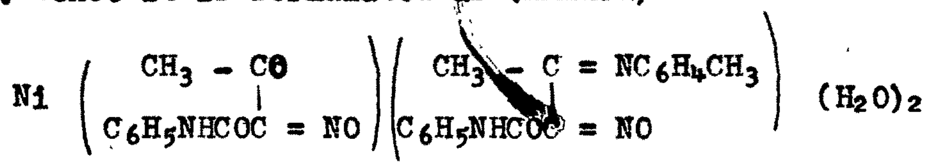
In continuation of our studies on the Schiff bases from diamines, we have studied the Schiff base from monoamine and related N-ligands.

(i) Ligands :

Schiff base from 2,3-dioxobutyranilide-2-oxime and p-toluidine was prepared from the above oxime-ketone and amine by the method of Talati and Patel.[143] 2,3-dioxobutyranilide-2-oxime-3-thiosemicarbazone was prepared from the oxime-ketone and thiosemicarbazide by the method of Patel and Mankad[144]; and 2,3-dioxobutyranilide-2-oxime-3-semicarbazone was prepared from oxime-ketone and semicarbazide also by the method of Patel and Mankad.[144] Cobalt and nickel complexes of these ligands are prepared by us. Their magnetic moments calculated from magnetic susceptibilities and diamagnetic corrections are presented in Table R-8.

(ii) Transition metal complexes :

(a) The complex (OT-Ni) (C) was prepared from nickel acetate, oxime-ketone and p-toluidine by keeping the mixture for sevaral days. On the basis of analysis, it is found to contain the ratio of metal to nitrogen as 1:5. Hence it is formulated as (XXXXIX)



$$\mathrm{Ni}\left(\begin{array}{c} CH_3 - CO \\ | \\ C_6H_5NHCOC = NO \end{array}\right)\left(\begin{array}{c} CH_3 - C = NC_6H_4CH_3 \\ | \\ C_6H_5NHCOC = NO \end{array}\right)(H_2O)_2$$

(XXXXIX)

Table R-8

Magnetic moments of the complexes

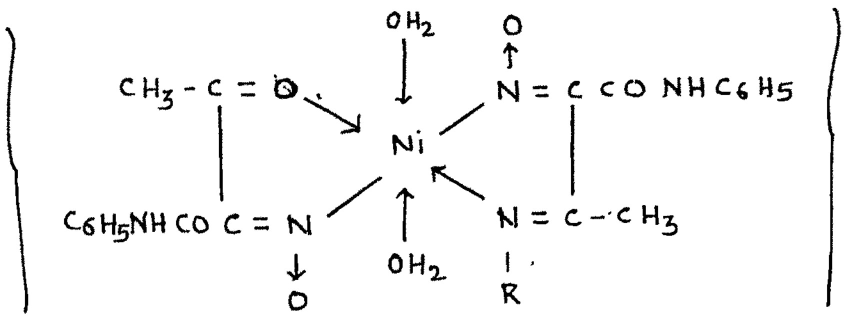
No.	Compound	Molarmagnetic susceptibility (per metal atom) $X_m \times 10^6$	Corrected Molar magnetic susceptibility (per metal atom) $X_m \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1 (a)	OT-Ni(C)	3254	3602	2.97
2 (b)	OT-Ni(R)	2725	3022	2.72
3 (a)	OT-Co(C)	2915	3212	2.80
4 (b)	OT-Co(R)	3191	3488	2.91
5	OTS-Ni	1054	1204	1.71
6	TSO-Ni	1310	1400	0.83
7	TSO-CO	102	333	1.03

It is insoluble in all common solvents except dimethylformamide and pyridine and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-32. It has continuous absorption.

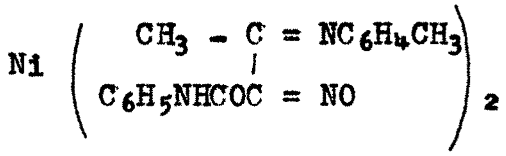
Its magnetic moment is found to be 2.9 B.M. It indicates the octahedral nature of the complex.

The complex may thus be represented as (XXXXX).



(XXXXX)

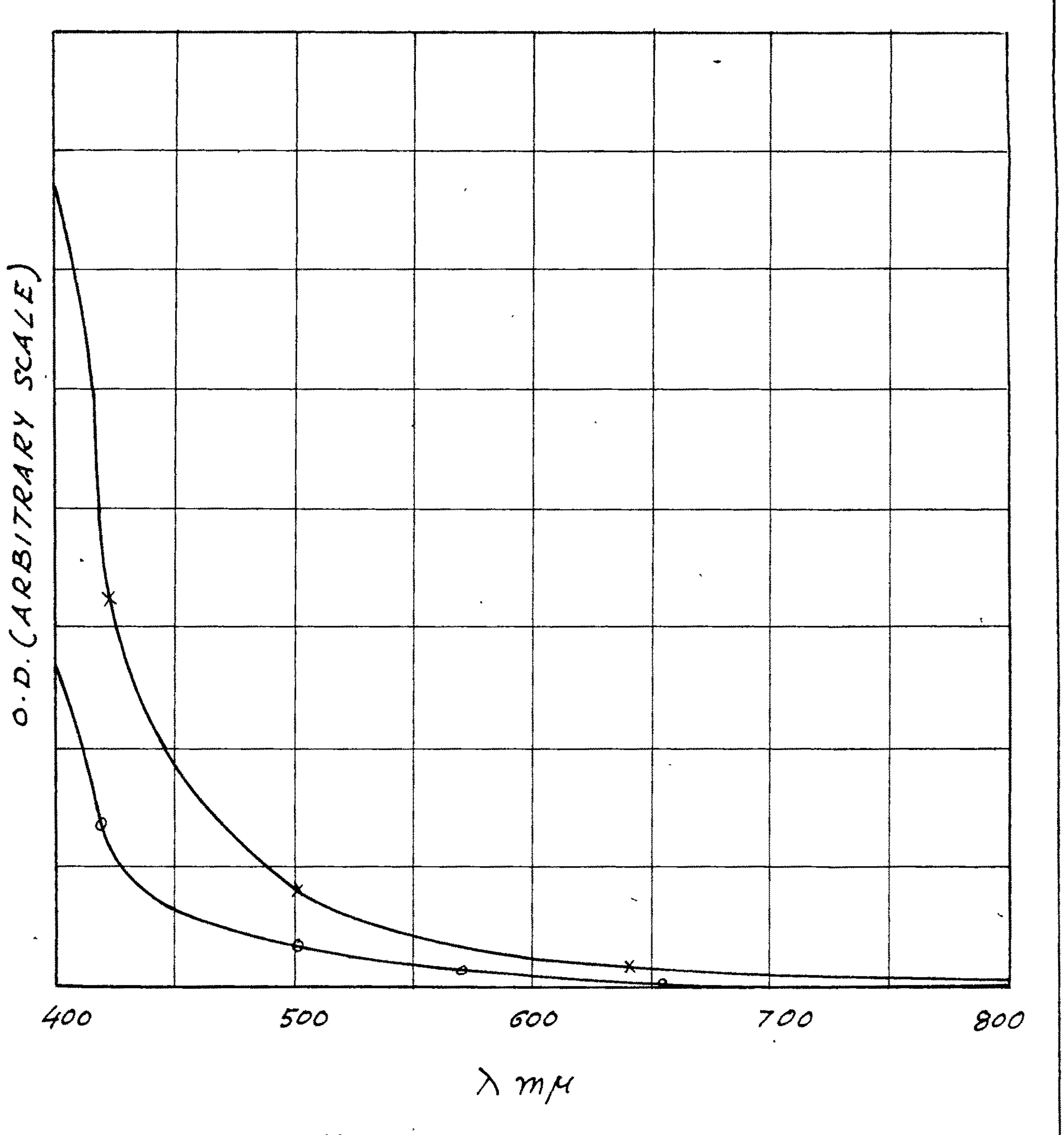
(b) The complex (OT-Ni) (R) was prepared by refluxing the mixture of nickel acetate, oxime-ketone, and p-toluidine. On the basis of analysis, it is found to contain the ratio of nickel to nitrogen as 1:6. Hence it is represented as (XXXXXI).



$$Ni\left(\begin{array}{l} CH_3 - C = NC_6H_4CH_3 \\ \qquad\ \ | \\ C_6H_5NHCOC = NO \end{array}\right)_2$$

(XXXXXI)

It is insoluble in all common solvents except dimethylformamide and pyridine and does not melt upto 300°C.

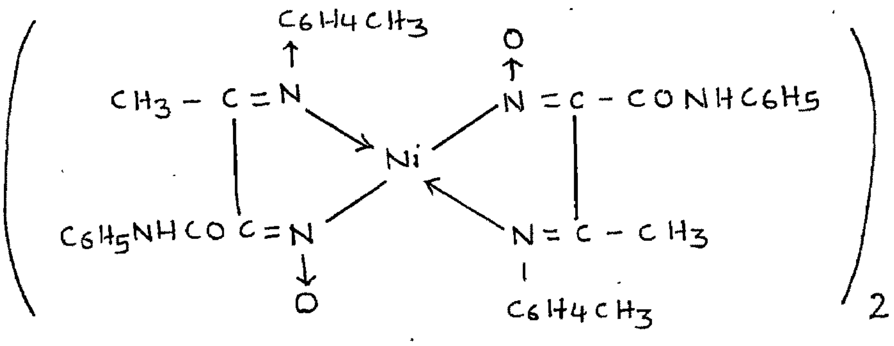


VISIBLE ABSORPTION SPECTRA OF OT-Ni(C) AND OT-Ni(R)

FIG-R-32

Its absorption spectrum in the visible region is presented in fig. R-32. It has continuous absorption.

