RESULTS

AND

DISCUSSION

PYROLYSIS OF POLYCHELATES

III RESULTS AND DISCUSSION

III.1 Polychelates of Chloranilic Acid and their Pyrolysis:

(i) General: Polychelates of dihydroxy quinones:

Polychelates of 2,5 dihydroxy-p-benzoquinone have been studied by Jain and Singhal (153), Kanda and co-workers (154 to 157), Frank and co-workers (158), Rose and co-workers (159), Bottei and Fangman (114) and Mistry (116).

Studies on polychelates of naphthazarin have been made by Underwood and co-workers (160), Mangini and Stratta (161), Bailes and Calvin (162), Bottei and Gerace (115), Akiyama and Mizutani (163) and Mistry (116). Polychelates of quinizarin and anthrarufin have been studied by Flumiani and Bajic (164), Knobloch and Rauscher (165), Korshak and co-workers (119, 120, 121), Slinkin and co-workers (166), Inoue and co-workers (117), Talati and Mistry (167,168), Coble and Holtzclaw (169), de Charentenary and Teyssie (170), Jackson and Leonard (171), Dzhusbalieva and co-workers (172), Issa and co-workers (173) and Maurya, Agarwala and Dey (174).

Studies on polychelates of chloranilic acid and bromanilic acid have been carried out by Kanda (154), Mckown and Swiger (175), Beg and Arshad (176), Yamadera and co-workers (177), Bianchi (178) and Krasockha and co-workers (179).

(ii) Polychelates of Chloranilic Acid:

Polychelates of chloranilic acid with cobalt(II), nickel(II), copper(II), iron(II), manganese(II), lead(II), and uranyl(II) have been prepared and their studies are presented below.

The magnetic moment, electrical conductivity, IR spectral bands, DTA peaks and TG weight loss of these polychelates are presented in tables III.1 (a) to (e).

From the analysis of these polychelates, the ratio of metal-to-ligand is suggested as one-to-one. They are represented as linear polymeric chain (I).

(a) Co(II)-polychelate

Bottei and co-workers (114,115) prepared cobalt polychelate of 2,5 dihydroxy p-benzoquinone (BQ) and

TABLE III.1(a)

Magnetic moments of polychelates of CA

No	Polychelate	Molar magnetic susceptibility (per metal ion) $X_m \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X_m' \times 10^6$	Magnetic moment (per metal ion) B.M.
1	CoCA	9464	9598	4.9
2	NiCA	4090	4226	3.2
3	CuCA	1500	1600	2.0
4	MnCA	14426	14541	5.9
5	FeCA	12695	12821	5.6
6	PbCA	Diam	Diam	Diam
7	UCA	Diam	Diam	Diam

TABLE III.1(b)

Solid State Electrical Resistivity of Polychelates of CA

No	Polychelate	Temperature (°C)	Resistivity ρ (ohm-cm)x10^{-10}	Conductivity σ (ohm^{-1} cm^{-1})x10^{13}
1	CoCA	32	1.040	962.0
2	NiCA	32	0.5634	1780.0
3	CuCA	32	46.11	21.70
4	MnCA	32	0.6863	1460.0
5	FeCA	32	0.6264	1600.0
6	PbCA	32	0.3545	2820.0
7	UCA	32	78.06	12.80

TABLE III.1(c)

Some Characteristic IR Frequencies (cm^{-1}) of the Polychelates

(i) Co CA

3400 s	2960 w	1985 w	1885 w(b)
1655 m	1610 (sh)	1580 m	1500 s(b)
1375 s	1305 w	1285 (sh)	1240 w
1110 w	1055 w	1005 w	970 w
850 s	8 20 w	770 w	690 m

(ii) Ni CA

3540 s	3390 s(b)	3260 s	2960 m
1890 w	1650 s	1610 s	1490 s(b)
1375 s	1300 s	1090 w	1000 m
960 w	850 s	780 w	

(iii) Cu CA

3490 m	2940 w	1900 w	1680 (sh)
1570 s	1365 s	1300 m	1080 w
995 w	850 s	820 w	790 w
755 w			

TABLE III. 1(c) continued

(iv) Mn CA

3420 s	2940 w	2840 w	1960 w
1880 w	1610 (sh)	1575 s	1490 s
1370 s	1345 (sh)	1290 w	1000 w
960 w	845 s	825 w	805 w
770 w	690 w(b)	645 m	595 m
570 m	470 w	395 w	

(v) Fe CA

3420 m	2940 w	1980 w	1570 m
1480 s	1355 m	1265 m	990 m
950 w	860 w	850 m	820 w
780 w	770 w	730 w(b)	660 w
650 w	560 m		

(vi) Pb CA

3520 m	3420 m	1980 w	1610 m
1485 s	1370 s	1300 m	1030 w
1000 m	965 w	850 s	820 w
760 w	645 m	595 m	

TABLE III.1(d)

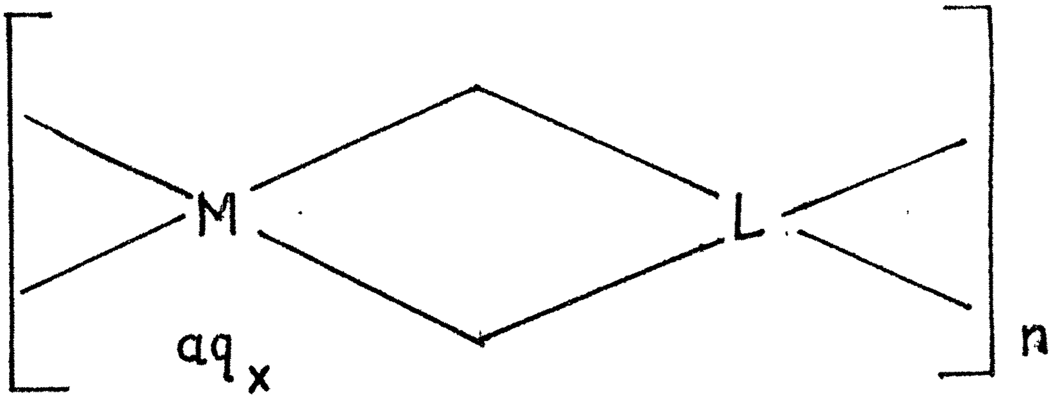
Endothermic and Exothermic peaks in DTA study of Polychelates of CA

No	Polychelate	Endothermic peak temp (°C) / onset temp (°C)	Exothermic peak temp (°C) / onset temp.(°C)
1	CoCA	(1) $\frac{185}{175}$, (2) $\frac{295}{275}$	(1) $\frac{345}{340}$
2	NiCA	(1) $\frac{225}{212}$, (2) $\frac{280}{265}$ (3) $\frac{300}{295}$	(1) $\frac{410}{400}$
3	CuCA	(1) $\frac{150}{145}$	(1) $\frac{390}{380}$
4	MnCA	(1) $\frac{225}{208}$	(1) $\frac{440}{410}$, (2) $\frac{460}{455}$
5	FeCA	(1) $\frac{155}{148}$, (2) $\frac{245}{210}$	(1) $\frac{310}{290}$, (2) $\frac{455}{445}$

TABLE III.1(e)

TG weight losses of Polychelates

No	Polychelate	Temperature range °C	% Weight loss
1	CoCA	180-230	6.3
		260-290	3.6
		298-405	1.0
		405-410	70.2
2	NiCA	192-210	4
		248-286	9
		300-277	3
		400-410	3
		435-470	3
		470-475	63
3	CuCA	370-418	2
		418-435	64
4	MnCA	204-248	13
		255-430	1
		430-435	70
5	FeCA	204-228	9
		285-360	6
		360-380	84
6	PbCA	150-170	2.5
		225-250	1.5
		290-345	2
		345-350	93



(I)

L : $C_6H_4Cl_2$

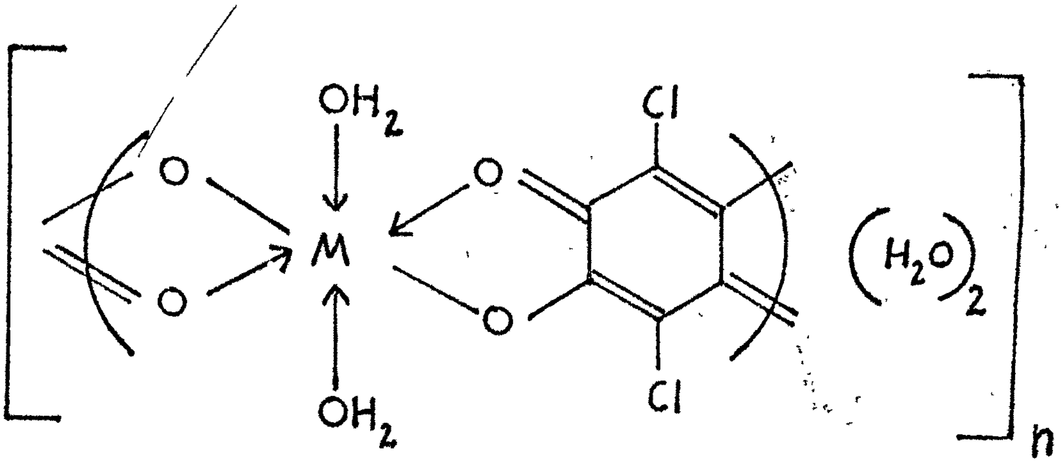
aq : H_2O

	M =	X =
(i)	Co(II)	4·0
(ii)	Ni(II)	4·0
(iii)	Cu(II)	1·0
(iv)	Fe(II)	3·5
(v)	Mn(II)	2·5
(vi)	Pb(II)	2·0
(vii)	UO_2(II)	0·5

5,8-dihydroxy naphthoquinone (NQ) and studied their IR spectra and DTA. Bailes and Calvin (162) studied oxygen-carrier characteristics of the cobalt polychelate of NQ. Korshak and co-workers (119) studied thermomechanical behaviour, average molecular weight and magnetic moment of the cobalt polychelate of quinizarin (AQ) and anthrarufin (AQR). Inoue and co-workers (117) studied electrical and thermal conductivity of cobalt polychelates of AQ and AQR. Mistry (116) studied electrical conductivity, DTA and IR spectra of cobalt polychelate of BQ, NQ, AQ and AQR. Cobalt polychelate of chloranilic acid (CA) has not been studied recently.

The magnetic moment of Co(II) polychelate (CoCA) is calculated as 4.9 B.M per metal atom. The metal ion is considered to be 6-covalent with octahedral ligand field. O - atoms of the ligand molecules and metal ions are considered to be in the same plane. It is suggested that monomeric metal chelate has trans octahedral configuration with coordinated and lattice water molecules as in (II). The solid state conductivity of the polychelate at room temp. is 0.96×10^{-10} ohm^{-1} cm^{-1}.

From the IR spectrum of the polychelate, it is suggested that (i) the band at 3400 cm^{-1} be attributed to chelated hydroxyl of end ligand molecules in a chain with the overlap for lattice and coordinated water, (ii) the

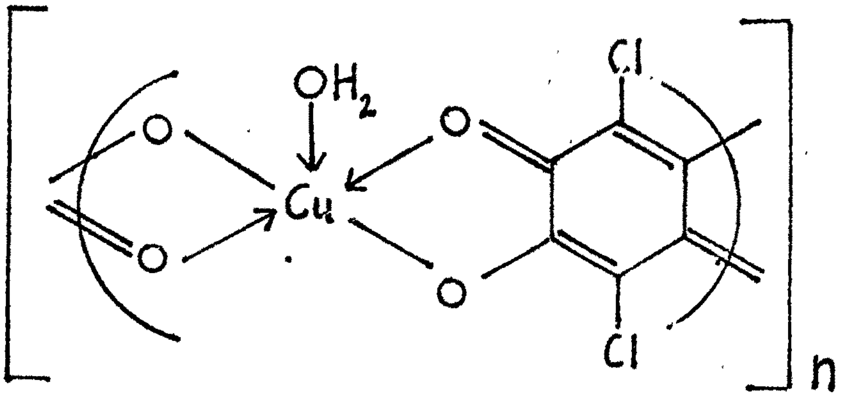


(II)

M =

(i) Co (II)

(ii) Ni (II)



(III)

band at 1580 cm^{-1} be attributed to coordinated quinonoid carbonyl, (iii) the band at 1005 cm^{-1} be attributed to C-Cl group, and (iv) the bands at 1500 cm^{-1} and 1375 cm^{-1} be attributed to ring deformations.

Endothermic DTA peaks at 185°C and 295°C are attributed to solid-state phase transitions involving lattice rearrangements with loss of water and the exothermic peak at 345°C is attributed to decomposition reactions. TG weight losses indicate loss of lattice water below 300°C. Heavy weight loss at 410°C, being associated with spurting of the powder from the micro crucible, cannot be attributed to definite decomposition reactions.

(b) Ni(II) Polychelate

Bottei and co-workers (114,115) prepared nickel chelates of BQ and NQ and studied their IR spectra and DTA. Kanda and co-workers (154,155) prepared nickel polychelates of BQ, chloranilic acid and bromanilic acid. Korshak and co-workers (119) studied the thermomechanical behaviour, average molecular weight and magnetic moment of the nickel polychelates of AQ and AQR. Inoue and co-workers (117) studied the electrical and thermal conductivity of the nickel polychelates of AQ and AQR. Mistry (116) investigated the electrical conductivity, DTA and IR spectra of the nickel polychelates of BQ, NQ, AQ and AQR. Knobloch and Rascher (165) studied IR spectra of the nickel polychelate of AQ and Slinkin and co-workers (166) studied the catalytic activity of the nickel polychelate of AQ.

The magnetic moment of nickel polychelate (NiCA) is calculated as 3.2 BM per metal atom. The metal ion is considered to be 6-covalent with octahedral ligand field. O-atoms of the ligand molecules and metal ions are considered to be in the same plane. It is suggested that the monomeric metal chelate has octahdral configuration with coordinated and lattice water molecules as in (II). The solid state conductivity of the polychelate is 1.78 x10^{-10} ohm^{-1} cm^{-1} at room temperature.

From the IR spectrum of the polychelate it is suggested that (i) the broad band at 3390 cm^{-1} be attributed to lattice water, (ii) the band at 1610 cm^{-1} be attributed to coordinated quinonoid carbonyl, (iii) the band at 1000 cm^{-1} be attributed to C-Cl group, (iv) the bands at 1490 cm^{-1} and 1375 cm^{-1} be attributed to ring deformations and (v) the band at 3540 cm^{-1} be attributed to hydroxyl of end ligand molecule in a chain.

Endothermic DTA peaks at 225°C, 280°C and 300°C are attributed to phase transitions involving lattice rearrangements with loss of water and the exothermic peak at 410°C is attributed to decomposition reactions. TG weight losses upto 410°C indicate loss of water molecules in steps. It indicates relatively loose binding of water molecules to metal ion. Above 410°C, heavy weight loss is observed due partly to the spurting of the powder from the micro-crucible and hence it could not be used to explain the decomposition reactions taking place at higher temperature. However, a speck of 2,5-dihydroxy p-benzoquinone could be observed on the wall of the glass-tube. It can be an indication of loss of the ligand resulting in the formation of a product with excess metallic ion (in oxide/ hydroxide form). It also indicates removal of Cl from chloranilate ion. Elimination of Cl may be related to the weak nature of C-Cl bond.

(c) Cu(II) Polychelate

Besides the studies made by Bottei and co-workers (114,115), Mistry (116), Knobloch and Rascher (165) Korshak and co-workers (119) and Inoue and co-workers (117), Copper polychelates of BQ, chloranilic acid and bromanilic acid have been extensively studied by Kanda and co-workers (154, 155) and Akiyama and Mizutani (163) have studied the electrical conductivity of the copper polychelate of NQ.

The magnetic moment of copper polychelate (CuCA) is calculated as 2.0 BM per metal atom. It is suggested that

O-atoms of the ligand molecules and metal ions be considered to lie in the same plane and that water molecule makes the metal ion 5-covalent so that the monomeric metal chelate be represented as square pyramid as in (III). The solid state conductivity of the polychelate is 0.02×10^{-10} ohm^{-1} cm^{-1} at room temperature.

From the IR spectrum of the polychelate it is suggested that (i) the band at 3490 cm^{-1} be attributed to coordinated/lattice water, (ii) the band at 995 cm^{-1} be attributed to C-Cl group and (iii) the bands at 1470 cm^{-1} and 1365 cm^{-1} be attributed to ring deformations.