Its magnetic moment is calculated as 2.72 B.M. It indicates the presence of two unpaired electron per nickel atom and the lower value indicates the formation of binuclear nickel complex. Hence the complex may be represented as (XXXXXII).



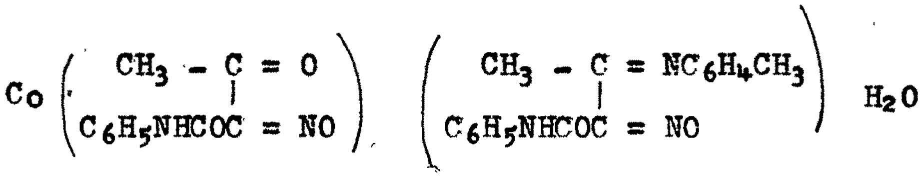
(XXXXXII)

Talati and Patel[165] prepared the nickel complex from nickel chloride and Schiff base. They formulated it as a monomer. In contrast to the paramagnetic nickel complexes of the vic-oxime-imines, the nickel complexes of vic-dioximes[166] and vic-oxime hydrazones[167] are diamagnetic.

Talati and Shah[168] prepared the nickel complex of vic-oxime ketone, Talati and Patel[165] obtained the nickel complex of vic-oxime-imine. We have been able to prepare the intermediate or mixed-ligand complex of nickel.

We also observe that when nickel salt, oxime-ketone and amine are mixed and refluxed, the complex obtained is the same as one prepared from nickel salt and preformed oxime-imine.

(c) The complex (OT-Co) (C) was prepared by keeping the mixture of cobalt acetate, oxime-ketone and p-toluidine for several days. On the basis of analysis it is found to contain the ratio cobalt to nitrogen as 1:5. Hence it is formulated as (XXXXXIII).



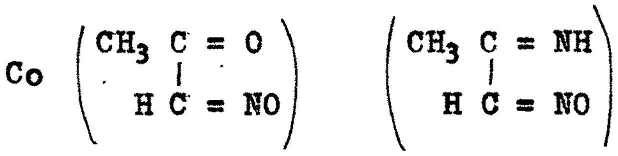
$$Co\left(\begin{array}{l} CH_3 - C = O \\ \qquad | \\ C_6H_5NHCOC = NO \end{array}\right)\left(\begin{array}{l} CH_3 - C = NC_6H_4CH_3 \\ \qquad | \\ C_6H_5NHCOC = NO \end{array}\right) H_2O$$

(XXXXXIII)

It is soluble in all common organic solvents except petroleum ether, and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-33. It has continuous absorption.

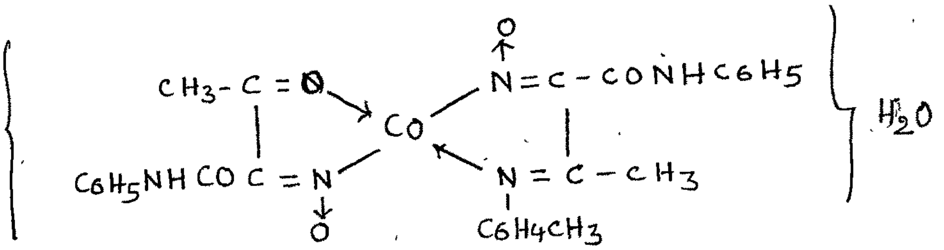
Its thermograms (D.T.A. and T.G.A.) are presented in fig. R-34. The results indicate that the complex decomposes in two major steps, leaving the residue of



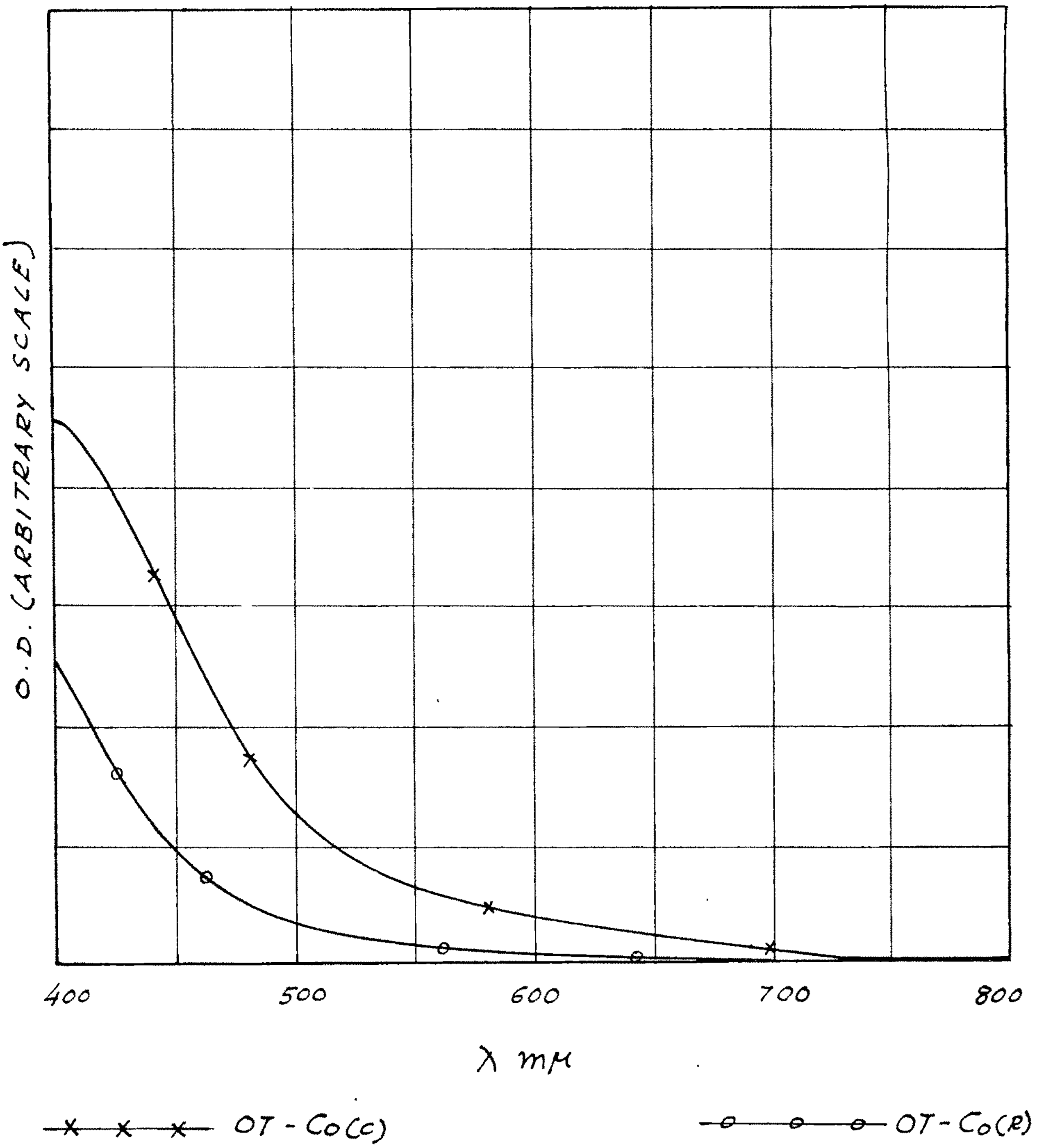
$$Co\left(\begin{array}{l} CH_3\ C = O \\ \quad\ | \\ \ \ H\ C = NO \end{array}\right)\left(\begin{array}{l} CH_3\ C = NH \\ \quad\ | \\ \ \ H\ C = NO \end{array}\right)$$

Its magnetic moment is calculated as 2.8 B.M. It indicates square planar nature of the complex.

On the basis of the above observations it may be representəd as (XXXXXIV).

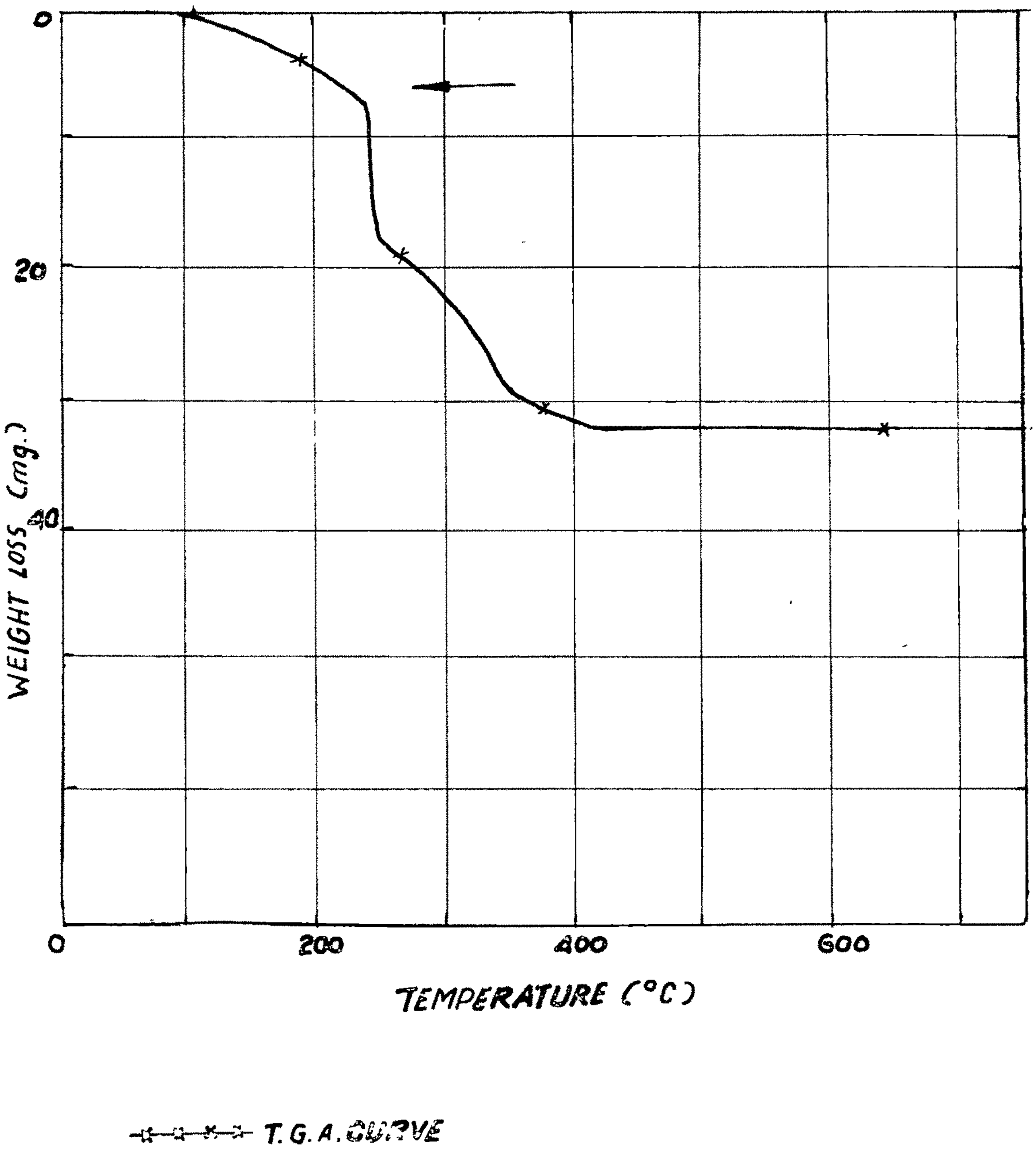


(XXXXXIV)



VISIBLE ABSORPTION SPECTRA OF
OT - Co(C) AND OT - Co(R)

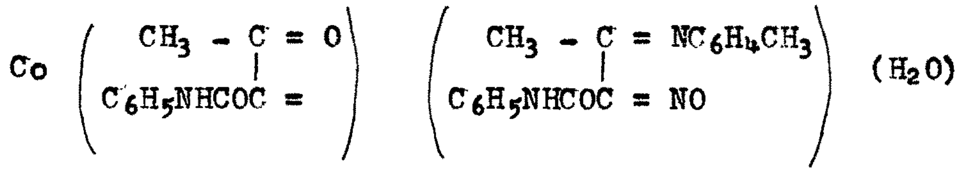
FIG. R-33



THERMOGRAM of OT-Co(C)

FIG. R-34

(d) The complex (OT-Co) (R) was prepared by refluxing the mixture of cobalt acetate, oxime-ketone, and p-toluidine. On the basis of analysis, it is found to contain the ratio of metal to nitrogen as 1:5. Hence it is represented as (XXXXXV).



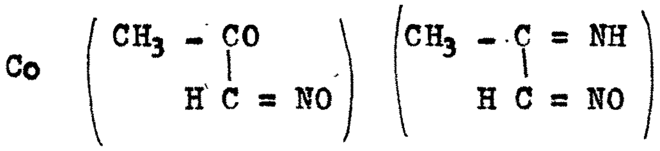
$$Co\left(\begin{array}{l} CH_3 - C = O \\ \qquad\;\; | \\ C_6H_5NHCOC = \end{array}\right)\left(\begin{array}{l} CH_3 - C = NC_6H_4CH_3 \\ \qquad\;\; | \\ C_6H_5NHCOC = NO \end{array}\right)(H_2O)$$

(XXXXXV)

It is soluble in all common organic solvents except petroleum ether and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-33. It has continuous absorption.

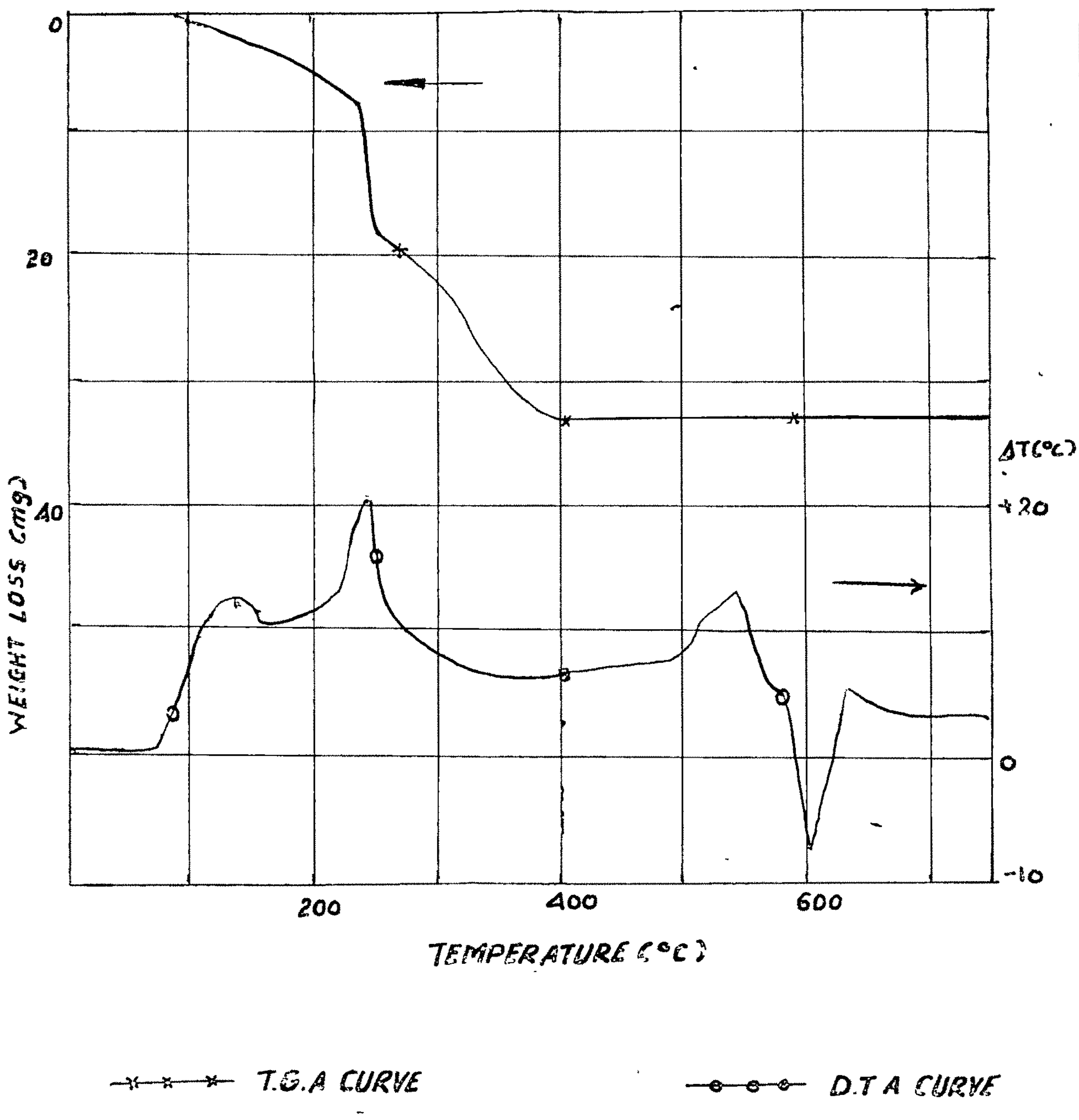
The thermograms (D.T.A. and T.G.A.) are presented in fig. R-35. The results indicate that the complex decomposes in to two major steps as in the case of (OT-Co(C) , leaving the residue of



$$Co\left(\begin{array}{l} CH_3 - CO \\ \qquad\;\; | \\ \qquad H\,C = NO \end{array}\right)\left(\begin{array}{l} CH_3 - C = NH \\ \qquad\;\; | \\ \qquad H\,C = NO \end{array}\right)$$

Its magnetic moment has been calculated as 2.91 B.M. The results show the similarity of the two complexes (OT-Co)(C) and (OT-Co)(R) prepared under different conditions, and the possibility of getting only mixed-ligand complexes under these conditions.

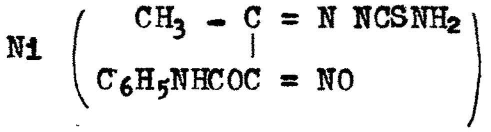
(e) The complex (OTS-Ni) was prepared by keeping the mixture of nickel acetate, oxime-ketone and thiosemicarbazide for several days. On the basis of analysis,



THERMOGRAMS OT-Co(R)

FIG. R-35

It is found to contain the ratio of metal to nitrogen as 1:5. Hence it is formulated as (XXXXXVI).