Endothermic DTA peak at 150°C can be attributed to phase transition involving lattice rearrangement. Exothermic peak at 390°C can be attributed to decomposition reaction. TG curve shows that there is no weight loss upto 370°C. At 435°C, weight loss is associated with decomposition and spurting of the powder from the micro-crucible. However, some 2,5-dihydroxy p-benzoquinone was identified from the particles deposited on the wall of the tube. It indicates (i) the removal of Cl from chloranilate ion and (ii) the loss of ligand by the polychelate.

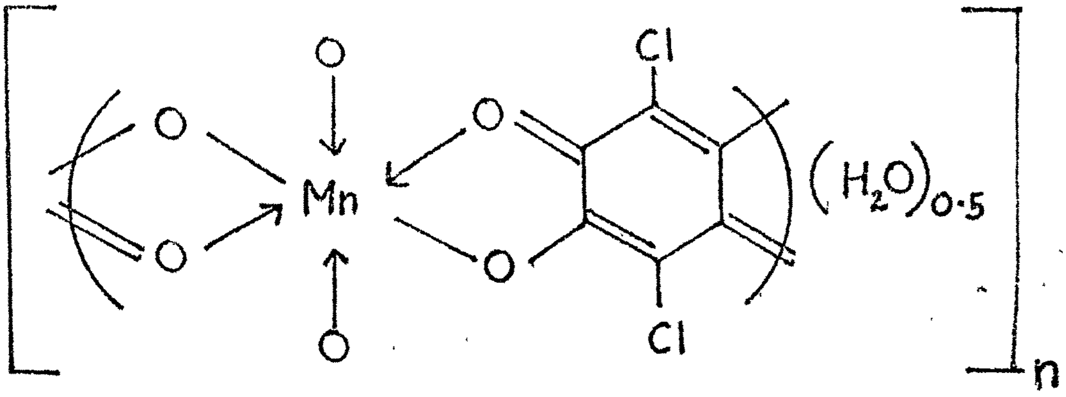
(d) Mn(II) Polychelate

Korshak and co-workers (119) have studied the manganese polychelate of AQ. No other studies on the Mn(II) polychelate of BQ, NQ, AQ, AQR or CA have been reported in recent years.

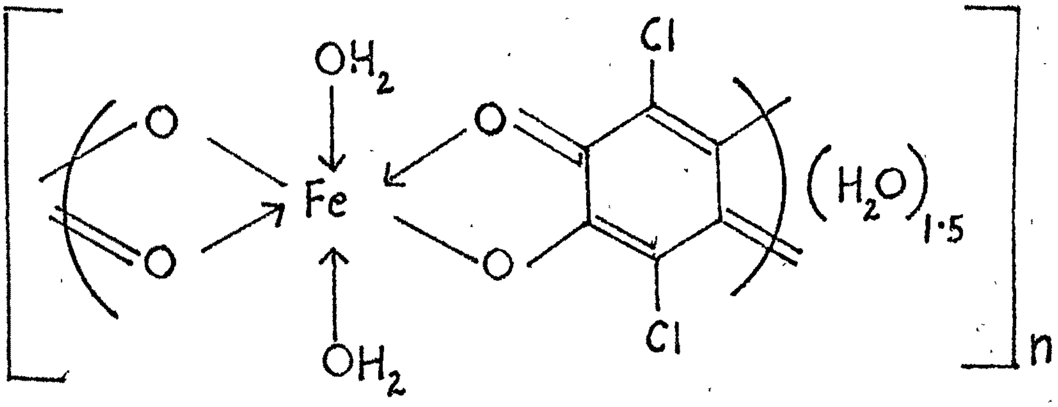
The magnetic moment of the polychelate is found to be 5.9 BM per metal atom. It is considered that the metal ion is 6-cavalent with octahedral ligand field. It is suggested that the monomeric metal chelate has trans octahedral configuration as in (IV). The solid state electrical conductivity of the polychelate is 1.46×10^{-10} ohm^{-1} cm^{-1} at room temperature.

From the IR spectrum of the polychelate it is suggested that (i) the band at 3420 cm^{-1} be attributed to hydroxyl of the end-ligand molecule in a chain with the overlap for coordinated and lattice water, (ii) the band at 1575 cm^{-1} be attributed to coordinated quinonoid carbonyl, (iii) the bands at 1490 cm^{-1} and 1370 cm^{-1} be attributed to ring deformations and (iv) the band at 1000 cm^{-1} be attributed to C-Cl group.

Endothermic DTA peak at $225^{o}C$ can be attributed to phase transition involving loss of water and exothermic peaks at $440^{o}C$ and $460^{o}c$ be attributed to decomposition



(IV)



(V)

reactions. TG weight losses upto 430°C indicate loss of water molecules. At 435°C, the weight loss is attributed to the decomposition and spurting of the powder.

(e) Fe(II) Polychelate

Inoue and co-workers (117) studied the electrical and thermal conductivity of iron polychelates of AQ and AQR. Mistry (116) studied the electrical conductivity, magnetic moment and IR spectrum of the iron polychelate of BQ. No work on the iron(II) polychelate of chloranilic acid has been reported recently.

The magnetic moment of the polychelate is calculated as 5.6 B.M. per metal atom. It is considered that the metal ion is 6-covalent with octahedral ligand field. It is suggested that the monomeric metal chelate has trans octahedral configuration as in (V[illegible]). The solid state electrical conductivity of the polychelate is 1.6×10^{-10} ohm^{-1} cm^{-1} at room temperature.

From the IR spectrum of the polychelate it is suggested that (i) the band at 3420 cm^{-1} be attributed to coordinated and lattice water, (ii) the bands at 1480 cm^{-1} and 1355 cm^{-1} be attributed to ring deformations, (iii) the band at 1570 cm^{-1} be attributed to coordinated quinonoid carbonyl and (iv) the band at 990 cm^{-1} be attributed to C-Cl group.

Endothermic DTA peaks at 155°C and 245°C can be attributed to phase transitions involving loss of lattice water. Exothermic DTA peaks at 310°C and 455°C can be related to decomposition reactions. TG weight losses upto 360°C indicate loss of lattice water. Heavy weight loss at 380°C is associated with decomposition and spurting of the powder.

(f) Pb(II) Polychelate

Inoue and co-workers (117) have studied the electrical and thermal conductivity of lead polychelates of AQ and AQR. No work on the lead polychelate of chloranilic acid has been reported in recent years.

The lead polychelate is diamagnetic. The solid state electrical conductivity of the polychelate is 2.82×10^{-10} ohm^{-1} cm^{-1}. From the IR spectrum of the polychelate, it is suggested that (i) the band at 1610 cm^{-1} be attributed to coordinated quinonoid carbonyl, (ii) the bands at 1485 cm^{-1} and 1370 cm^{-1} be attributed to ring deformations and (iii) the band at 1000 cm^{-1} be attributed to C-Cl group.

TG weight losses upto 340°C indicate loss of water. Heavy weight loss at 350°C is associated with decomposition reactions and spurting of the powder.

(g) UO_2(II) Polychelate

The polychelate is diamagnetic. The solid state electrical conductivity of the polychelate is 0.0128×10^{-10} ohm^{-1} cm^{-1}. No other studies of the polychelate have been made.

(h) General Considerations:

All the polychelates under study contain coordinated/lattice water. The magnetic moment of manganese(II), iron(II), cobalt(II) and nickel(II) polychelates indicates 6-covalent nature of the metal ion, with octahedral ligand field surrounding the ion. Lead and uranyl polychelates are diamagnetic as anticipated. There is no spin-pairing in any of these polychelates indicating weak crystal field of the ligand atoms surrounding the metal ion. The studies also indicate the absence of superexchange coupling in these polychelates.

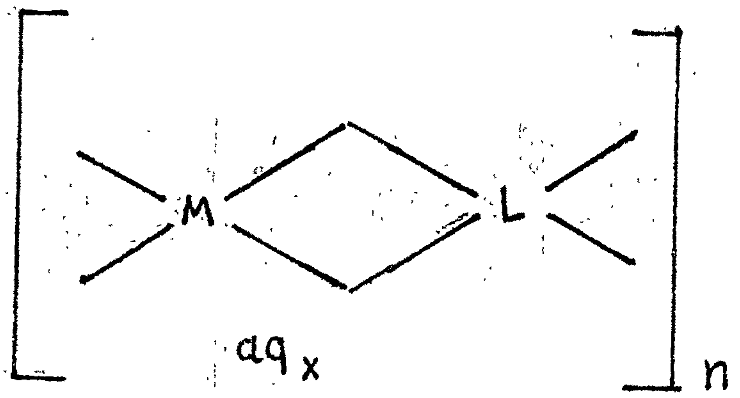
The IR spectra of the polychelates, in general, have a band-structure which can be related to $D_{\infty h}$ point group. The spectrum would have a three-band pattern in band regions - 1600 cm^{-1}, 800 cm^{-1} and 3200 cm^{-1}.

The thermal studies (DTA and TGA) show that both coordinated and lattice water may be considered lost in cases of NiCA and MnCA. In these cases, water-coordination to metal ion may not be strong and heating may lead to tetragonal distortions. Weak water-coordination to metal ion is not envisaged from magnetic studies. Further, DTA studies of CuCA and FeCA show endothermic peak at/near 150°C. There is no weight loss at this temperature in the corresponding TGA studies. Meso phase formation may be a possibility and the peak may be attributed to solid-smectic transition.

(iii) Pyrolyzed Polychelates of CA (Pyrolyzed at 310-30°C):

The polychelates of CA were pyrolyzed at 310-30°C under continuous evacuation. The residual products were washed, dried and analysed. On the basis of analysis, they are represented as in (VI). There is a difference in the amount of lattice/ coordinated water between MCA(PL) and MCA in general.

The magnetic moments of CoCA(PL), NiCA(PL), CuCA(PL) and MnCA(PL) (table III.1(f)) are comparable to those of CoCA, NiCA, CuCA and MnCA respectively. In case of FeCA(PL), the magnetic moment has a somewhat higher value. The diamagnetic PbCA has become paramagnetic on pyrolysis. The magnetic moment of PbCA(PL) is calculated as 2.1 B.M per metal atom. It may be related to the formation of free radical from the ligand or of lower valent lead ion.



(VI)

$L = C_6O_4Cl_2$

$aq = H_2O$

	M =	X =
(i)	Co(II)	7
(ii)	Ni(II)	5
(iii)	Cu(II)	1
(iv)	Fe(II)	2
(v)	Mn(II)	0
(vi)	Pb(II)	0

TABLE III.1(f)

Magnetic Moments of Pyrolyzed Polychelates of CA

No.	Polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X'_M \times 10^6$	Magnetic moment (per metal ion) B.M.
1	CoCA (PL)	9798	9961	5.0
2	NiCA (PL)	4268	4410	3.3
3	CuCA (PL)	1731	1831	2.1
4	MnCA (PL)	12913	13002	5.7
5	FeCA (PL)	14942	15052	6.1
6	PbCA (PL)	1615	1716	2.1

(iv) Pyrolyzed Polychelates of CA (Pyrolyzed at 530-60°C):

The polychelates of CA were pyrolyzed at 530-60°C under continuous evacuation. During pyrolysis, evolution of water and hydrochloric acid was observed. The residual products were washed, dried and analysed. The magnetic moment and IR spectral bands of these products are presented in tables III.1(g) and (h). Solid state electrical conductivity of these products could not be determined as they could not be obtained in pellet form.

(a) CoCA(PH):

The product, on analysis, indicates a ratio of metal-to-ligand (C_6) as one-to-one, and is represented as in (VII).

The magnetic moment of the product is calculated as 5.0 B.M. per metal atom. The metal ion is considered 6-covalent, being surrounded by weak octahedral ligand field.

From the IR spectral data of the pyrolyzed polychelate, it is suggested that (i) the product has amorphous character, (ii) the band due to C-Cl group is absent, and (iii) a new band due to C-H group is not observed.

TABLE III 1(g)

Magnetic Moments of Pyrolyzed Polychelates of CA

No	Polychelate	Molar Magnetic susceptibility (per metal ion) X_m x10^6	Molar Corrected magnetic susceptibility (per metal ion) X_m' x 10^6	Magnetic moment (per metal ion) B.M.
1	CoCA(PH)	10032	10103	5.0
2	NiCA(PH)	4406	4462	3.3
3	CuCA(PH)	1228	1270	1.8
4	MnCA(PH)	14277	14338	5.9
5	*FeCA(PH)	17678	17710	6.6
6	*PbCA(PH)	2663	2814	2.6

TABLE III.1(h)

Some characteristic IR frequencies (cm^{-1}) of CoCA(PH), NiCA(PH), CuCA(PH), MnCA(PH), FeCA(PH) and PbCA(PH)

(i) CoCA(PH)

3540 s	3400 m	2905 w	1970 w(b)
1680 (sh)	1640 m(b)	1530 w(b)	1420 w
1350 w(b)	1290 w(b)	955 m	940 m
790 m	770 (sh)	725 m	680 w(b)
590 w(b)	540 w		

(ii) NiCA(PH)

3340 s	1980 w	1610 s	1500 s(b)
1380 s	1300 w(b)	1240 w	850 m
810 m	770 m	725 m(b)	690 m(b)
645 m	590 w		

(iii) CuCA(PH)

3440 s	3360 s	1980 w(b)	1600 m
1340 m	1260 m(b)	975 w	910 w(b)
845 w	780 w	725 w	645 w
590 w	475 w	440 w	

TABLE III.1(h) (continued)

(iv) MnCA(PH)

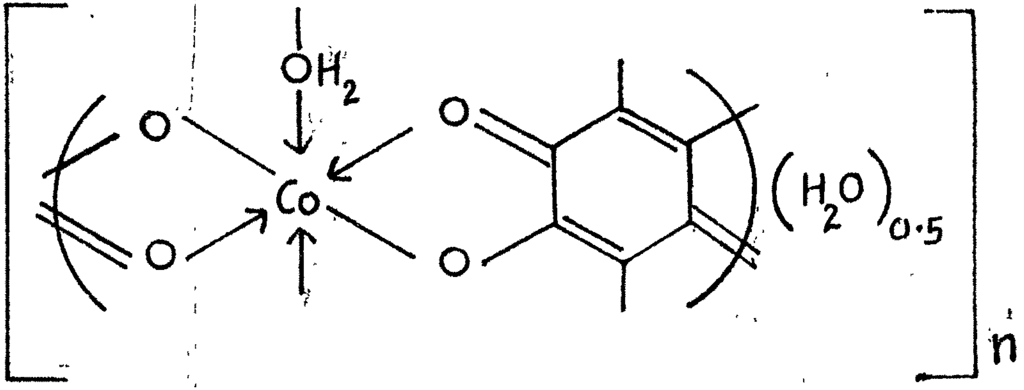
3420 s(b)	1610 s	1570 m	1500 s
1370 m	1320 w(b)	1290 w(b)	1220 w(b)
1160 w(b)	1100 w(b)	990 w	840 m
815 w	640 m	590 m	475 w
390 w			

(v) FeCA(PH)

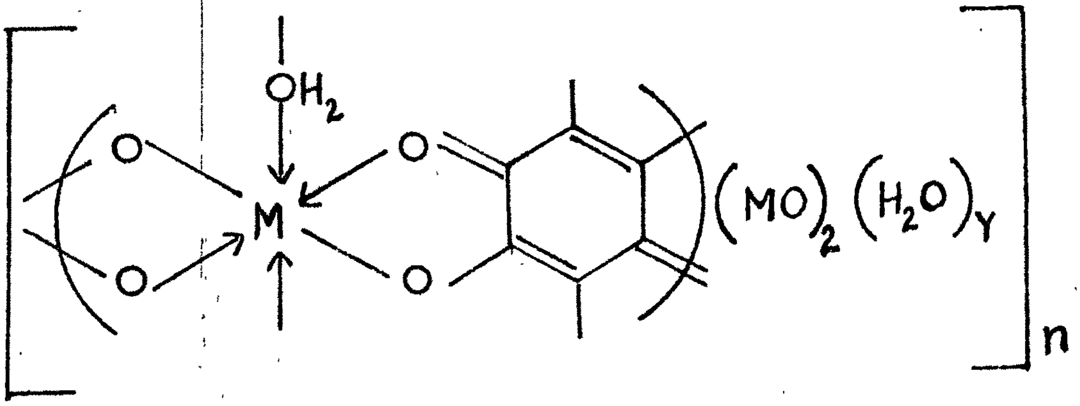
3390 w(b)	1990 m	1590 m(b)	1430 w(b)
1360 w(b)	1280 w(b)	760 w	645 m
590 m	480 w	460 w	410 w(b)
370 m			

(vi) PbCA(PH)

3560 s	3460 s	1970 m	1565 s
1350 m(b)	620 m	565 m	480 m
375 m			



(VII)



(VIII)

	M =	Y =
(i)	Ni	6
(ii)	Fe	0

(b) NiCA(PH):

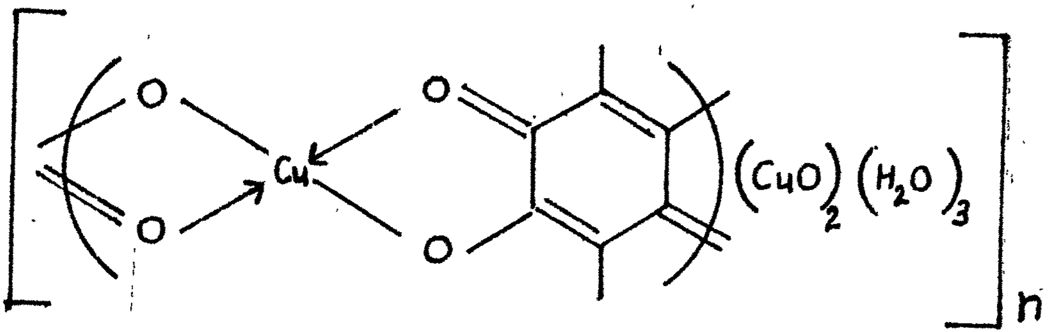
The product, on analysis, indicates a ratio of metal-to-ligand (C_6) as three-to-one, and is represented as in (VIII). The magnetic moment of the product is calculated as 3.3 B.M. per metal atom. If the ligand is considered to provide square planar crystal field around one metal ion, the remaining two sites of the octahedral field around the ion can be associated to O-atoms.