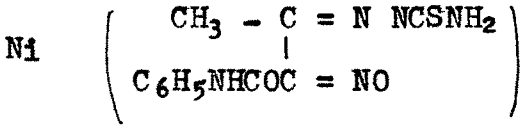
$$\mathrm{Ni}\left(\begin{array}{l} CH_3 - C = N\ NCSNH_2 \\ \qquad\quad | \\ C_6H_5NHCOC = NO \end{array}\right)$$

(XXXXXVI)

Its magnetic moment is found to be 1.71 B.M. The value is abnormal for bivalent nickel. It indicates the mixture of spin paired and spin-free complexes in the product and needs further investigation.

Its absorption spectrum in the visible region is presented in fig. R-36. It has continuous absorption.

(f) The complex (TSO-Ni) was prepared by refluxing a mixture of nickel acetate and oxime-thiosemicarbazone. On the basis of the analysis, the ratio of metal to nitrogen is found as 1:5. Hence it is formulated as (XXXXXVII)



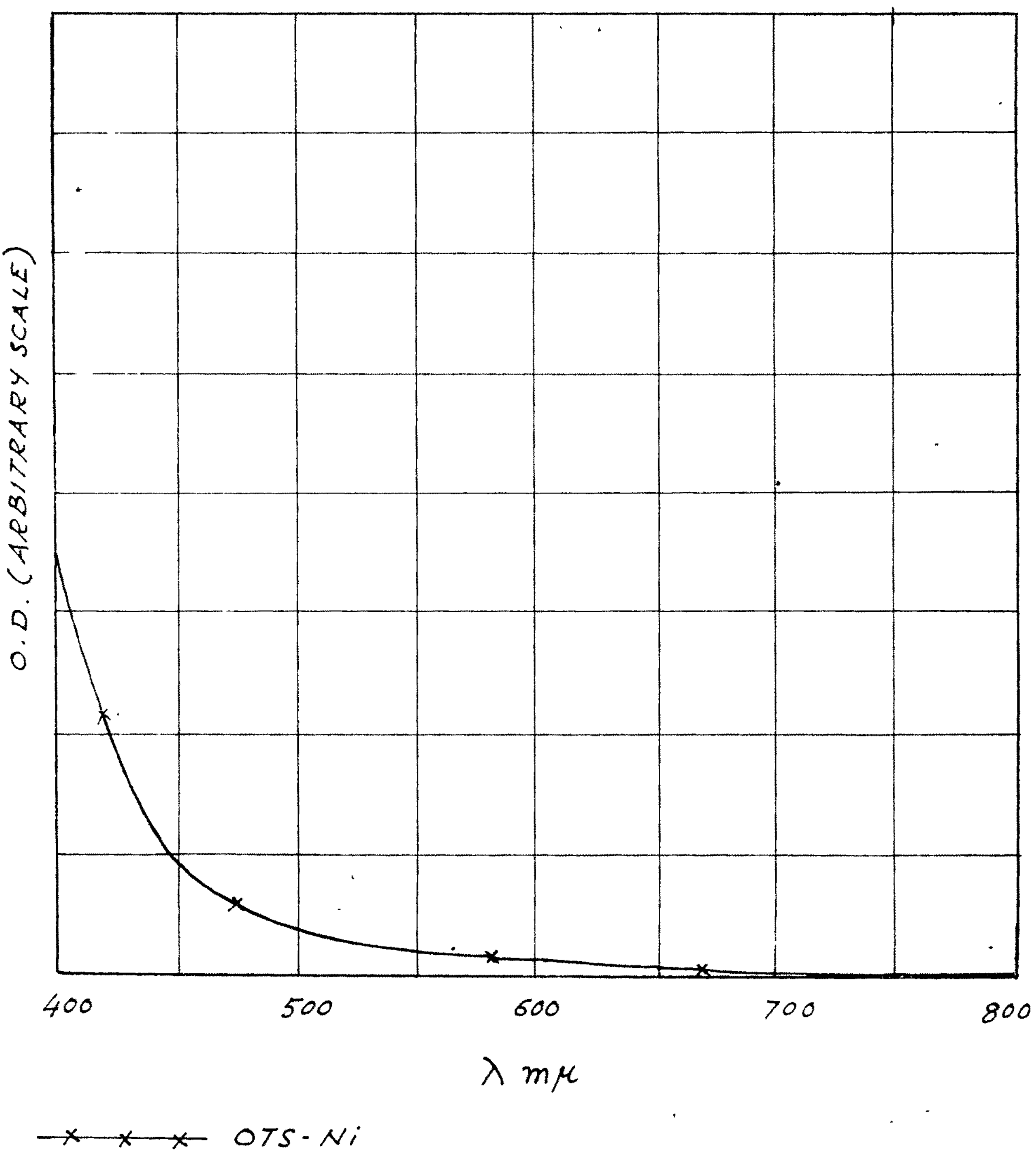
$$\mathrm{Ni}\left(\begin{array}{l} CH_3 - C = N\ NCSNH_2 \\ \qquad\quad | \\ C_6H_5NHCOC = NO \end{array}\right)$$

(XXXXXVII)

Its absorption spectrum in the visible region is presented in fig. R-37.

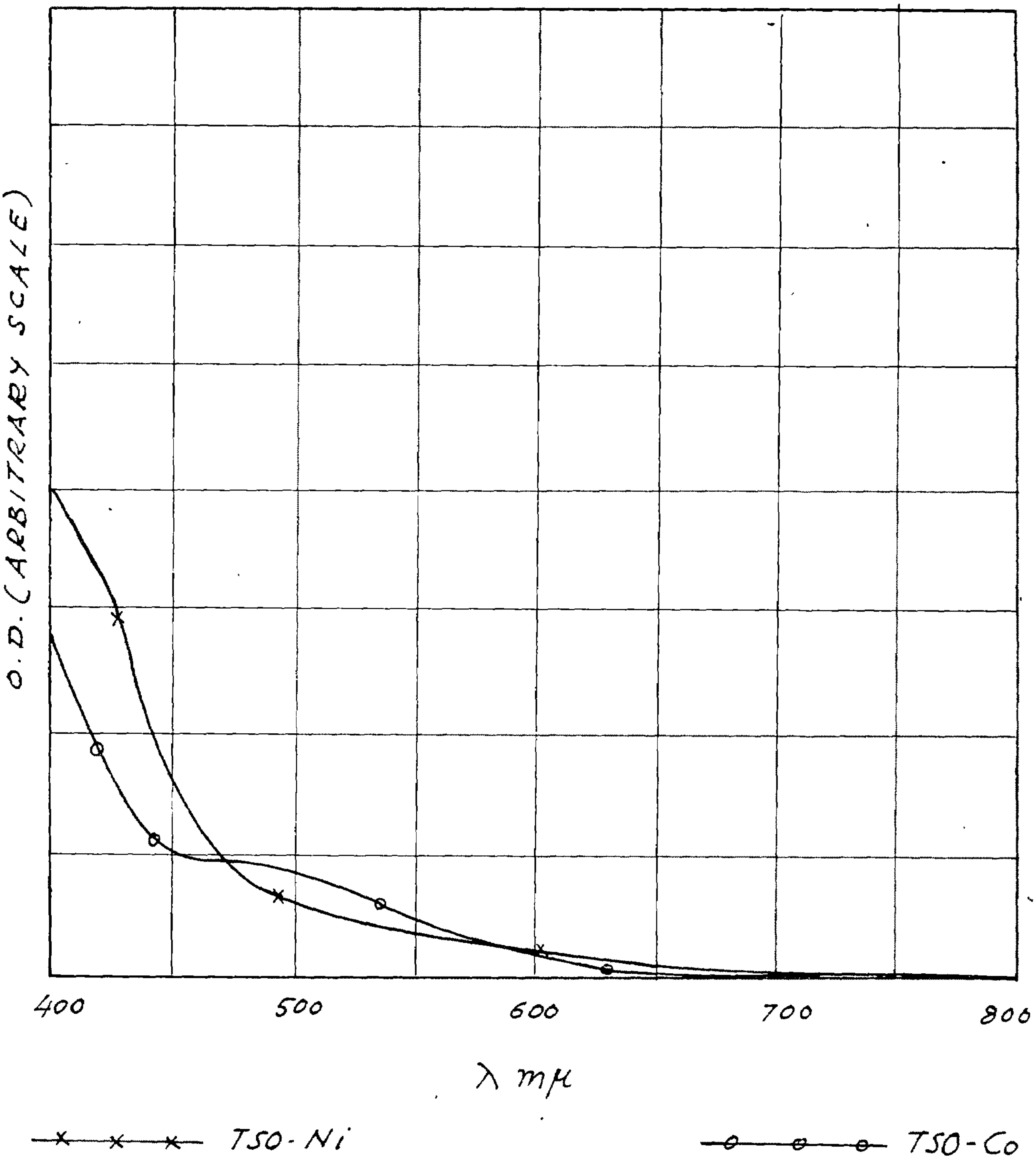
Its magnetic moment is found as 0.83 B.M. The value is abnormal for bivalent nickel. It indicates the mixture of spin paired and spin free complexes, and needs further investigation.