From the IR spectral data of the pyrolyzed product, it is suggested that (i) the band due to C-Cl group is absent, and (ii) a new band due to C-H group is not observed. The fine structure of the spectrum observed in case of NiCA is lost on pyrolysis; however, the three-band pattern is maintained.

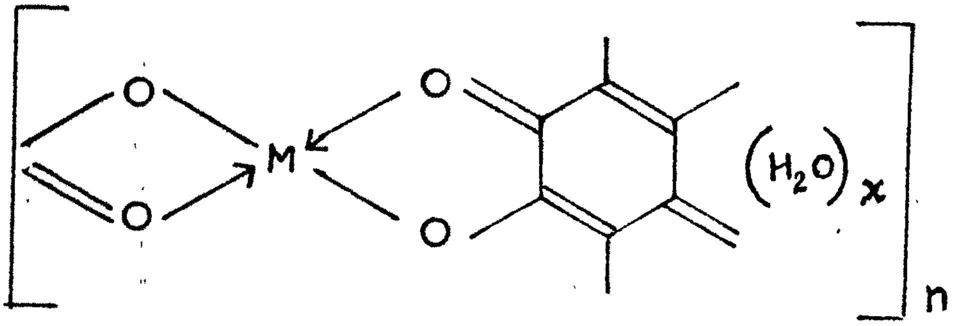
(c) CuCA(PH):

The product, on analysis, indicates a ratio of metal-to-ligand (C_6) as three-to-one and is represented as in (IX). The magnetic moment of the product is calculated as 1.8 B.M. per metal atom. The ligand is considered to provide square planar crystal field around the metal ion.

From the IR spectral data of the pyrolyzed product, it is suggested that (i) the band due to C-Cl group is

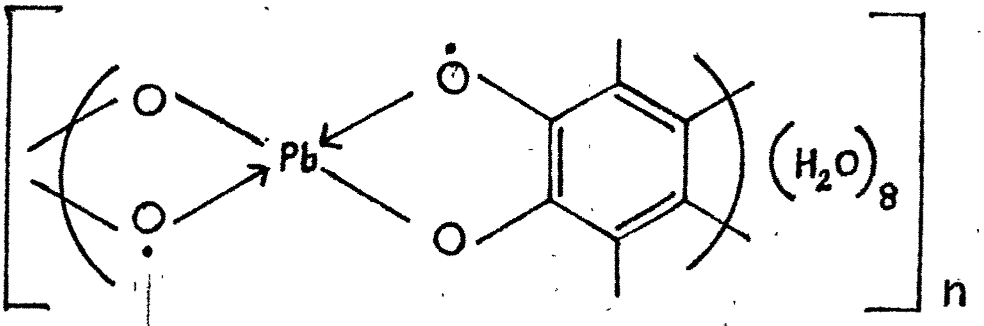


(IX)



(X)

	M	x
(i)	Mn	0·5
(ii)	Pb	8



(XI)

absent and (ii) a new band attributable to C-H group is not observed. Further the bands attributable to Cu-O bond in copper oxide are not observed.

(d) FeCA(PH):

The product, on analysis, gives a ratio of metal-to-ligand (C_6) as three-to-one and is represented as in (VIII). The magnetic moment of the product is calculated as 6.6 B.M. per metal atom. The ligand is considered to provide square planar crystal field around one metal ion. Ferromagnetic interactions may be expected to exist between different iron atoms.

From the IR spectral data of the pyrolyzed product, it is suggested that (i) the band attributable to C-Cl group is absent and (ii) a new band attributable to C-H is not observed. The spectrum is indicative of amorphous nature of the product.

(e) MnCA(PH):

The product, on analysis, gives a ratio of metal-to-ligand (C_6) as one-to-one and is represented as in (X). The magnetic moment of the product is calculated as 5.9 B.M. per metal atom. The ligand is considered to provide weak square planar crystal field around the metal ion.

From the IR spectral data of the pyrolyzed product, it is suggested that (i) the band attributable to C-Cl group is absent and (ii) a new band attributable to C-H is not observed. The spectrum is a structured one.

(f) PbCA(PH):

The product, on analysis, indicates a ratio of metal-to-ligand (C_6) as one-to-one and is represented as in (X). The magnetic moment of the product is calculated as 2.6 B.M. per metal atom. It indicates the formation of a stabilized biradical as in (XI).

From the IR Spectral data of the pyrolyzed product, it is suggested that (i) the band due to C-Cl group is absent and (ii) a new band attributable to C-H is not observed. Further the spectrum seems to have changed to benzenoid structure from quinonoid structure.

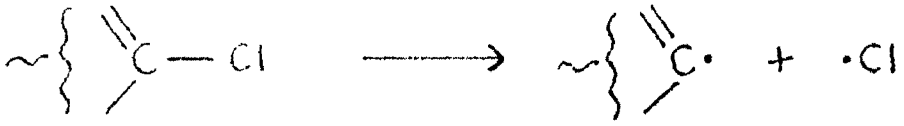
(g) General Considerations: MCA(PH):

When coking coals are pyrolyzed, polynuclear quinone-type compounds are considered to be formed (180,181,182). Garten and Weiss (183) proposed the presence of polynuclear quinonoid structures in H-carbons to explain their behaviour as an O-electrode in alkaline solutions.

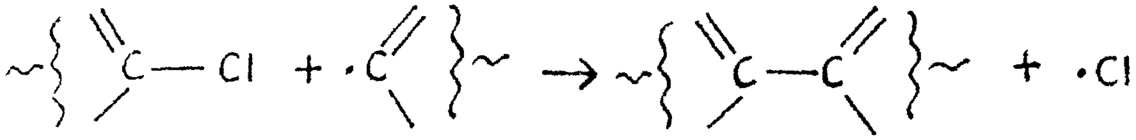
It has been observed from the present studies that the polychelates of chloranilic acid undergo dechlorination on pyrolysis under continuous evacuation. Formation of free radicals may be suggested as in E (i). The active centres may propagate the reaction leading to cross-polymerisation as in E (ii) and (iii). Cross-polymerisation may also result from the recombination reaction as in E (iv).

Presence of moisture can lead to termination reaction for the active site in a chain, as in E (v). The reaction E (v) will lead to the formation of metal polychelates of 2,5-dihydroxy p-benzoquinone, which in specific cases (M=Ni, Cu, Fe), may be considered to undergo hydrolysis forming basic polychelates and releasing 2,5-dihydroxy p-benzoquinone (BQ). The last product (BQ) is obtained as a sublimate on the wall of the tube during pyrolysis. (This reaction is not considered to take place to any appreciable extent in the case of polychelates of Co, Mn and Pb).

The pyrolysis, thus, may involve depolymerisation eliminating modified ligand monomer and cross-polymerisation extending cross-conjugation. The relative occurrence of depolymerisation and cross-polymerisation in the pyrolysis of copper, nickel and iron polychelates is two-to-one.

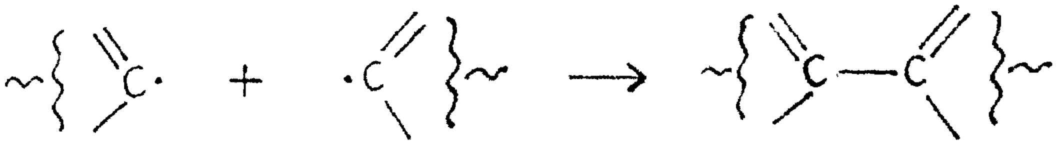


E(i)

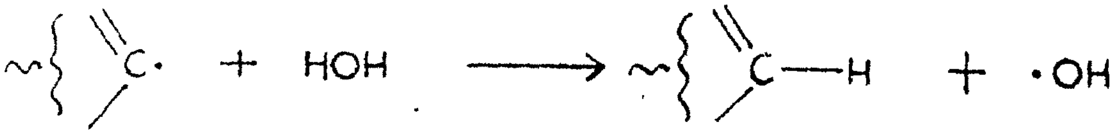


E(ii)

E(iii)



E(iv)

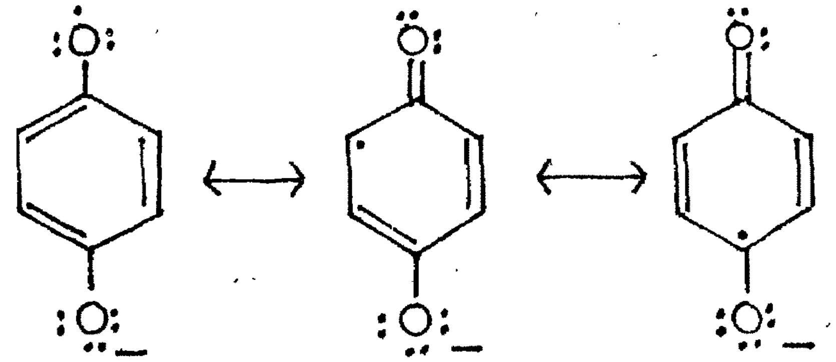


E(v)

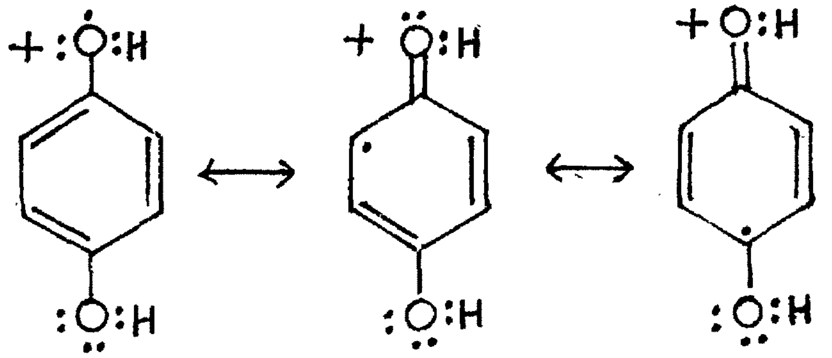
The comparison of the IR spectra of MCA and MCA(PH) suggests that a band observed in 2000 to 1800 cm^{-1} region in the spectra of NiCA and MnCA is not observed in the spectra of NiCA(PH) and MnCA(PH).

The magnetic studies of PbCA, PbCA(PL) and PbCA(PH) produced some unusual and interesting results. Although PbCA is diamagnetic, PbCA(PL) has a magnetic moment of 2.1 B.M. per metal atom and PbCA(PH) has a magnetic moment of 2.6 B.M. per metal atom. These results indicate the presence of unpaired electrons in the pyrolyzed products and can be related to the radical formation and trapping in the solid state. Studies on Pb^{2+} doped meta phosphate glass showed that (i) an optical absorption is developed on irradiation by high energy radiation, (ii) new ill-defined absorption in UV region is observed on X-ray irradiation, and (iii) comparing ESR spectra of irradiated glasses with and without Pb^{2+} shows that the electron signal has disappeared (184). These results suggest Pb^{2+} affects the colouration by trapping electrons and undergoing reduction to Pb^{+}. This conclusion is supported by recent experiments (185, 186) which also indicate the possibility of Pb^{0}.

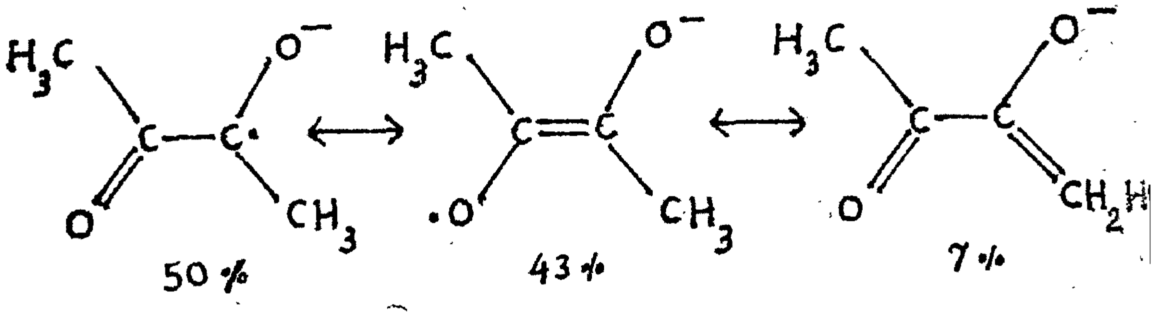
The formation of organic radicals in the pyrolyzed products is also a possibility. Formation of p-benzo semiquinone anion (XII) or diprotonated p-benzo semiquinone



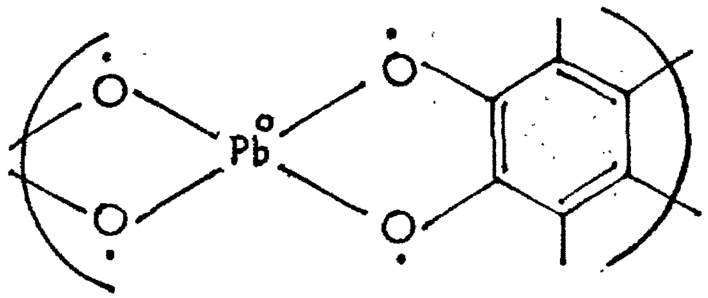
(XII)



(XIII)



(XIV)



(XV)

anion (XIII) has been well established in p-benzoquinone system (187 to 190). The preferred route to semi-dione is through alpha-hydroxy ketone (191). Treatment of 1,3-dihydroxy acetone with base and air yields a radical now recognised as 2,5-dihydroxy-p-benzo semiquinone. The bi-acetyl radical anion is suggested to have various ketyl type structures as in (XIV) (192).

In the present studies 2,5-dihydroxy-p-benzoquinone unit can be considered to be transformed on pyrolysis in presence of lead into (i) radical trianion (ii) bis-biradical or (iii) biradical dianion. The trianion cannot be formed as it would involve the oxidation of lead to trivalent state. The formation of bis-biradical can take place by oxidation with simultaneous reduction of lead(II) to lead (0) (XV). The formation of biradical dianion is suggested in (XI). The magnetic moment of the product favours (XI) which will be resonance-stabilised. It needs confirmation from EPR studies.

The high magnetic moment of FeCA(PH) may now be attributed nnt only to the ferromagnetic interactions between iron atoms but also to the free-radical nature of the ligand and its magnetic interactions with iron atoms.

The cross-polymerisation through quinonoid rings of different linear polymeric chains brings about ordered orientation of two-dimensional net-works formed, favouring coplanarity of linked rings. The pyrolysis therefore, would increase the electrical conductivity of the polymer on the basis of increased conjugation and coplanarity and decrease the energy gap for conduction on the basis of reduced energy barriers. Attempts were made to prepare pellets of the pyrolyzed products under different conditions. However, a pellet believed to be formed on compression, increased in its volume on the release of pressure and turned into powder on handling. Attempts to use a suitable binding material for pelletizing also failed.