The thermograms (D.T.A. and T.G.A.) are presented



VISIBLE ABSORPTION SPECTRA OF OTS-Ni

FIG. R-36



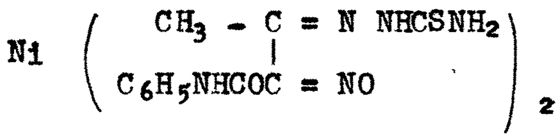
VISIBLE ABSORPTION SPECTRA OF

TSO-Ni AND TSO-Co

FIG. R-37

in fig.38. The results show that the complex decomposes in two steps, the final product left being the residue of nickel. The results indicate low thermal stability of the complex.

Patel and Mankad[144] obtained the complex which is represented by them as (XXXXXVIII).

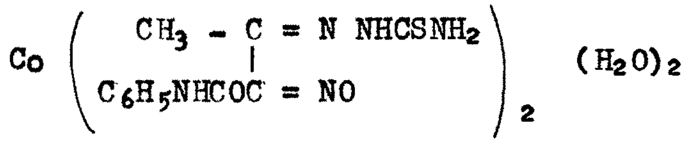


$$Ni\left(\begin{array}{l} \quad CH_3 - \underset{|}{C} = N\ NHCSNH_2 \\ C_6H_5NHCOC = NO \end{array}\right)_2$$

(XXXXXVIII)

However, Hovocka and Hotz-becher[169] obtained the nickel complex of diacetyl-oxime-thiosemicarbazone which was shown to contain the ratio of nickel to ligand as 1:1.

(g) The complex (TSO-Co) was prepared by refluxing the mixture of cobalt acetate and oxime-thiosemicarbazone. On the basis of analysis the ratio metal to nitrogen is suggested as 1:10. Hence it is formulated as (XXXXXIX).

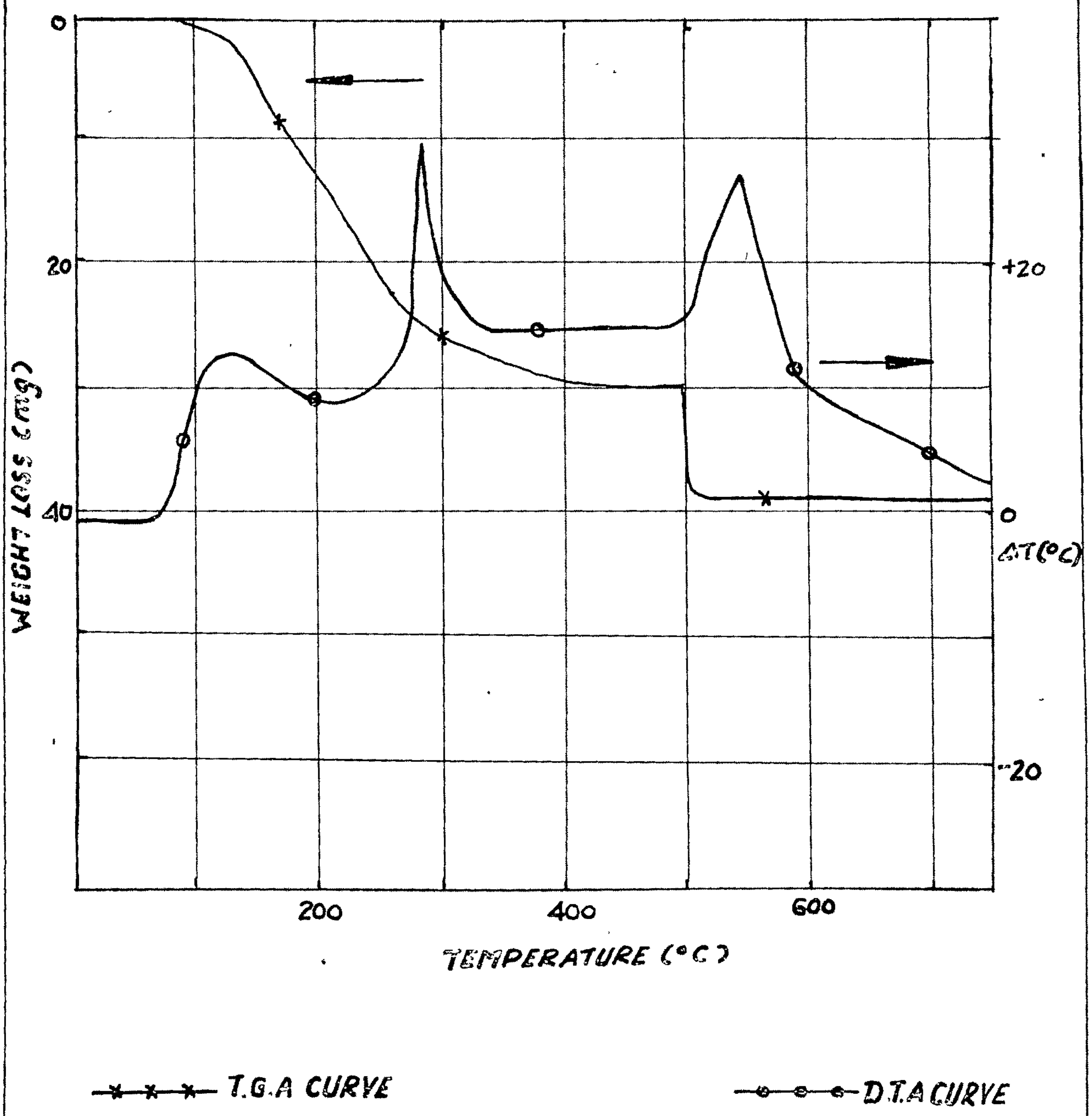


$$Co\left(\begin{array}{l} \quad CH_3 - \underset{|}{C} = N\ NHCSNH_2 \\ C_6H_5NHCOC = NO \end{array}\right)_2 (H_2O)_2$$

(XXXXXIX)

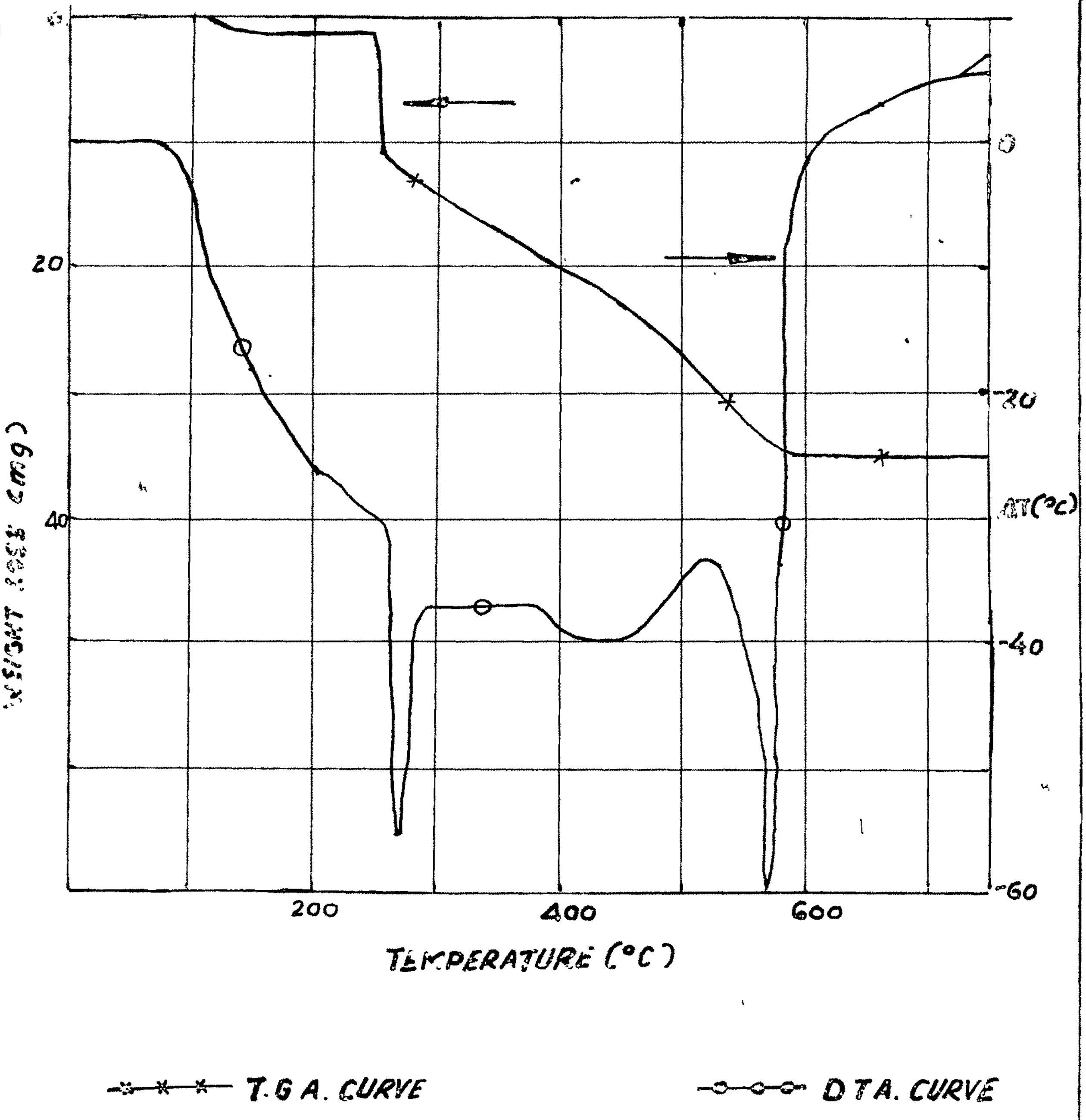
Its absorption spectrum in the visible region is presented in fig. R-37. It has continuous absorption.