III. 2 Polychelates of 3,3'-diacetyl 4,4'-dihydroxy diphenyl sulphone (DAS) and their pyrolysis:

(i) General: Polychelates of bis (O-acyl phenol):

Terentev and co-workers (106,107) and Marvel and Tarkoy (108) studied thermal stability, reflectance and luminescence spectra and magnetic moment of the polychelates of copper, nickel, cobalt and iron with 3,3'-diformyl 4,4'-dihydroxy diphenyl methane and its Schiff bases and hydrazone. Goodwin and Bailar (Jr) (193) studied the polychelates of copper, nickel, cobalt and iron with Schiff bases and hydrazones of 3,3'-diformyl 4,4'-dihydroxy diphenyl methane and of 3,3'-diformyl 4,4'-dihydroxy diphenyl sulphone. Belskii and Tsikunov (194) studied EPR spectra of the polychelates of iron, cobalt, copper, zinc and cadmium with the Schiff bases and hydrazone of 3,3'-diformyl 4-4'-dihydroxy diphenyl methane. Kapadia (109) studied the the polychelates of copper, nickel and cobalt with salicylaldehyde coupled with tetrazotised benzidine.

(ii) Polychelates of DAS:

Polychelates of DAS with cobalt(II) nickel(II) and copper(II) have been prepared in presence of ammonia and the results of the studies are presented and discussed below.

The magnetic moment, electrical conductivity, IR spectral bands, DTA peaks and TG weight loss of these polychelates are presented in tables III.2(a) to (e).

The ratio of metal to ligand is found from the analysis of these polychelates as one-to-one. They are represented as a linear polymeric chain (XVI).

(a) CoDAS:

The magnetic moment of CoDAS is calculated as 5.1 B.M per metal atom. The metal is considered to be 6-covalent with octahedral ligand field. O-atoms of the ligand

TABLE III. 2(a)

Magnetic Moment of Polychelates of DAS

No	Polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X'_{M'} \times 10^6$	Magnetic moment (per metal ion) B.M.
1	CoDAS	10623	10841	5.1
2	NiDAS	5606	5823	3.8
3	CuDAS	1564	1781	2.1

TABLE III.2(b)

Solid State Electrical Resistivity of Polychelates of DAS

No	Polychelate	Temperature (°C)	Resistivity (ohm cm)x10^{-10}	Conductivity (ohm^{-1} cm^{-1})x10^{13}
1	CoDAS	33	0.3253	3070
2	NiDAS	33	3.521	284
3	CuDAS	33	0.7557	1320

TABLE III.2(c)

Some characteristic IR frequencies (cm^{-1}) of CoDAS

3400 s	3100 (sh)	2900 m	2200 w
1640 s	1560 w	1520 m	1505 m
1470 m	1380 m	1330 m	1240 w
1190 s	1170 m	1150 w	1130 w
1115 w	980 m	925 m	880 w
840 w	810 w	775 m	705 m

TABLE III 2(d)

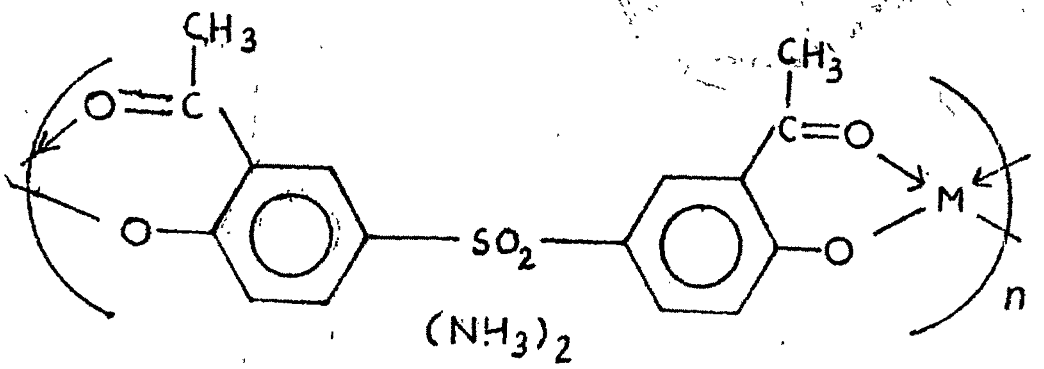
Endothermic and Exothermic Peaks in DTA Study of Polycheates of DAS

No	Polychelates	Endothermic $\frac{\text{peak temp (°C)}}{\text{onset temp(°C)}}$	Remark
1	CoDAS	1) $\frac{145}{140}$ (2) $\frac{305}{285}$ (3) $\frac{425}{420}$	second order changes
2	NiDAS	(1) $\frac{160}{155}$ (2) $\frac{185}{175}$ (3) $\frac{465}{440}$	-
3	CuDAS	(1) $\frac{180}{175}$ (2) $\frac{332}{327}$	second order changes

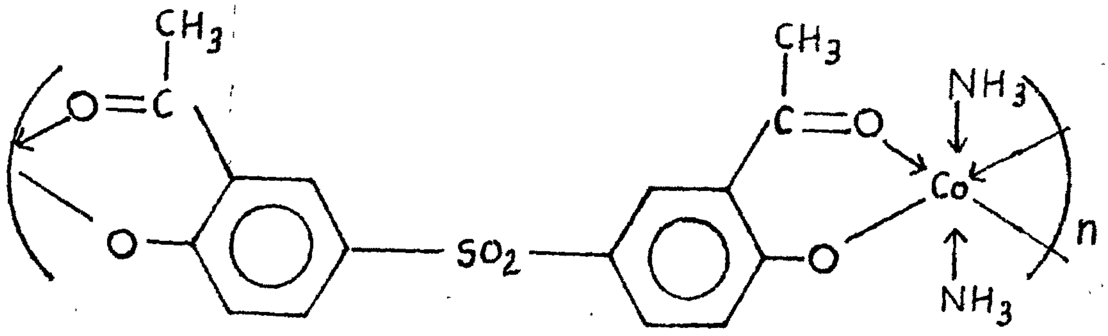
TABLE III. 2(e)

TG weight losses of the polychelates

No	Polychelate	Temperature range	% Weight loss
1	CoDAS	110-340	21
		370-392	1.5
		* 392-405	24
2	NiDAS	320-412	5
		* 412-430	57
3	CuDAS	160-330	5
		* 3 30-348	50



(XVI) M = Cu, Ni, Co



(XVII)

molecules and metal ions are considered to be in the same plane. It is suggested that monomeric chelate has trans octahedral configuration with coordinated ammonia molecules as shown in (XVII). The solid state conductivity of the polychelate is 3.07×10^{-10} ohm^{-1} cm^{-1}.

From the IR spectral data of the polychelate, it is suggested that (i) the band at 3400 cm^{-1} be attributed to weakly coordinated N-H bonds, (ii) the band at 1640 cm^{-1} be attributed to coordinated CO groups, (iii) the bands at 1330 cm^{-1} and 1170 cm^{-1} be attributed to SO_2 group (iv) the bands at 1380 cm^{-1} and 1470 cm^{-1} be attributed to CH_3group. (v) the band at 1115 cm^{-1} be attributed to Ph.S bond and (vi) the bands at 775 cm^{-1} and 705 cm^{-1} be attributed to 1,2,4 trisubstituted phenyl ring.

Endothermic DTA peaks at 145°C, 305°C and 425°C indicate both phase transitions and decomposition reactions. Second order changes are also considered to take place. TG weight losses indicate loss of ammonia and sulphur dioxide, upto a temperature of 392°C and above this temperature complex oxidation reactions are considered to occur.

(b) NiDAS and CuDAS:

The magnetic moment of NiDAS and CuDAS has been calculated as 3.8 and 2.1 B.M. per metal ion respectively.

The results indicate tetrahedral and square planer nature of monomeric NiDAS and CuDAS respectively.

Endothermic DTA peaks are at (i) 160°C, 185°C and 465°C for NiDAS and (ii) 180°C and 332°C for CuDAS. The results are indicative of phase transitions and decomposition reactions. TG weight losses indicate loss of ammonia molecules upto 412°C for NiDAS and upto 330°C for CuDAS. Above these temperatures, compounds undergo complex oxidation reactions.

Further, for DTA peaks at 160°C and 185°C for NiDAS, there is no corresponding weight loss in this temperature range in its TGA studies. Mesophases may be considered a possibility in these phase transitions.

(c) General considerations:

All the polychelates under study contain ammonia; however, in case of CoDAS, two ammonia molecules are considered to be coordinated to a cobalt ion, whereas in case of NiDAS and CuDAS, two ammonia molecules present per metal atom are considered to be in the lattice.

Further, magnetic studies indicate a different stereochemical arrangement of ligand fields for cobalt and nickel. The degree of coplanarity of the chelate molecule is lower for NiDAS (tetrahedral) than for CoDAS (octahedral) and can explain lower value of electrical conductivity of NiDAS than of CoDAS.

Thermoanalytical studies show that in all three cases there is loss of ammonia on heating. Loss of sulphur dioxide is a possibility on heating upto 330°C in case of CoDAS but not in case of NiDAS or CuDAS, thereby indicating that the thermal stabilization of the ligand is greater in NiDAS and CuDAS than in CoDAS. Results also show that the degradation/oxidation reactions are all endothermic.

(iii) Pyrolyzed Polychelates of DAS:

The polychelates of DAS were pyrolyzed at 410-30°C under continuous evacuation. During pyrolysis, evolution of ammonia was observed. The residual products were washed, dried and analysed. The magnetic moments and IR spectral bands of some of these products are presented in tables III.2(f) and (g). Solid state electrical conductivity of these products could not be determined as they could not be obtained in pellet form.

(a) CoDAS(P):

The product on analysis, indicates a ratio of metal-to-ligand (C_{16}) as one-to-one. The magnetic moment of the product is calculated as 5.1 B.M. per metal atom. The metal

TABLE III.2(f)

Magnetic Moments of Pyrolyzed Polychelates of DAS

No	Polychelate	Molar maggetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X_M' \times 10^6$	Mangetic moment (per metal ion) B.M.
1	CoDAS(P)	10253	10436	5.1
2	NiDAS(P)	5006	5184	3.6
3	CuDAS(P)	1949	2117	2.3

TABLE III. 2(g)

Some characteristic IR frequencies (cm^{-1})
of CoDAS(P)

3400 m(b)	2910 s	2850 m	2350 w
1590 m	1550 (sh)	1530 (sh)	1440 m
1370 w	1290 w	1215 w	1115 w(b)

ion is considered 6-covalent, being surrounded by weak octahedral ligand field. From the IR spectral data, it is suggested that (i) the broad band at 3400 cm^{-1} be attributed to water and ammonia molecules in the product (ii) the bands at 775 cm^{-1} and 705 cm^{-1}, attributed to trisubstituted phenyl ring in CoDAS are not observed, (iii) the band at 1115 cm^{-1} be attributed to Ph.S bond (iv) the band at 1590 cm^{-1} be attributed to coordinated CO group, and (v) the band at 1370 cm^{-1} be attributed to CH_3 + SO_2 groups. The spectrum indicates amorphous nature of the product.

(b) NiDAS(P) and CuDAS(P):

The products, on analysis, give a ratio of metal-to-ligand (C_{16}) as one-to-one. The magnetic moment is calculated as 3.6 B.M. per metal atom for NiDAS(P) and 2.3 B.M. per metal atom for CuDAS(P). The results indicate tetrahedral and square planar nature of the crystal field around nickel and copper ions respectively.

(c) General Considerations:

The IR spectral data of CoDAS(P) indicate that the phenyl rings are highly substituted. To understand this, the ligand was pyrolyzed under continuous evacuation, analysed and studied for its reactions. It was observed that (i) the product gives reactions for phenolic and acetyl groups and (ii) hydrogen content is reduced by four hydrogen atoms per ligand molecule. Hence it is suggested that the ligand is dimerised with the abstraction of hydrogen atoms in its pyrolyzed polychelates as in (XVIII).

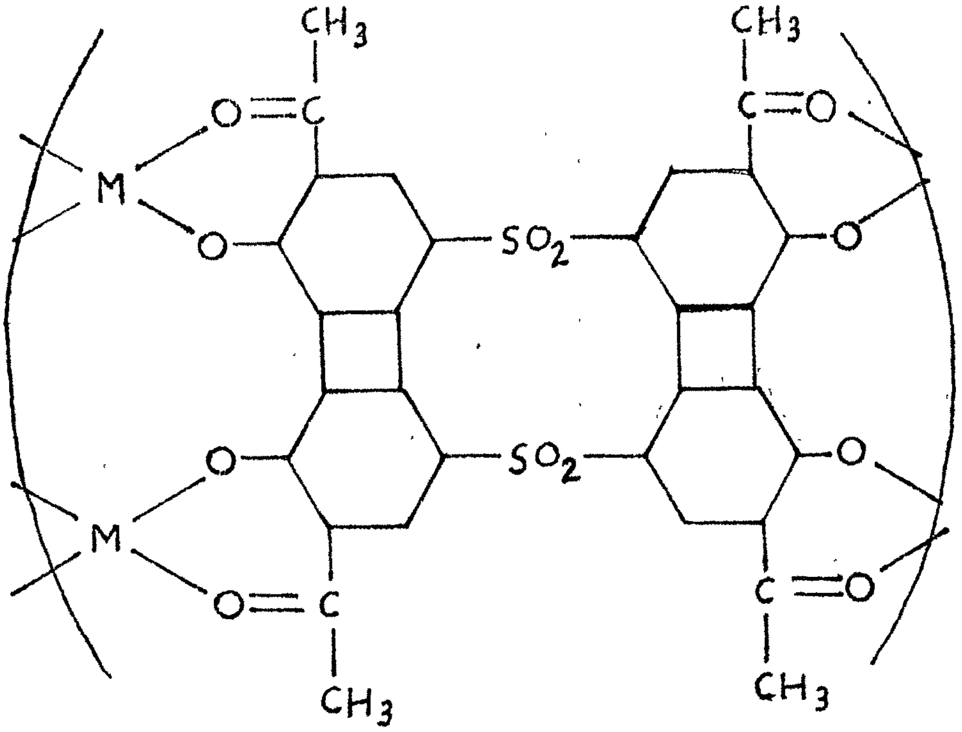
Pyrolysis, thus, is considered to involve loss of ammonia and abstraction of hydrogen by the radical mechanism. The formation of free radical may be suggested as in E(vi). The cyclized product may be formed through propagation and recombination reactions as in E(vii) to (x). (Involvement of CH_3 group at some stages of radical mechanism of reaction may be a possibility).

It has been observed recently (195) that carbon-carbon bond formation takes place on sulphone-pyrolysis. However, in the present studies it is observed that carbon-carbon bond formation is not associated with the loss of SO_2 or the breaking of C-S bond.

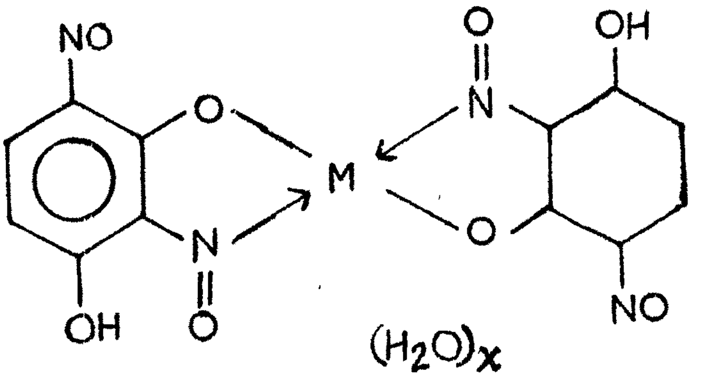
III.3 Polychelates of dinitroso resorcinol and their pyrolysis:

(i) General: Chelates of dinitroso resorcinol (DNR):

Issa et al (196) suggested from spectrophotometric studies that palladium(II) forms three complexes with dinitroso resorcinol (DNR) with Pd-to-DNR ratio as

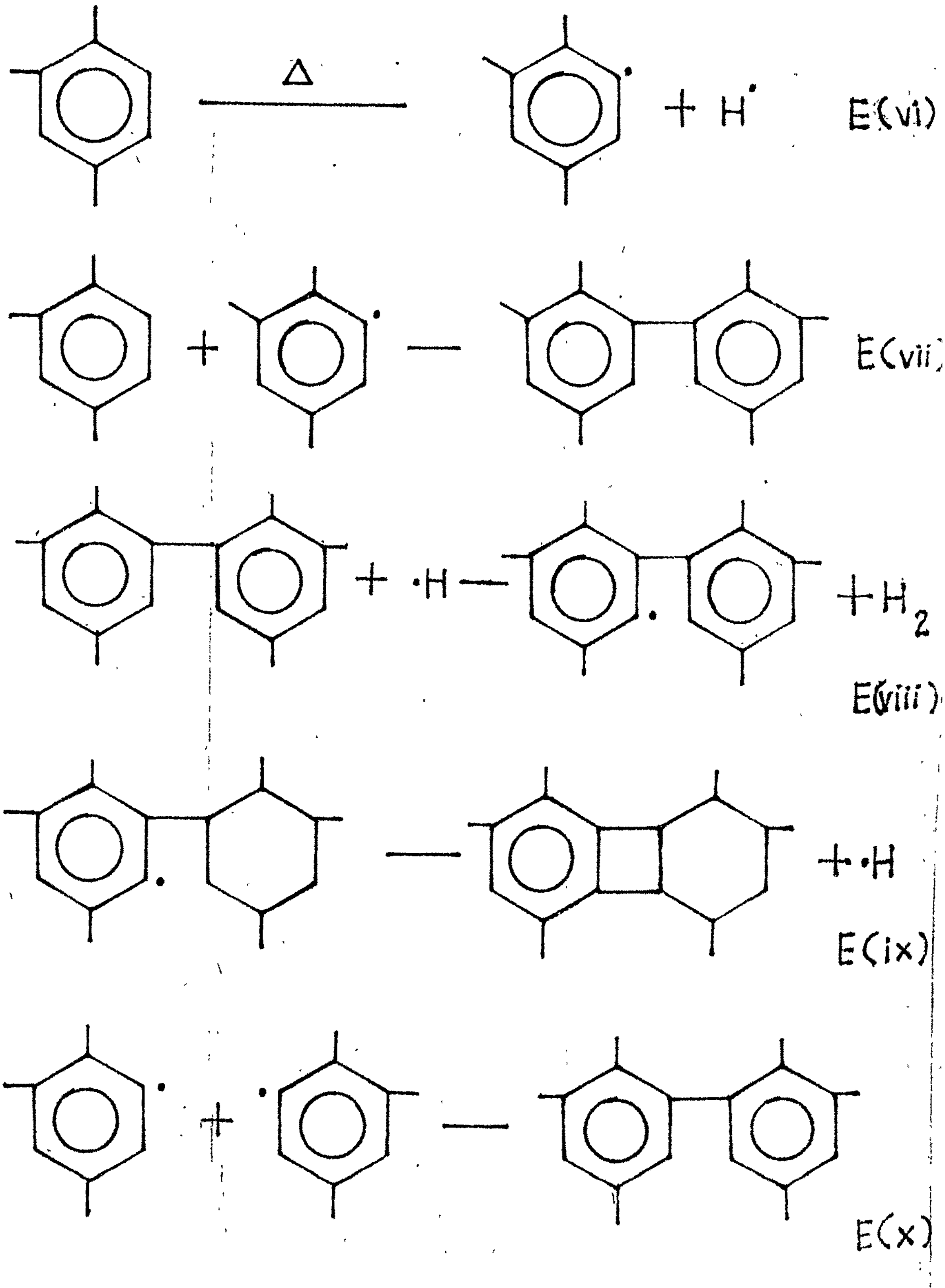


(XVIII)



(XIX)

	M =	x =
(i)	Fe	1
(ii)	Pb	0


Δ
+ H˙
E(vi)
+
E(vii)
+ ·H
+H2
E(viii)
+·H
E(ix)
+
E(x)

two-to-three, one-to-one and one-to-two. Bottie and McEachern (197) prepared copper(II), nickel(II) cobalt(II) zinc(II), lead(II), cadmium(II) and mercury(II) chelates of DNR and studied their thermal and spectral characteristics. Zayan et al (198,199) used DNR for the spectrophotometric micro determination of copper(II) and iron(II) and suggested the formation of three complexes of copper(II) with DNR with Cu-to-DNR ratio as two-to-one, one-to-one and one-to-two. Shebaldov (200) obtained a linear coordination polymer of palladium(II) with DNR with the ratio of Pd-to-DNR as one-to-one and studied its catalytic activity. Masoud et al (201) prepared copper, nickel, cobalt, iron and zinc chelates of DNR and studied their magnetic and spectral properties. Masoud et al (202) also studied the solvent extraction of metal-DNR complexes. Peshkova and co-workers (203,204) studied the in-situ formation of copper, nickel and cobalt complexes of DNR using resorcinol and nitrite ion.

(ii) Chelates of DNR:

Chelates of DNR with cobalt(II), nickel(II) copper(II) iron(II) and lead(II) have been prepared and their studies are presented below.

The magnetic moment, electrical conductivity, IR spectral bands and TG weight loss of these chelates are presented in tables III.3 (a) to (d).

TABLE III.3(a)

Magnetic Moments of Polychelates of DNR

No	Polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X_M' \times 10^6$	Magnetic moment (per metal ion) B.M.
1	CoDNR	1433	1509	1.9
2	NiDNR	3790	3887	3.1
3	CuDNR	Diam	Diam	Diam
4	FeDNR	8116	8252	4.5
5	PbDNR	Diam	Diam	Diam

TABLE III.3 (b)

Solid State Electrical Resistivity of Polychelates of DNR

No	Polychelate	Temperature (°C)	Resistivity ϱ (ohm-cm) $\times 10^{-10}$	Conductivity σ ($ohm^{-1} cm^{-1}$) $\times 10^{13}$
1	CoDNR	28	8.0	125
2	NiDNR	28	80.8	12.4
3	CuDNR	28	313.5	3.19
4	FeDNR	28	8.58	117
5	PbDNR	28	270.8	3.69

TABLE III.3(c)

Some characteristic IR frequencies (Cm^{-1}) of DNR, CuDNR, CoDNR and PbDNR

(i) DNR

3500 s	3400 s	3150 s	2960 w
2800 m	2740 m	2675 m	2040 w
1990 w	1680 (sh)	1650 s	1590 s
1530 w	1480 m	1385 s	1360 (sh)
1300 w	1270 w	1200 m	1120 m
1090 w	1020 s	960 s	900 w
840 m	780 m	720 w	650 w

(ii) CuDNR

3425 s(b)	3350	2920 m	2850 m
2300 w	1580 s	1530 m	1460 m
1440 m	1390 s	1340 (sh)	1260 m
1150 m	1040 m	960 (sh)	820 m
670 m	630 w		

TABLE III. 3(c) (continued)

(iii) CoDNR

3450 s(b)	3075 s	2900 m	1620 (sh)
1565 s	1500 m	1430 (sh)	1375 s
1340 s	1280 (sh)	1060 w	810 m
690 m	650 m		

(iv) PbDNR

3480 m (?)	3260 m	3220 m	3080 s
2960 (sh)	2480 w	1620 m	1580 s
1510 m	1410 s	1380 (sh)	1340 s
1270 s	1250 m	1110 m	1070 m
930 s	840 m	790 w	740 m
710 m			

TABLE III.3(d)

TG weight loss of chelates of DNR

No	Chelate	Temperature range (°C)	% weight loss
1	CoDNR	100-260	15
		260-375	38
		375-380	27
2	NiDNR	85 -175	8
		180-285	9
		285-370	21
		400-500	17
3	CuDNR	175-280	12
		290-292	81
4	FeDNR	140-325	32
		335-350	35

The ratio of metal-to-ligand in case of FeDNR and PbDNR is one-to-two and the compounds are represented as non-polymeric chelates as in (XIX). The ratio of metal-to-ligand in case of CoDNR, NiDNR and CuDNR is one-to-one and they are represented as linear polymeric chain (XX). This is in analogy with chelates of o-nitroso phenols wherein coordination is believed through nitrogen of nitroso group.

(a) <u>CoDNR</u>:

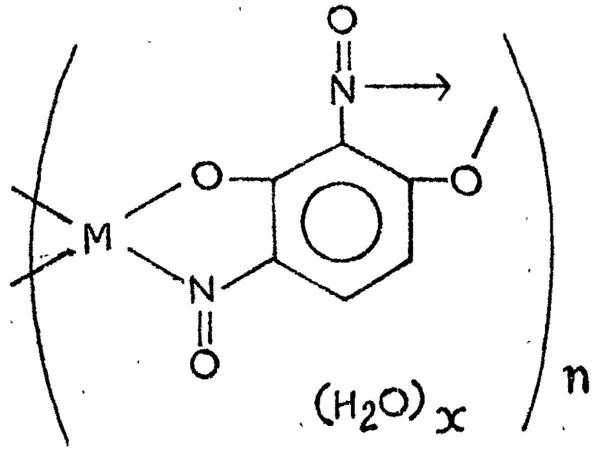
The magnetic moment of CoDNR is calculated as 1.9 B.M. per metal atom. It is suggested that cobalt ion is 5-covalent, being surrounded by square pyramidal crystal field. The solid state electrical conductivity is 0.125×10^{-10} ohm^{-1} cm^{-1} at room temperature.

It is suggested from its IR spectral data that (i) broad band at 3450 cm^{-1} be attributed to water present in the chelate and (ii) bands attributable to free phenolic groups are not observed.

TG weight loss upto 260°C indicates loss of water and above this temperature complex oxidative decomposition reactions are considered to take place.

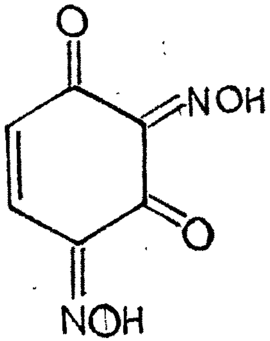
(b) <u>NiDNR</u>:

The magnetic moment of NiDNR is calculated as 3.1 B.M. per metal atom. It is suggested that nickel ion

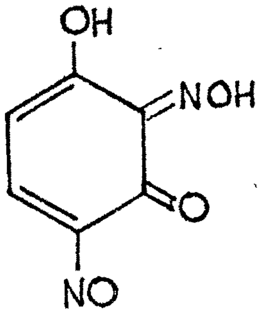


(XX)

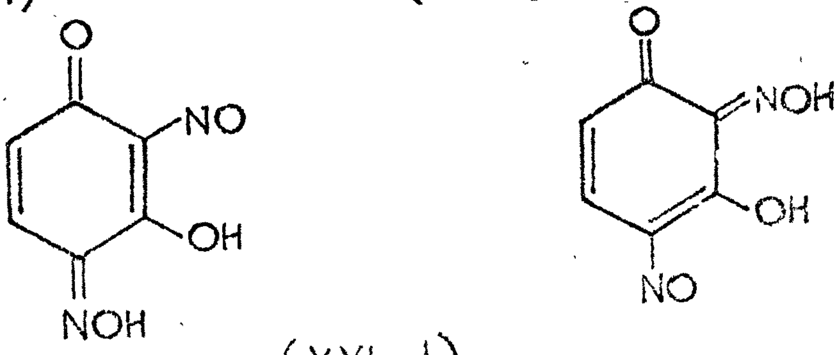
	M	x
(i)	Co	1
(ii)	Ni	3
(iii)	Cu	3



(XXI)



(XXI-a)



(XXI-b)

is 6-covalent, being surrounded by octahedral crystal field. Two water molecules may be considered coordinated to metal ion in monomeric chelate.

TG weight losses upto 285°C indicate loss of water and above this temperature oxidative decomposition reactions occur.

(c) CuDNR:

The magnetic moment studies of CuDNR show that it is diamagnetic. Diamagnetic complexes of copper have been observed for various ligands, wherein Cu-Cu interaction would be considered.

From its IR spectral data, it is suggested that (i) the broad band at 3425 cm^{-1} be attributed to water present in the chelate and (ii) no bands attributable to free phenolic groups are observed.

TG weight losses indicate loss of water upto 280°C and above this temperature, decomposition is vigorous and explosive.

(d) PbDNR and FeDNR :

PbDNR is diamagnetic as anticipated. From its IR spectrum, it is suggested that no water is present in the chelate.

The magnetic moment of FeDNR is calculated as 4.5 B.M. per metal atom. TG weight losses indicate decomposition reactions.

(e) General Considerations:

Bottei and McEachern (197) observed that when metal chelates were heated at a rate of 5°C per minute in nitrogen, they exploded. Their relative thermal stability (observed from TGA) was decreasing in order Ni $>$ Cd $>$ Zn $\sim$ Co $>$ Cu $\sim$ Hg $>$ Pb. They attributed IR spectral bands at 3520 cm^{-1} and 3400 cm^{-1} for DNR to oxime and hydrogen-bonded phenolic group respectively. They concluded from mass spectrometric studies that (i) chelates of nickel and zinc did not explode when heated under vacuum in the oil-bath, (ii) gaseous products consist mainly of carbon dioxide, (iii) no NO or NO_2 was detected and (iv) a trace of benzene was detected in the pyrolysis gases of NiDNR.

It is observed that DNR provides strong crystal field to (i) cobalt ion leading to electron-spin-pairing in the ion, (ii) copper ion leading to electron-spin-pairing in the ion pair or ion-cluster and (iii) iron ion leading to some electron-spin-pairing in the ion or ion-cluster. The ligand which melts at 152°C is stabilised by complex formation with metal ions. From the total weight loss observed in TGA studies, the relative stability of the chelates is considered decreasing in the order NiDNR > FeDNR > CoDNR > CuDNR.

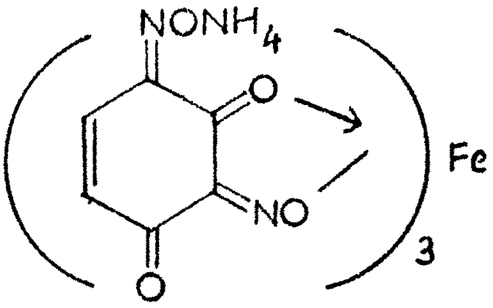
The relative thermal stability on the basis of onset temperature for the first phase of decomposition is decreasing in order CuDNR > FeDNR > CoDNR > NiDNR.

Explosive nature of PbDNR is comparable to that of lead-azide, lead styphnate, lead complex of nitro resorcinol, etc.

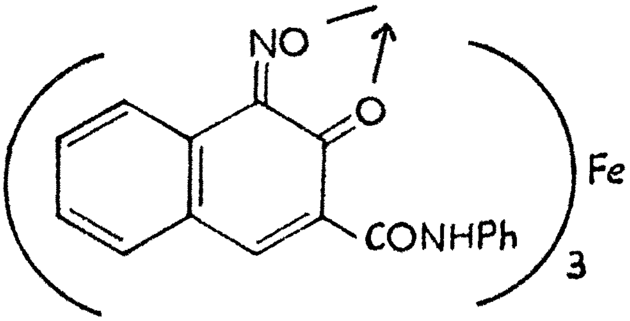
The ligand can be represented as quinone-oxime as in (XXI). IR spectrum of the ligand shows the presence of both oxime and phenolic hydroxyl groups. Hence the ligand may be considered to be a tautomeric mixture of nitroso phenol and quinone-oxime. Morgan and Moss (205) suggested the structure of ferric lake of DNR prepared in presence of ammonia as (XXII-a). Naphthol-AS when heated with ferric salt in presence of nitrous acid formed a chelate (XXII-b) (206). Naphthol green-B (XXII-c) is used for accelerating solar evaporation of water of Dead sea for the manufacture of salts (207).

(iii) <u>Pyrolyzed Polychelates of DNR</u>:

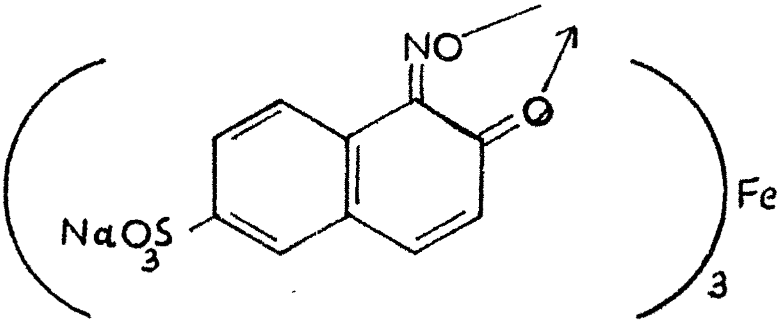
The pyrolysis of polychelates was very difficult to control; the system would often detonate with explosive violence. Hence very small quantities of samples were



(XXII—a)



(XXII—b)



(XXII—c)

used with low rate of heating. The magnetic moments and IR spectral data of some of these products are presented in tables III.3(e) and (f). Solid state electrical conductivity of these products could not be determined.