The thermograms (D.T.A. and T.G.A.) are presented in fig. R-39. The results indicate that the complex decomposes in two major steps leaving the residue of



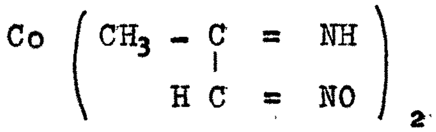
THERMOGRAMS OF TSO-Ni

FIG. R-38



THERMOGRAMS of TSO-Co

FIG. R-39



$$\mathrm{Co}\left(\begin{array}{ccc} CH_3 - C & = & NH \\ | & & \\ HC & = & NO \end{array}\right)_2$$

The magnetic moment of the complex is found to be 1.03 B.M. The value is low for spin paired bivalent cobalt complexes.

The cobalt and nickel complexes of oxime-thiosemicarbazone possesses low value of magnetic moment. It may be attributed to the antiferromagnetic coupling of spin-spin interactions.

Further the ligand behaves differently with cobalt and nickel. Thus it acts as a monobasic acid with cobalt and as a dibasic acid with nickel. Similar observations have been made by Hovocka and Hotzbechen for diacetyl oxime thiosemicarbazone ligand.

III 7 Transition metal complexes of oxime-azine (oxime-hydrazone) and hydroxyazine :

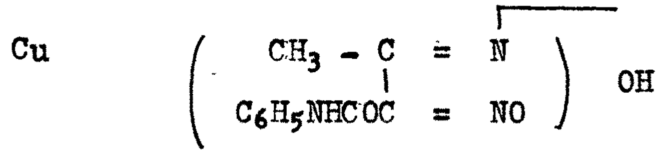
In continuation of our studies on the complex of salicylaldimines and oxime-anils, we have investigated the complexes of oxime-azines and resorcylaldazine, Cu, Ni and Co complexes of oxime-azine or oxime-hydrazone and Cu and Co complexes of β-resorcylaldazine are obtained. Their magnetic moments calculated from magnetic susceptibilities and diamagnetic corrections are presented in Table R-9.

(a) The complex OZ-Cu was prepared from copper acetate, oxime-ketone and hydrazine. It is found from analysis that it contains the ratio of copper to nitrogen as 1:3 hence it is formulated as LXI(a).

Table R-9

Magnetic moments of the complexes

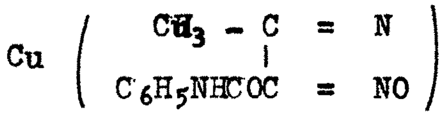
No.	Compound	Molar magnetic susceptibility (per metal atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $X_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1	OZ-Cu	1455	1590	1.97
2	OZ-Co	7941	8191	4.46
3	OZ-Ni	3981	4173	3.20
4	OZ-Fe	10460	10647	5.07
5	RZ-Cu	48450	48597	1.37
6	RZ-Co	4167	4335	3.25



$$Cu \left(\begin{array}{ccc} CH_3 - \overset{}{C} & = & N \\ \vert & & \\ C_6H_5NHCOC & = & NO \end{array} \right) OH$$

(LXI) (a)

It may be remarked, however, that the preferred formula on the basis of analysis would be (LXI)(b).



$$Cu \left(\begin{array}{ccc} CH_3 - C & = & N \\ \vert & & \\ C_6H_5NHCOC & = & NO \end{array} \right)$$

(LXI)(b)

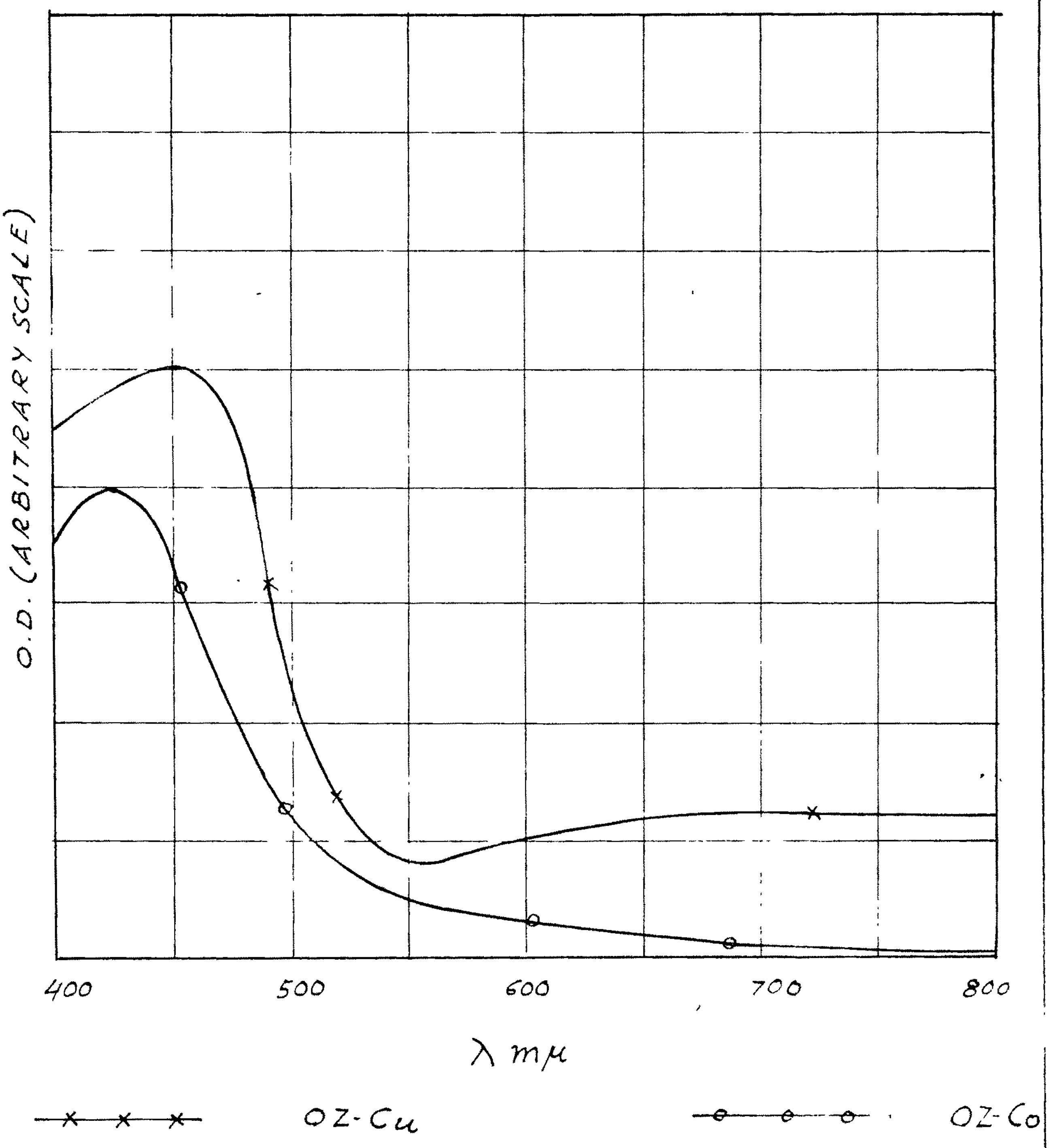
It indicates the presence of monovalent copper and the complex should be diamagnetic. As the complex is paramagnetic the (above) formula is discarded.

It is insoluble in various solvents except dimethylformamide and pyridine and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-40. It has an absorption band at 440-60 mμ.

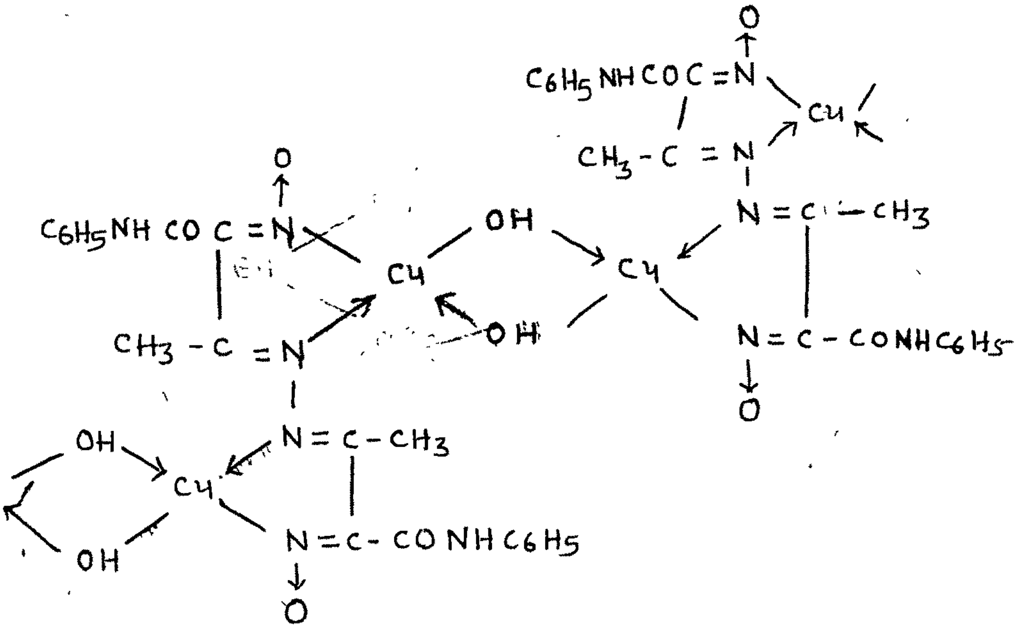
Its magnetic moment has been calculated as 1.97 B.M. It suggests the square planar nature of monomeric complex.