On the basis of analysis, (i) CoDNR(P) and NiDNR(P) are considered to have the metal-to-ligand (C_6) ratio as one-to-one and are represented as in (XXIII-a,b) and (ii) CuDNR(P) is found to have metal-to-ligand ratio as two-to-one and is represented as (XXIII-c).

(a) CoDNR(P), NiDNR(P) and CuDNR(P):

The magnetic moment of CoDNR(P) and NiDNR(P) are calculated as 4.1 B.M. and 3.7 B.M. per metal ion respectively. It indicates tetrahedral stereochemical nature of cobalt and nickel. Pyrolysis has resulted in weakening and reorientation of the crystal field. IR spectral data of CoDNR(P) indicate the existence of free phenolic group (3560 cm^{-1}).

CuDNR is considered to lose the ligand on pyrolysis increasing metal-to-ligand ratio. However, the pyrolyzed product is still diamagnetic.

(b) General Considerations:

Explosive degradation could be avoided in the above cases by adjusting the conditions of pyrolysis after repeate

TABLE III3(e)

Magnetic Moments of Pyrolyzed Polychelates of DNR

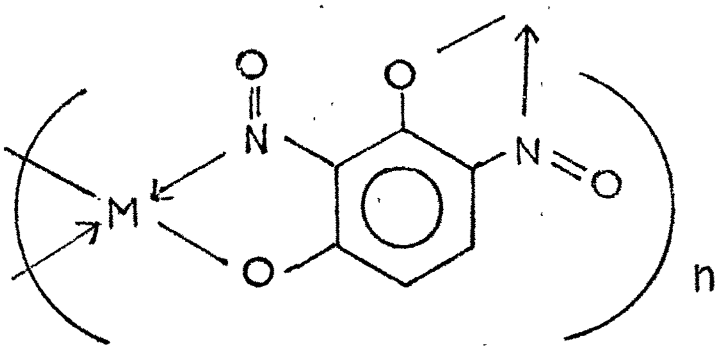
No	Polychelate	Molar Magnetic Susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X_M' \times 10^6$	Magnetic moment (per metal ion) B.M.
1	CoDNR(P)	6688	6767	4.1
2	NiDNR(P)	5568	5646	3.7
3	CuDNR(P)	Diam	Diam	Diam

TABLE III.3(f)

Some characteristic IR frequencies (cm^{-1})
of CoDNR(P)

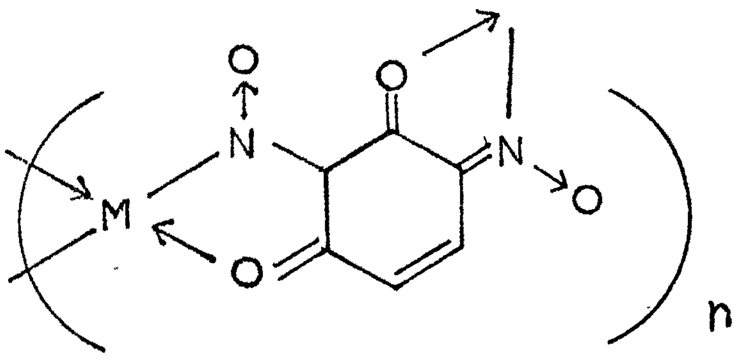
CoDNR(P)

3560 m
2940 m
2920 m
2860 w
1600 s(b)
1380 (sh)
1320 w
840 (sh)
730 w



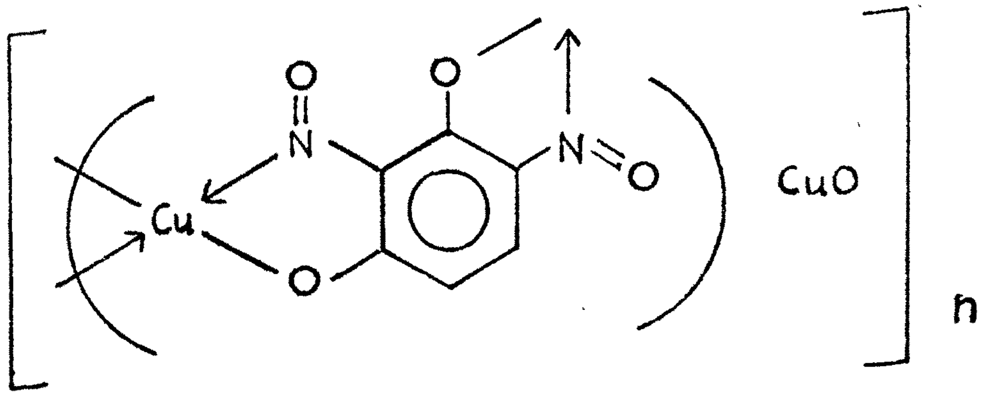
(XXIII-a)

M = Co, Ni



(XXIII-b)

M = Ni, Co



(XXIII-c)

trials. DNR provided a strong crystal field around the metal ion in chelation; the field weakened on pyrolysis. It has resulted in various structural changes. Weakening of the field is considered to have helped the process of degradation. In case of CuDNR, the ligand has separated out in part on pyrolysis indicating depolymerisation. In case of CoDNR(P), the presence of free phenolic groups observed in IR spectrum is an indication of degradation leading to the formation of shorter polymeric chains. In case of CoDNR(P) and NiDNR(P) there is also reorientation of crystal field around metal ion.

PbDNR(P) could not be prepared. It is believed that if it can be prepared, it would exhibit free radical nature.

III.4 Polychelates of azo resorcinols and their pyrolysis:

(i) General:

(a) Chelates of azoresorcinols:

4-(2-pyridyl azo) resorcinol (PAR) has been investigated widely for its chelating characteristics. Spectrophotometric determination of (i) silver, (ii)manganese and (iii) palladium, rhodium and ruthenium with PAR was studied by Eshwar and Subramanyan (208), Yotsuyanagi et al (209) and Kodama and Kodama (210) respectively. Kinetics of the reaction of a nickel complex with PAR was studied by Funahashi and Tanaka (211). Chelate formation of PAR with (i) uranyl, (ii) iron and (iii) titanium was investigated by Sommer et al (212), Nonova and Evlimova, (213) and Lobanov et al (214) respectively. Polarographic studies of PAR with cobalt were made by Toyokichi and Hisao (215).

Chelates of 4-(2-thiazolylazo) resorcinol (TAR) with cobalt and zinc were prepared by Kiryukhina (216) and Navratil et al (217). Analytical determinations of uranium, osmium and ruthenium with TAR were made by Gusev et al (218) and Ivanov et al (219).

Chelates of PAR and TAR with cobalt, nickel, zinc and manganese were studied by Stanley and Cheney (220), Herman and Norman (221) and Busev et al (222).

Two complexes of zirconium with 1-(2,4-dihydroxy benzene azo)2-naphthol-4-sulphonic acid were prepared and the mechanism of formation was studied by Mandzhgalaze and Nazarenko (223). Palladium complex of 4-(N-methyl anabasine 2'-azo) resorcinol was prepared by Talipov and Nigai (224). Chaprasova et al (225) studied the extraction and photometric determination of cobalt chelate with picraminazo-4-cyclohexyl resorcinol.

Planarity of hydroxy-azo compounds and their metal complexes was discussed by Salikhov (226).

(b) Polychelates of azo resorcinols:

Metallised hydroxy-azo compounds have been widely investigated and patented as dyes. Atkinson and Plant (227) prepared iron, copper and nickel chelates obtained by nitrosation and metallisation of aryl azo resorcinols. Kracker, Mohr and Ribka (228) described cobalt, nickel and copper chelates of azo resorcinols and azo dihydroxy benzoic acid. Sailer and Frank (229) patented nitroso azo dye prepared by coupling tetrahydroxy diphenyl methane with diazotised sulphanilic acid and nitrosating it. It gave iron complex with iron (III). Wicki (230) patented one-to-two metal-ligand complexes based on resorcinol coupled with diazotised amino dinitro phenol.

Bauman (231) claimed a series of disazo and polyazo resorcinol dyes by dimerising the azo dye with aldehyde and preparing their metal complexes with iron, cobalt and copper. A number of patents (232 to 234) has been issued claiming diazo couplings with resorcinol and forming their metal complexes.

Tris-azo dyes based on resorcinol coupler and their metallic complexes have been patented (235, 236). Poly azo resorcinol dyes have been prepared either by coupling first and reacting the dye with aldehyde or by coupling with resorcinol aldehyde condensate (237).

(ii) Polychelates of BAR and SAR:

Polychelates of BAR with cobalt(II), nickel(II), copper(II), iron(II), manganese(II) and lead(II) and of

SAR with cobalt(II), nickel(II) and copper(II) have been prepared and the results of the studies are presented and discussed below.

The magnetic moment, electrical conductivity, IR spectral bands, DTA peaks and TG weight loss of these polychelates are presented in tables III.4(a) to (e).

On the basis of analysis, (i) CoBAR is found to have metal-to-ligand (C_{24}) ratio of one-to-one and is represented as (XXIV), (ii) CuBAR, NiBAR, FeBAR and MnBAR are found to have metal-to-ligand (C_{24}) ratio of two-to-one and are represented as (XXV), (iii) PbBAR is found to have metal-to-ligand (C_{24}) ratio of two-to-three and is represented as (XXVI), (iv) CoSAR is found to have metal-to-ligand (C_{26}) ratio of three-to-one and is represented as (XXVII), and (v) NiSAR and CuSAR are found to have metal-to-ligand (C_{26}) ratio of two-to-one and are represented as (XXVIII).

(a) CoBAR:

The magnetic moment of CoBAR is calculated as 5.2 B.M. per metal atom. The metal is considered to be 4-covalent with tetrahedral ligand field. Its solid state electrical conductivity is 6.7×10^{-13} ohm^{-1} cm^{-1} at room temperature.

The endothermic peak at 170°C indicates the possibility of phase transistion associated with

TABLE III.4(a)

(i) Magnetic Moments of Polychelates of BAR

No	Polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X'_M \times 10^6$	Magnetic moment (per metal ion) B.M.
1	CoBAR	10625	10871	5.2
2	NiBAR	4647	4794	3.4
3	CuBAR	945	1108	1.6
4	MnBAR	12565	12695	5.6
5	FeBAR	11963	12094	5.4
6	PbBAR	Diam	Diam	Diam

TABLE III.4(a)(continued)

(ii) Magnetic Moments of Polychelates of SAR

No	Polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X_M' \times 10^6$	Magnetic moment (per metal ion) B.M.
1	CoSAR	7875	7989	4.4
2	NiSAR	6347	6509	4.0
3	CuSAR	1250	1411	1.9

TABLE III.4(b)

(i) Solid State Electrical Resistivity of Polychelates of BAR

No	Polychelate	Temperature (°C)	Resistivity ρ (ohms-cm)x10^{-10}	Conductivity σ (ohm^{-1}-cm^{-1})x10^{13}
1	CuBAR	28	149.3	6.7
2	CoBAR	28	213.5	4.68
3	MnBAR	28	27.85	35.9
4	FeBAR	28	1.5	666
5	PbBAR	28	229.5	4.36

TABLE III.4(b)(continued)

(ii) Solid State Electrical Resistivity of Polychelates of SAR

No	Polychelate	Temperature (°C)	Resistivity ρ (ohm-cm)x10^{-10}	Conductivity σ ($ohm^{-1}cm^{-1}$)x10^{13}
1	CoSAR	28	4.624	216
2	NiSAR	28	26.23	38.1
3	CuSAR	28	11.3	88.5

TABLE III.4(c)

Some characteristic IR frequencies (cm^{-1}) of BAR, CoBAR, FeBAR and SAR

(i) BAR

3100 s(b)	1580 m	1460 m	1390 m
1295 m	1230 s	1185 s	1090 m
980 w	800 m		

(ii) CoBAR

3350 s(b)	3150 m	2950 m	1560 s
1540 s	1420 m(b)	1020 (sh)	820 m
650 m			

(iii) FeBAR

3350 s(b)	3050 s(b)	2900 m	2840 m
2750 w	1610 m(b)	1485 m	1425 w
1390 w	1120 s(b)	1070 s	1000 m
980 m	810 m	660 m	610 m

(iv) SAR

3400 m(b)	3075 s	2900 s	2500 (sh)
1600 m(b)	1550 m(b)	1460 m	1380 w
1305 s	1175 s	1120 m	1060 s
1010 s	950 (sh)	820 w	780 w
700 m	620 m		

TABLE III.4(d)

(i) Endothermic and Exothermic Peaks in DTA Study of Polychelates of BAR

No	Polychelates	Endothermic peak temp (°C) / onset temp (°C)	Exothermic peak temp (°C) / onset temp (°C)
1	CoBAR	(1) $\frac{170}{148}$	(1) $\frac{470}{430}$
2	NiBAR	(1) $\frac{155}{135}$ (2) $\frac{290}{252}$	(1) $\frac{460}{440}$
3	CuBAR	(1) $\frac{165}{145}$	(1) $\frac{310}{280}$
4	MnBAR	(1) $\frac{160}{145}$	(1) $\frac{460}{440}$
5	FeBAR	(1) $\frac{180}{170}$ (2) $\frac{290}{265}$ (3) $\frac{410}{370}$ (4) $\frac{510}{485}$	
6	PbBAR	(1) $\frac{175}{160}$	(1) $\frac{425}{410}$

TABLE III.4(d)(continued)

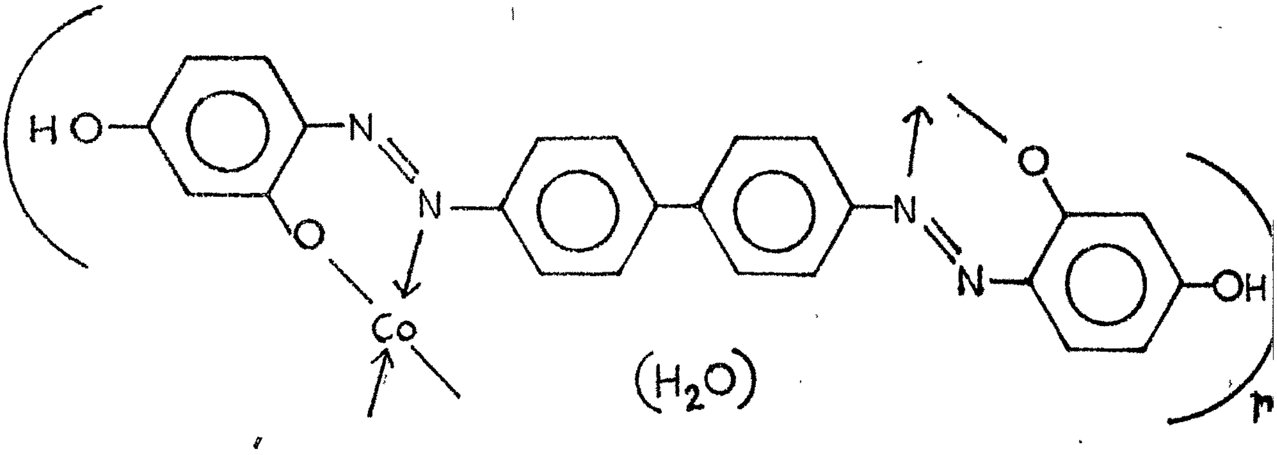
(ii) Endothermic and Exothermic Peaks in DTA study of Polychelates of SAR

No	Polychelates	Endothermic $\frac{\text{peak temp (°C)}}{\text{onset temp (°C)}}$	Exothermic $\frac{\text{peak temp (°C)}}{\text{onset temp (°C)}}$
1	CoSAR	(1) $\frac{160}{152}$ (2) $\frac{300}{280}$	(1) $\frac{480}{450}$
2	NiSAR	(1) $\frac{170}{140}$ (2) $\frac{380}{360}$	(1) $\frac{460}{435}$
3	CuSAR	(1) $\frac{180}{150}$ (2) $\frac{330}{300}$	(1) $\frac{500}{460}$

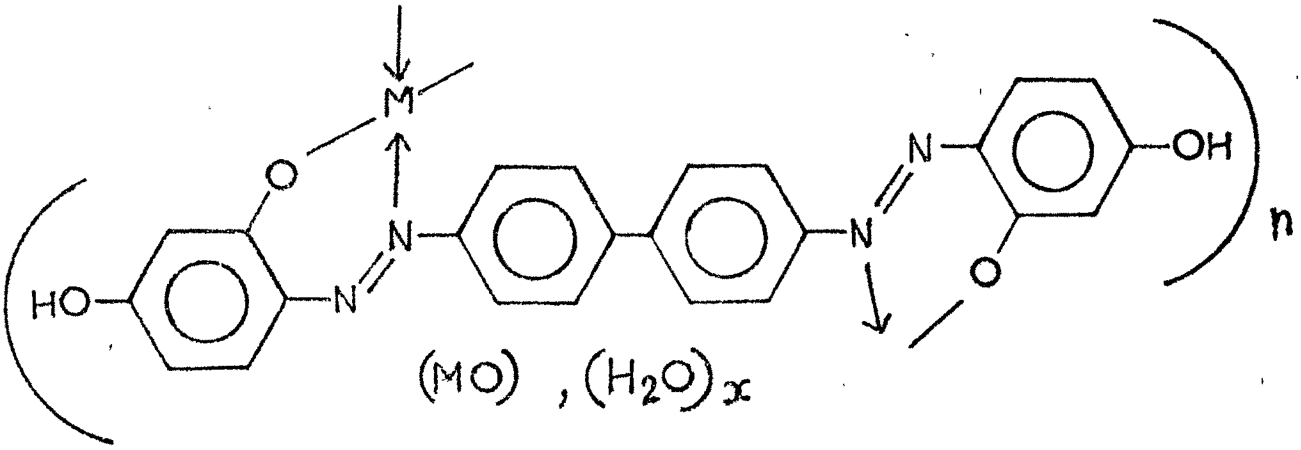
TABLE III.4(e)

TG weight loss of BAR and Polychelates of BAR and SAR

No	Ligand and Polychelates	Temperature range	% weight loss
1	BAR	175-270	2
		270-540	60
2	CoBAR	175-185	4
		250-270	4
		275-430	15
		*430-480	67
3	NiBAR	160-510	40
		510-540	20
4	FeBAR	310-330	7
		350-385	8
		*385-410	35
5	CuSAR	225-325	5
		325-375	6
		420-450	3
		*450-550	12
6	CoSAR	180-275	4
		275-340	6
		340-470	16
		*470-530	34

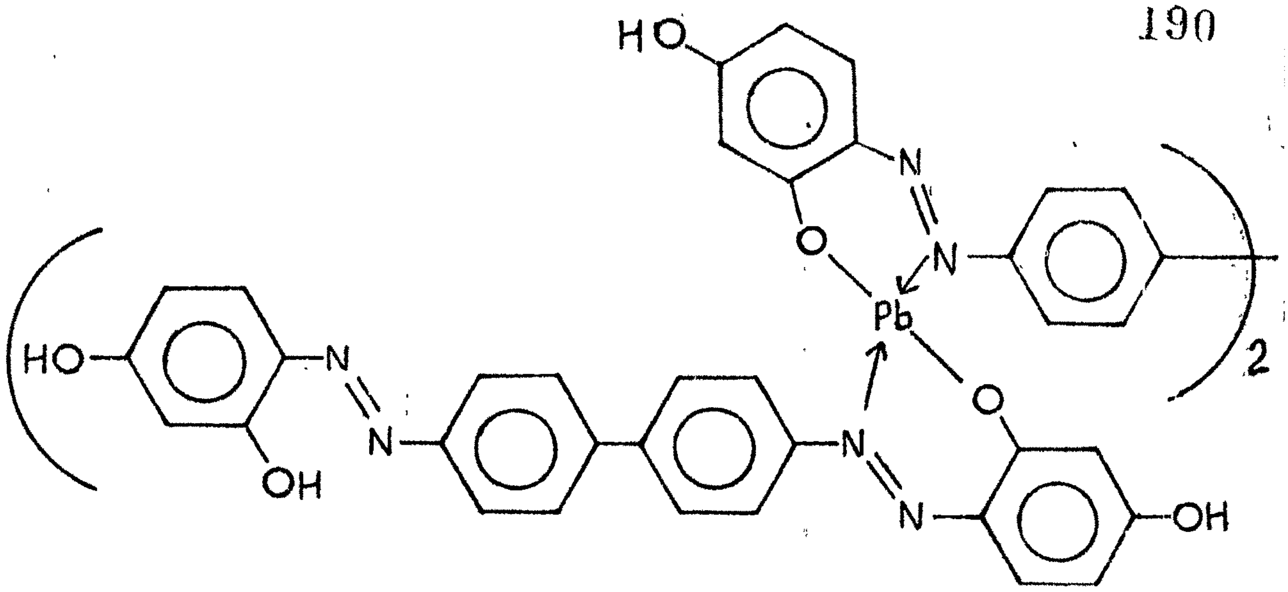


(XXIV)

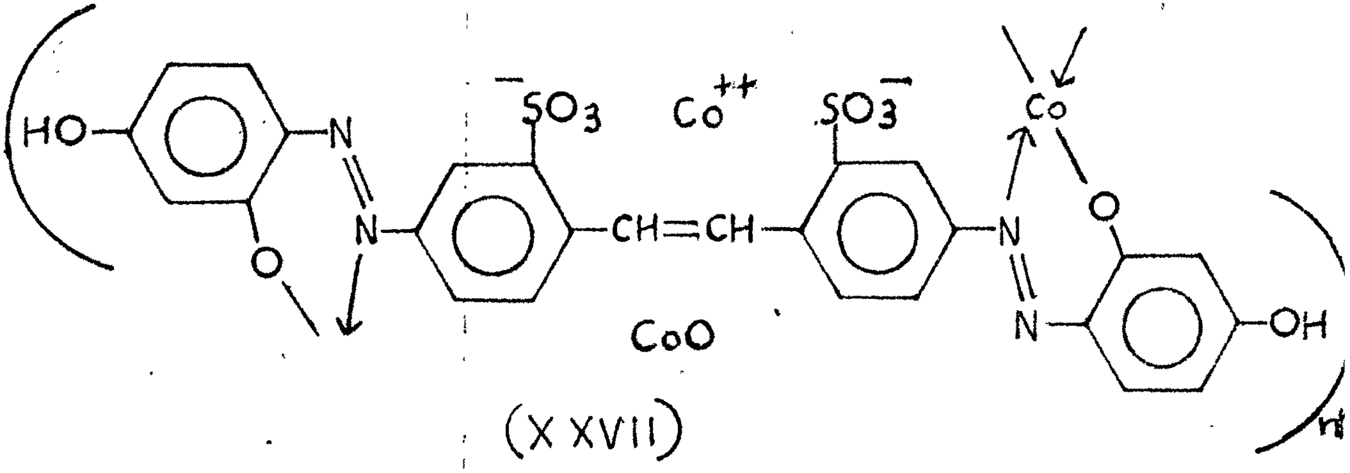


(XXV)

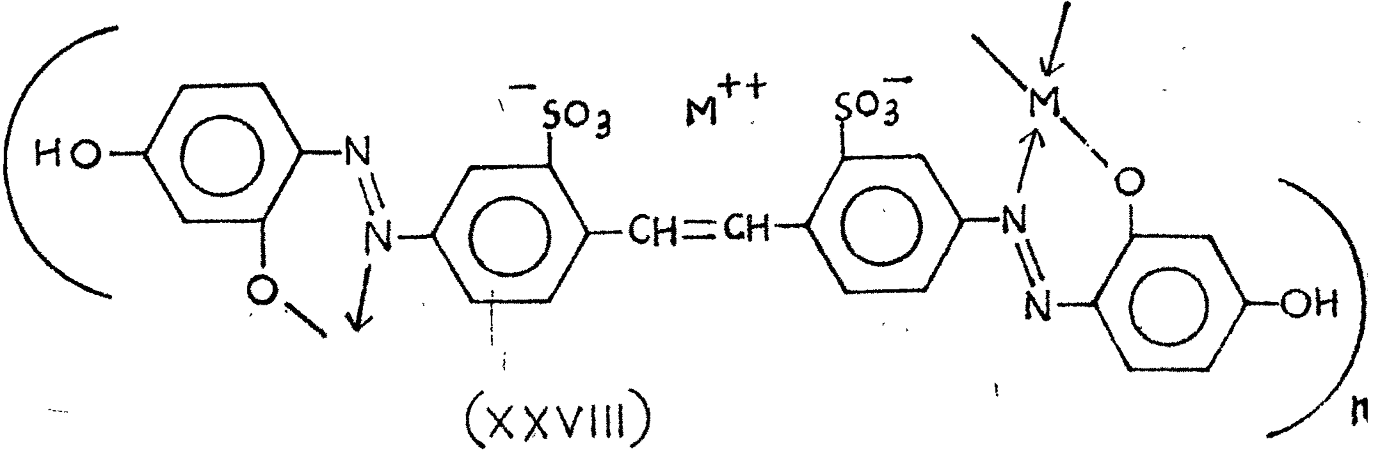
	M =	x =
(i)	Ni	3
(ii)	Cu	6
(iii)	Fe	0
(iv)	Mn	0



(XXVI)



(XXVII)



(XXVIII)

M = Ni, Cu

decomposition and the exothermic peak at 470°C can be related to oxidative decomposition. TG weight losses indicate loss of nitrogen upto 270°C and above this temperature the system decomposes leaving the residue of cobalt.

From the IR spectral data, it is suggested that (i) the band at 820 cm^{-1} be attributed to p-substituted aromatic rings, (ii) the bands at 1540 cm^{-1} and 1420 cm^{-1} be attributed to phenyl rings and (iii) the band at 1020 cm^{-1} be attributed to azo group.

(b) NiBAR:

Its magnetic moment is calculated as 3.4 B.M. per metal atom. It indicates octahedral crystal field around the metal ion.

Endothermic peaks at 155°C and 290°C and exothermic peak at 460°C are attributed to decomposition reactions. TG weight losses indicate overlap of decomposition reactions.

(c) CuBAR:

Its magnetic moment is calculated as 1.6 B.M. per metal atom. The system may be considered to have Cu-Cu interactions leading to electron-spin-pairing in paramagnetic centres.

Endothermic peak at 165°C and exothermic peak at 310°C are attributed to decomposition reactions.

(d) FeBAR:

Its magnetic moment is calculated as 5.4 B.M. per metal atom. It indicates octahedral crystal field around metal ion.

Endothermic peak at 180°C may be related to phase transition whereas peaks at 290°C, 390°C and 510°C to decomposition reactions. TG weight losses indicate complex decomposition reactions.

From the IR spectral data, it is suggested that (i) the broad band at 3350 cm^{-1} be attributed to water present in the chelate, (ii) the band at 810 cm^{-1} be attributed to p-substituted aromatic rings and (iii) the band at 980 cm^{-1} be attributed to azo group.

(e) MnBAR and PbBAR:

The magnetic moment of MnBAR is 5.6 B.M. per metal atom.

Endothermic peak at 160°C and exothermic peak at 460°C may be attributed to decomposition reactions in MnBAR.

PbBAR is diamagnetic. Endothermic peak at 175°C and exothermic peak at 425°C may be related to decomposition reactions,

(f) Polychelates of SAR:

The magnetic moment of CoSAR, NiSAR and CuSAR has been calculated as 4.4 B.M. per metal atom, 4.1. B.M. per metal atom and 1.9 B.M. per metal atom respectively. The magnetic moments of CoSAR and NiSAR may be related to the ionic and tetrahedral chelated metal ion contributions.

Thermal studies indicate the following:

Endothermic peak at 160°C, 170°C or 180°C indicate phase transition. Other endothermic and exothermic peaks are indicative of degradation reactions. TG weight losses indicate decomposition reaction involving loss of nitrogen and oxidative degradation reactions.

(g) General Considerations:

Azo-resorcinol dyes and their metallised products are in use as leather dyes. Azo phenol dyes can exist in their tautomeric quinone-hydrazone forms. However, in the present studies, azo-phenol structures are considered in general.

The relative thermal stability on the basis of onset temperature for the first phase of degradation is decreasing in order

$$\text{FeBAR} > \text{PbBAR} > \text{CoBAR} \sim \text{CuBAR} \sim \text{MnBAR} > \text{NiBAR}$$

$$\text{NiSAR} > \text{CuSAR} > \text{CoSAR}$$

From TG weight losses, the relative stability of the polychelates is considered decreasing in order

$$\text{FeBAR} > \text{NiBAR} > \text{CoBAR}$$

$$\text{CuSAR} > \text{CoSAR}$$

(iii) Pyrolyzed polychelates of BAR and SAR:

The pyrolysis of the polychelates of BAR and SAR was carried out under continuous evacuation. The magnetic moments and IR spectral data of some of these pyrolyzed products are presented in tables III.4(f) and (g). Solid state electrical conductivity of these products could not be determined.

On the basis of analysis, (i) CoBAR(P) is found to have metal-to-ligand (C_{24}) ratio of one-to-one and is represented as (XXIX), (ii) NiBAR(P), CuBAR(P), FeBAR(P) and MnBAR(P) are found to have metal-to-ligand (C_{24}) ratio of two-to-one and are represented as (XXX), (iii) CoSAR(P) is found to have metal-to-ligand (C_{26}) ratio of three-to-one and is represented as (XXXI) and (iv) NiSAR(P) and CuSAR(P) are found to have metal-to-ligand ratio of two-to-one and are represented as (XXXII).

The magnetic moments of CoBAR(P), FeBAR(P), CoSAR(P) and NiSAR(P) are not evaluated as they exhibit ferromagnetism which could not be studied. The magnetic moment of NiBAR(P) is calculated as 2.7 B.M. per metal atom. It indicates that the nickel ions in the polychelate maintain octahedral stereochemistry and undergo dimerisation through Ni-Ni cross-linking. The magnetic moment of CuBAR(P) is

TABLE III, 4(f)

(i) Magnetic Moments of Pyrolyzed Polychelates of BAR

No	Polychelate	Molar magnetic susceptibility (per metal ion) X_M x10^6	Corrected molar magnetic susceptibility (per metal ion) X'_M x 10^6	Magnetic moment (per metal ion) B.M.
1	*CoBAR(P)	-	-	-
2	NiBAR(P)	2758.5	2879.5	2.7
3	CuBAR(P)	695.5	816.5	1.4
4	MnBAR(P)	11834	11955	5.4
5	*FeBAR(P)	-	-	-

TABLE III.4(f) (continued)

(ii) Magnetic Moments of Pyrolyzed Polychelates of SAR

No	Polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X'_M \times 10^6$	Magnetic moment (per metal ion) B.M.
1	*CoSAR(P)	-	-	-
2	*NiSAR(P)	-	-	-
3	CuSAR(P)	1442	1602	2.0

TABLE III.4(g)

Some characteristic IR frequencies (cm^{-1}) of CoBAR(P), FeBAR(P), CoSAR(P) and NiSAR(P)

(i) CoBAR(P)

3400 m (b)	3100 m	2920 m	2850 m
2790 w	2675 w	1585 m(b)	1560 m
1540 m	1400 m	1375 m	1360 w
1140 m			

(ii) FeBAR(P)

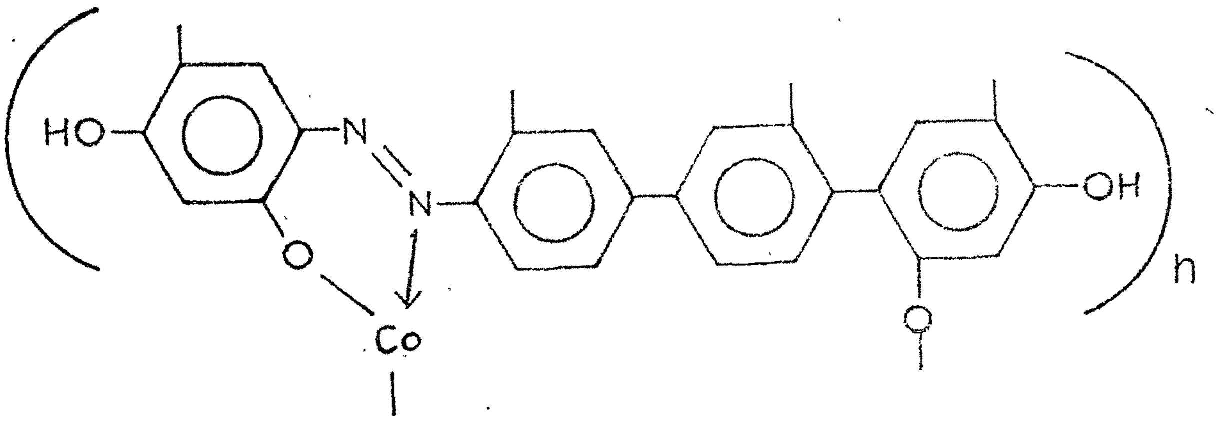
3100 w	2900 s	2850 m	1580 w(b)
1440 m	1370 w	1140 w	1100 w
1080 w	1020 w		