On the basis of above observations the complex may be considered to be dimeric with reference to bis(bidentate) ligand and hence polymeric through the formation of OH bridges (LXII).



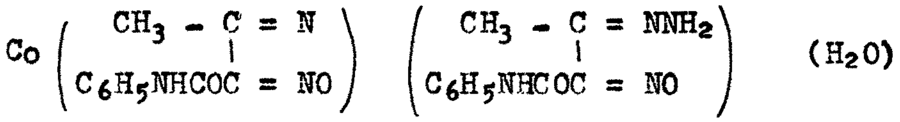
VISIBLE SABSORPTION SPECTRA OF
OZ - Cu AND OZ - Co

FIG. R - 40



(LXII)

(b) The complex(OZ-Co)was prepared from cobalt acetate, oxime-ketone and hydrazine. It is found from analysis that the ratio of cobalt to nitrogen is 1:7. Hence it is formulated as (LXIII).



$$Co\left(\begin{array}{c}CH_3 - \overset{}{C} = N \\ | \\ C_6H_5NHCOC = NO\end{array}\right)\left(\begin{array}{c}CH_3 - C = NNH_2 \\ | \\ C_6H_5NHCOC = NO\end{array}\right)\quad(H_2O)$$

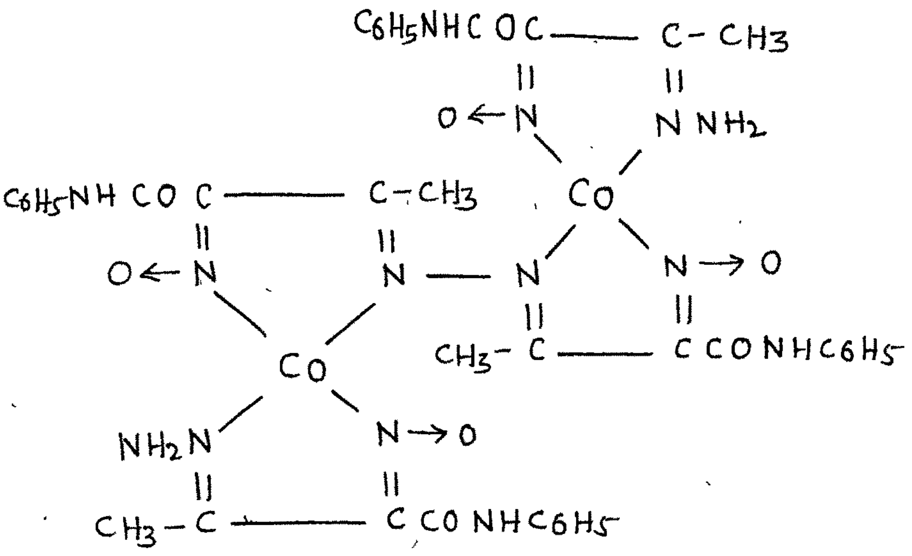
(LXIII)

It is insoluble in various solvents except dimethylformamide and pyridine and does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-40. It has an absorption band at 420-30 mμ.

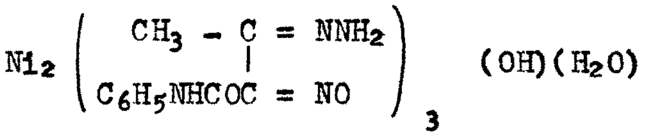
Its magnetic moment has been calculated as 4.46 B.M. It indicates the tetrahedral nature of the complex.

On the basis of the above observations, the complex is considered to be dimeric (LXIV).



(LXIV)

(c) The complex(OZ-Ni)was prepared from nickel acetate oxime-ketone and hydrazine. It is found from analysis that it contains the ratio of nickel to nitrogen as 1:6. Hence it is formulated as (LXV).



$$Ni_2\left(\begin{array}{c} CH_3 - \underset{|}{C} = NNH_2 \\ C_6H_5NHCOC = NO \end{array}\right)_3 \quad (OH)(H_2O)$$

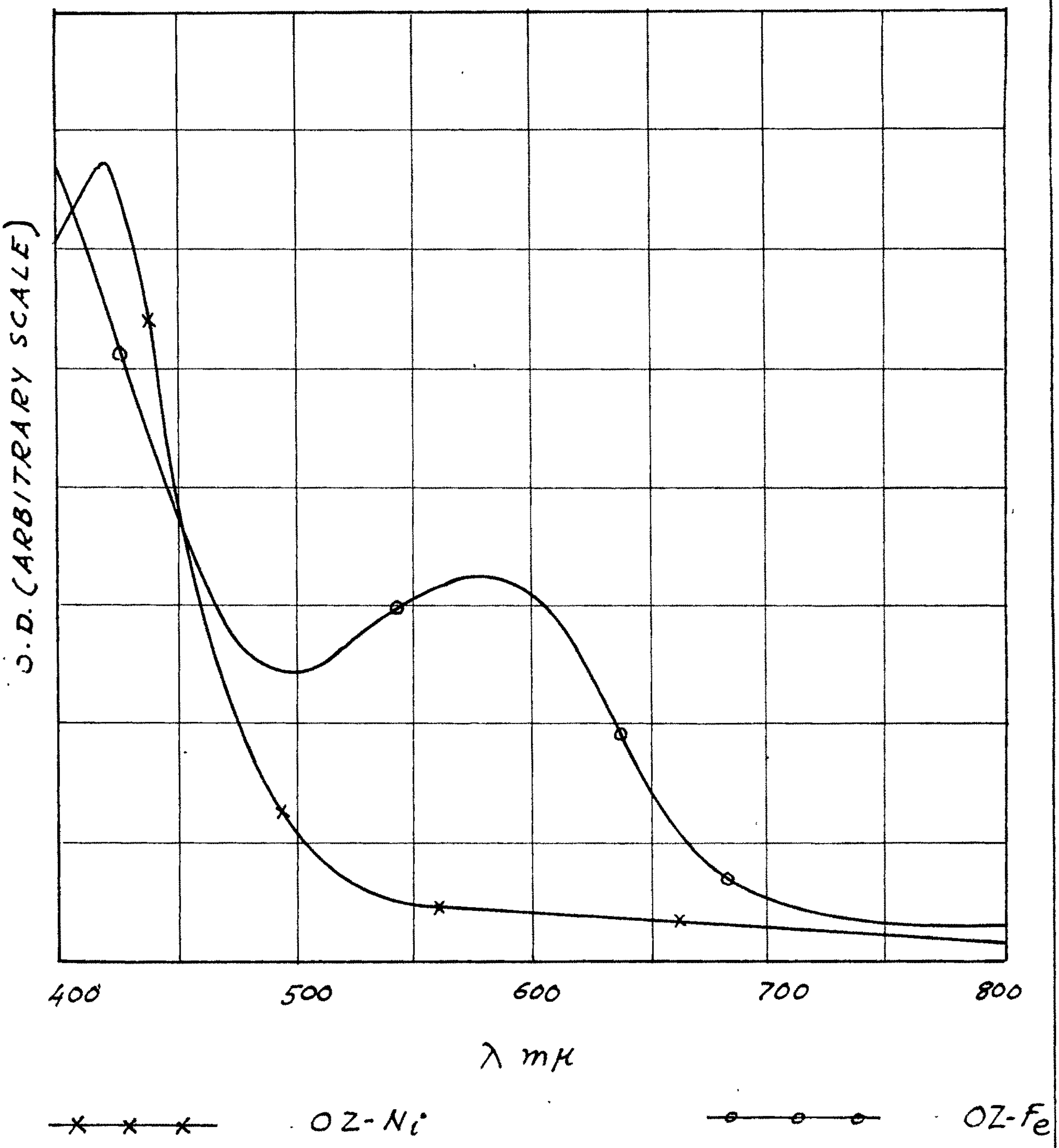
(LXV)

It is insoluble in various solvents and does not melt upto 300°C.

Its absorption spectrum in the visible region is given in fig. R-41. It has an absorption band at 420 mμ.

Its magnetic moment per nickel atom is calculated as 3.20 B.M. Hence the complex is considered to possess octahedral ligand field around nickel atom.

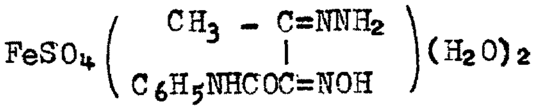
(d) The complex(OZ-Fe) was prepared from Iron(II) sulphate, oxime-ketone and hydrazine. It is found from



VISIBLE ABSORPTION SPECTRA OF OZ-Ni AND OZ-Fe

FIG. R-41

analysis that it contains sulphate and that the ratio of iron to nitrogen is 1:4. Hence it is formulated as (LXVI).



$$FeSO_4\left(\begin{array}{c} CH_3 - C{=}NNH_2 \\ | \\ C_6H_5NHCOC{=}NOH \end{array}\right)(H_2O)_2$$

(LXVI)

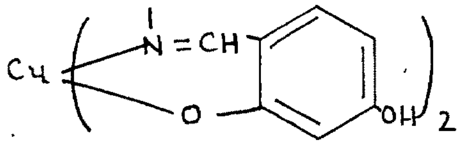
It is a blue coloured complex soluble in various organic solvents. It does not melt upto 300°C.

Its absorption spectrum in the visible region is presented in fig. R-41. It has an absorption band at 580 mμ.

Its magnetic moment is calculated as 5.07 B.M.

The results suggest that hydrazone is formed in the case of nickel and Fe complexes, azine is formed in the case of copper complex, whereas both azine and hydrazone are formed in the case of cobalt complex.

(e) The complex (RZ-Cu) was prepared from copper acetate, and β-resorcylaldazine.on the basis of analysis, it is formulated as (LXVII).



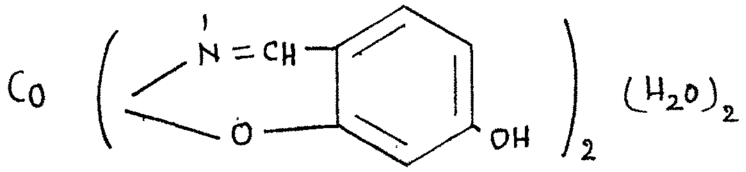
(LXVII)

It is insoluble in all common solvents except pyridine and dimethylformamide and does not melt upto 300°C.

Its magnetic moment has been calculated as 1.37 B.M.

The value is low and would indicate M-M bonding or antiferromagnetic coupling of spin-spin interactions.

(f) The complex (RZ-Co) was prepared from cobalt acetate and β-resorcylaldazine. On the basis of analysis it is formulated as (LXVIII).



(LXVIII)

It is insoluble in various solvemts and does not melt upto 300°C.

Its magnetic moment has been calculated as 3.25 B.M. It suggests the octahedral nature of the complex.

It may be suggested that these last two complexes may be represented as monomers or dimers.

III 8. Oxalyldihydrazide and its transition metal complexes :

Acyl hydrazides are known to exist in enolic form and to act as bidentate ligand. Sacconi[170] showed that salicylalhydrazide derivatives act as tridentate ligand. We believed that oxalyldihydrazide can act as bis(bidentate) or tetradentate ligand and hence may give rise to polymeric metal complexes. Cu, Ni and Co complexes of oxalyldihydrazide were prepared and their magnetic moment calculated from magnetic susceptibilities and diamagnetic corrections are presented in Table R-10.

(a) The complex (BZ-Cu) was prepared from copper acetate,

Table R-10

Magnetic moments of the complexes

No.	Compound	Molar magnetic susceptibility (per metal atom) $X_m \times 10^6$	Corrected Molar magnetic susceptibility (per metal atom) $X_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1	DZ-Cu	1281	1341	1.81
2	DZ-Co	1176	1256	1.75
3	DZ-Ni	5031	5134	3.54

oxalylaldihydrazide and ammonia. It is found from analysis that it contains the ratio of copper to nitrogen as 1:2. Hence it is formulated as (LXIX).

$$Cu\ (CH_3CO_2)\ (\underset{|}{C}ONNH_2)$$

(LXIX)

It is insoluble in various solvents and does not melt upto 300°C.

Its magnetic moment has been calculated as 1.81 B.M. Hence the complex may be considered to axist as dimer.

(b) The complex (DZ-Co) was prepared from cobalt acetate, oxalyldihydrazide and ammonia. It is found from analysis that the ratio of cobalt to nitrogen is 1:3. Hence it is formulated as (LXXX).

$$Co(CH_3CO_2)\ (\underset{|}{C}ONNH_2)\ (NH_3)\ (H_2O)$$

(LXXX)

It is insoluble in various solvents and does not melt upto 300°C.

Its magnetic moment has been calculated as 1.75 B.M. Hence the complex is considered to be octahedral and dimeric.

(c) The complex (DZ-Ni) was prepared from nickel acetate, oxalyldihydrazide and ammonia. It is found from analysis that the ratio of nickel to nitrogen is 1:3. Hence it is formulated as (LXXXI)

$$Ni\ (CH_3CO_2)\ (CONNH_2)\ (NH_3)\ (H_2O)_2$$

(LXXXI)

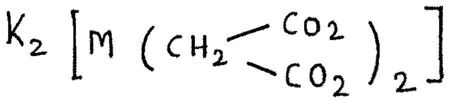
It is insoluble in various solvents and does not melt upto 300°C.

Its magnetic moment has been calculated as 3.54 B.M. The complex is considered to be oxtahedral and dimeric.

All these complexes are considered to exist as dimers. Further work is necessary to remove acetate from these complexes.

III 9. Polymerisation of malenates :

It is shown that malonic acid readily reacts vigorously with formaldehyde forming poly-acids. The reaction is controllable with ethyl malonate so that tetra-acid can be obtained. Little is known about the polymerisation of the simple and complex salts of malonic acid. We have carried out some preliminary work on this aspects. The double malonates of the type (LXXXII) were prepared and their polymerisation with formaldehyde was attempted. Their magnetic moments calculated from magnetic susceptibilities and diamagnetic corrections are presented in Table R-11.



$$K_2\left[M\left(CH_2\begin{matrix}\diagup CO_2\\ \diagdown CO_2\end{matrix}\right)_2\right]$$

(LXXXII)

(a) Double malonates of Cu, Ni and Co:

These complexes were prepared by the reaction of metal Cu, Ni and Co carbonate with malonic acid in presence of K_2CO_3.On the basis of analysis, they are formulated as (LXXXIII).

$$K_2\left[M-(C_3H_2O_4)_2\right](H_2O)_x$$

(LXXXIII)

Table B-11

Magnetic moments of the complexes

No.	Compound	Molar magnetic susceptibility (per metal atom) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per metal atom) $X_m' \times 10^6$	Magnetic moment (per metal atom) (μ) B.M.
1	Mal Co K	10890	11070	5.11
2	Mal Ni K	6310	6485	3.99
3	Mal F Co K	7079	7203	4.25
4	Mal F Ni K	6515	6665	4.15

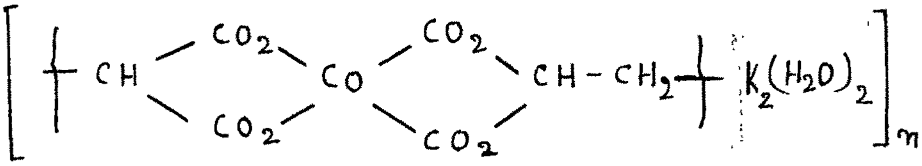
	M =	X =
(a)	Cu	5
(b)	Ni	3
(c)	Co	8

The magnetic moments of Ni and Co complexes are found to be 3.99 and 2.85 B.M. respectively.

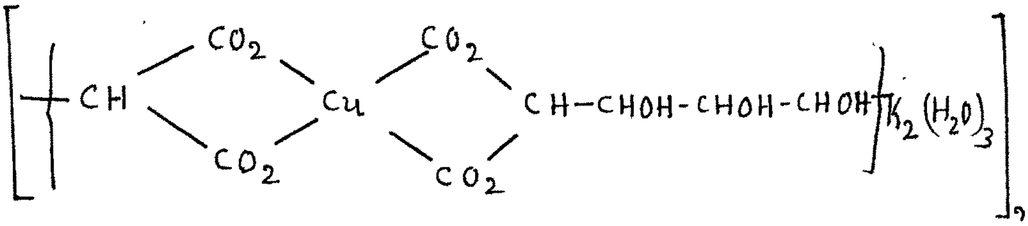
(b) Polymerisation of double malonates of Cu, Ni and Co :

Attempt was made to polymerise the above double malonate with formaldehyde. Gummy mass was obtained; it could not, however, be satisfactorily fractionated or purified. Hence the following suggestions are tentative and of a preliminary nature.

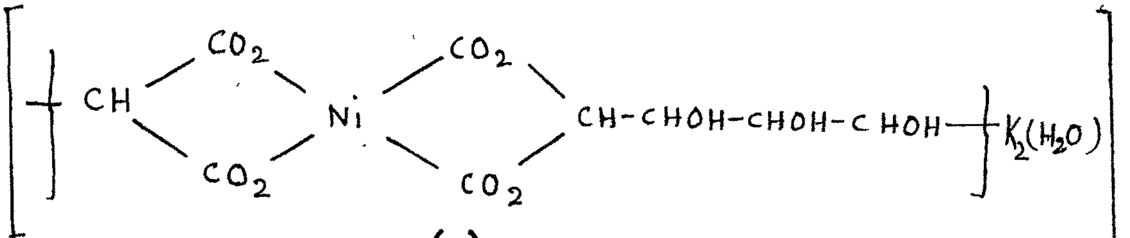
On the basis of analysis, they are formulated as follows :



(a)



(b)



(c)

The possibility that the products are mixtures of double malonates and ketonic glasses cannot be eliminated.

The magnetic moments of nickel and cobalt complexes for transition metal atom have been calculated as 4.15 and 4.25 B.M. respectively.