(iii) CoSAR(P)

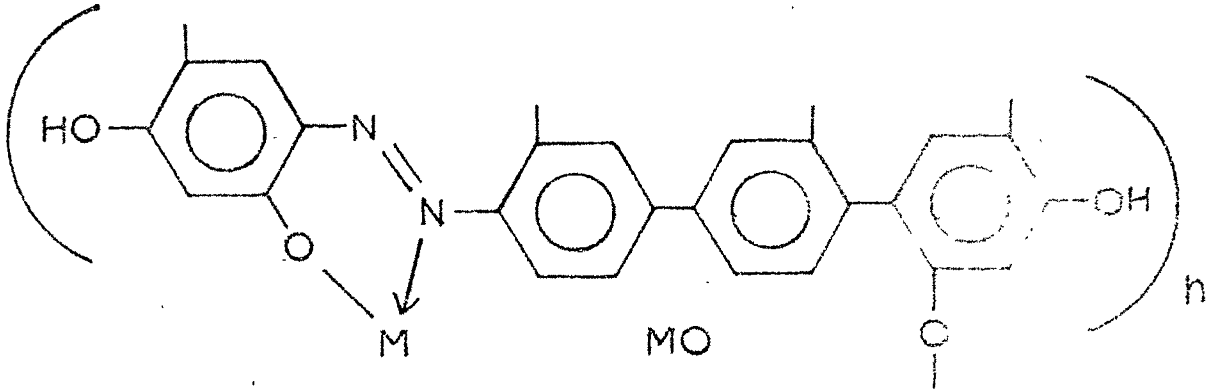
3100 w	2900 m	2825 w	1560 m(b)
1540 w(b)	1490 w	1380 w	1180 m
1020 w	800 w	780 w	

(iv) NiSAR(P)

2850 m	1140 m

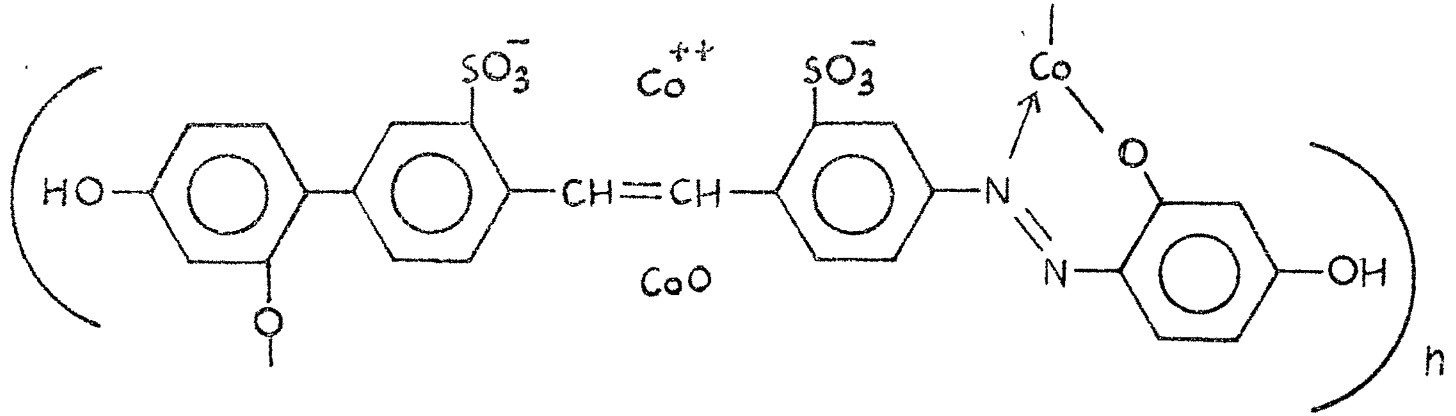


(XXIX)

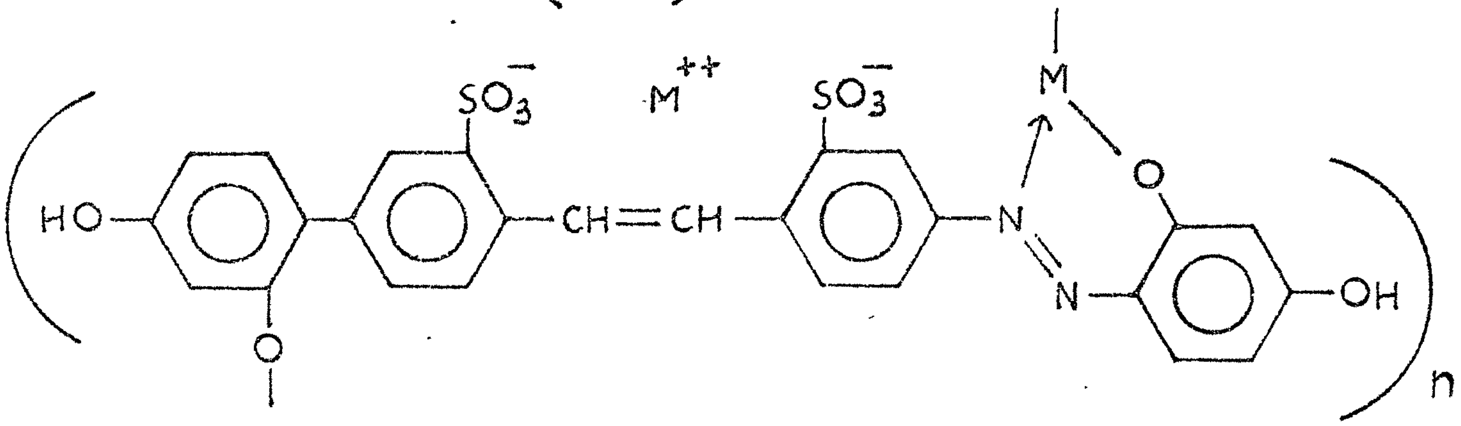


(XXX)

M = Ni , Cu , Fe , Mn



(XXXI)



(XXXII)

M = Ni , Cu

calculated as 1.4 B.M. per metal atom. Low value is indicative of antiferromagnetic interactions which would take place amongst copper ions. The magnetic moment of MnBAR(P) is calculated as 5.4 B.M. per metal atom and suggests no change in the magnetic nature of the polychelate on pyrolysis. The magnetic moment of CuSAR(P) is calculated as 2.0 B.M. per metal atom and indicates no change in paramagnetic nature on pyrolysis.

From the IR spectral data of CoBAR(P) and FeBAR(P), it is suggested that (i) the band at 820 cm^{-1}/810 cm^{-1} attributed to p-substituted aromatic rings is not observed and (ii) the band at 1020 cm^{-1}/1000 cm^{-1} attributed to azo group is not observed.

From the IR spectral data of CoSAR(P) and NiSAR(P), it is suggested that (i) the band at 1010 cm^{-1} attributable to azo group is very weak in CoSAR(P) and not observed in NiSAR(P).

The radical mechanism of decomposition of azo compounds is well known. Thilo and Hauser (238) described in 1896 the quantitative evolution of nitrogen according to the equation

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

and the formation of products by transfer and recombination reactions. Kapadia (109) suggested that the thermal fission involving the evolution of nitrogen is catalysed by the metal ion chelated to the salicylaldehyde moiety of the azo ligand. The fission reaction was facilitated by nickel and inhibited by cobalt. In the present studies azo group is considered involved in complex formation and in none of the polychelates there is inhibition of thermal fission evolving nitrogen, by the metal ion chelated to the azo group.

Azo-compounds are known as initiators of polymerisation through radical mechanism. IR spectra of the polymerized products suggest further substitution in the phenyl rings. It may indicate the formation of polynuclear compounds through hydrogen-abstraction, facilitated by the free radicals formed in the fission of azo compounds.

The ferromagnetism suggested for various pyrolyzed products may be attributed not only to the M-M interactions but also to M - L interactions where L (ligand) has attained some free radical nature.

III.5 Polychelates of BAN and SAN and their Pyrolysis:

(i) General : Chelates of azo naphthols:

Bamberger (239) prepared copper, nickel and cobalt chelates of hydroxy azobenzenes and azo-naphthols. Lassettre (240) and Walf and Liddell (241) studied the stereochemical properties of metal chelated azo phenols and their azo phenol and quinone-hydrozone resonating structures. Drew and Landquist (242) prepared copper chelates of hydroxy azo benzenes and naphthalenes and considered the planarity of metal chelate rings. Wark (243) observed that azo group in azo salicylic acid is not involved in chelate ring formation with copper. Morgan and Mainsmith (244) found that while many 0,0'-dihydroxy azo dyes took up metal ions, some underwent oxidation to quinonoid forms which were involved in chelate formation. Beech and Drew (245) studied the formation of copper complex with hydroxy azo compounds containing sulphonic acid group.

Chelates of 1-azo-2-naphthol derivatives and their tautomerism have been studied by Toshio et al (246), Kawase (247), Korshanov (248), Schetty (249), Pilipenko and Savranskii (250), Domagalina and Zareba (251), Garnovskii et al (252), Pilipenko et al (253), Garvanska et al (254), Beffa and Fasciati (255), Saikina et al (256), Budnikov et al (257), Zimmermann et al (258), and Shimidzu and Uno (259).

1-azo-2 hydroxy-3-naphthoic acid (AHN) derivatives have been found as (i) a reagent for calcium (260), (ii) an indicator for titrations of copper and nickel against EDTA (261), (iii) a chelating agent for copper, nickel and zinc (262), (iv) a lake-former (263, 264) and (v) a complexing agent for various metal ions (265).

(ii) Polychelates of BAN and SAN:

Polychelates of BAN with cobalt and copper were prepared from dimethyl formamide solutions and polychelates of SAN with cobalt,nickel and copper were prepared from ammoniacal solutions. The results of their studies are presented and discussed below.

The magnetic moment, electrical conductivity, IR spectral data, DTA peaks and TG weight loss of these polychelates are presented in tables III.5(a) to (e).

On the basis of analysis (i) CoBAN and CuBAN are found to have metal-to-ligand (C_{34}) ratio of one-to-one and are represented as (XXXIII), (ii) CoSAN is found to have metal-to-ligand (C_{36}) ratio of two-to-one and is represented as (XXXIV), (iii) NiSAN is found to have metal-to-ligand ratio of four-to-one and is represented as (XXXV) and (iv) CuSAN is found to have metal-to-ligand (C_{36}) ratio of three-to-one as.

TABLE III.5(a)

Magnetic moments of polychelates

No	polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	corrected molar magnetic susceptibility (per metal ion) $X_M' \times 10^6$	Magnetic moment (per metal ion) B.M.
	(i) Polychelates of BAN			
1	CoBAN	14568	14905	6.1
2	CuBAN	1930	2268	2.4
	(ii) Polychelates of SAN			
3	CoSAN	11262	11470	5.3
4	NiSAN	4672	4804	3.4
5	CuSAN	1266	1406	1.9

TABLE III.5(b)

Solid State Electrical Resistivity of Polychelates

No	Polychelate	Temperature (°C)	Resistivity ρ (ohm-cm)x10^{-10}	Conductivity σ (ohm^{-1} cm^{-1})x10^{13}
	(i) Polychelates of BAN			
1	CuBAN	28	13.91	71.9
2	CoBAN	28	140.3	7.13
	(ii) Polychelates of SAN			
3	CoSAN	28	89.80	11.1
4	NiSAN	28	16.47	60.7
5	CuSAN	28	54.19	19.4

TABLE III.5(c)

Some Characteristic IR Frequencies (cm^{-1}) of CoBAN and CoSAN

(i) CoBAN

2900 s	2850 s	1640 (sh)	1600 s(b)
1530 s	1470 s	1438 s	1365 s
1340 s	1300 m(b)	1240 m	1180 m
1125 m	998 w	802 m	725 m

(ii) CoSAN

3350 s(b)	2900 m	2350 m	1600 m
1560 (sh)	1540 s	1480 s	1440 s
1380 vs	1366 s	1320 m	1295 w
1258 m	1180 vs	1145 s	1070 m
1018 s	980 (sh)	880 m	820 m
750 m	705 m	615 m	

TABLE III.5(d)

(i) Endothermic and Exothermic peaks in DTA Study of Polychelates of BAN

No	Polychelates	Endothermic $\frac{\text{peak temp (°C)}}{\text{onset temp (°C)}}$	Exothermic $\frac{\text{peak temp (°C)}}{\text{onset temp (°C)}}$
1	CoBAN	(1) $\frac{160}{140}$ (2) $\frac{270}{225}$	(1) $\frac{335}{315}$
2	CuBAN	(1) $\frac{170}{155}$ (2) $\frac{270}{235}$	(1) $\frac{355}{350}$

TABLE III. 5(d) (cpntinued)

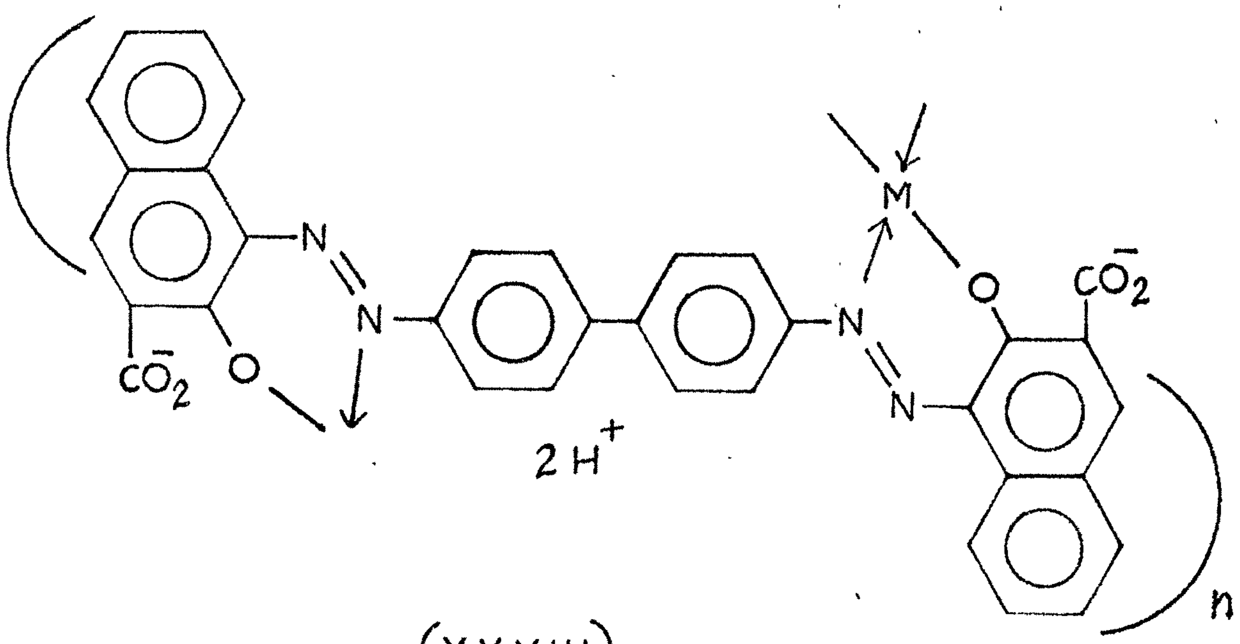
(ii) Endothermic and Exothermic Peaks in DTA Study of Polychelates of SAN

No	Polychelates	Endothermic $\frac{\text{peak temp (°C)}}{\text{onset temp (°C)}}$	Exothermic $\frac{\text{peak temp (°C)}}{\text{onset temp (°C)}}$	Remarks
1	CoSAN	(1) $\frac{160}{140}$ (2) $\frac{305}{275}$	(1) $\frac{450}{425}$	-
2	NiSAN	(1) $\frac{130}{100}$ (2) $\frac{390}{350}$	(1) $\frac{460}{440}$	second order changes
3	CuSAN	(1) $\frac{160}{140}$	(1) $\frac{295}{285}$	-

TABLE III.5(e)

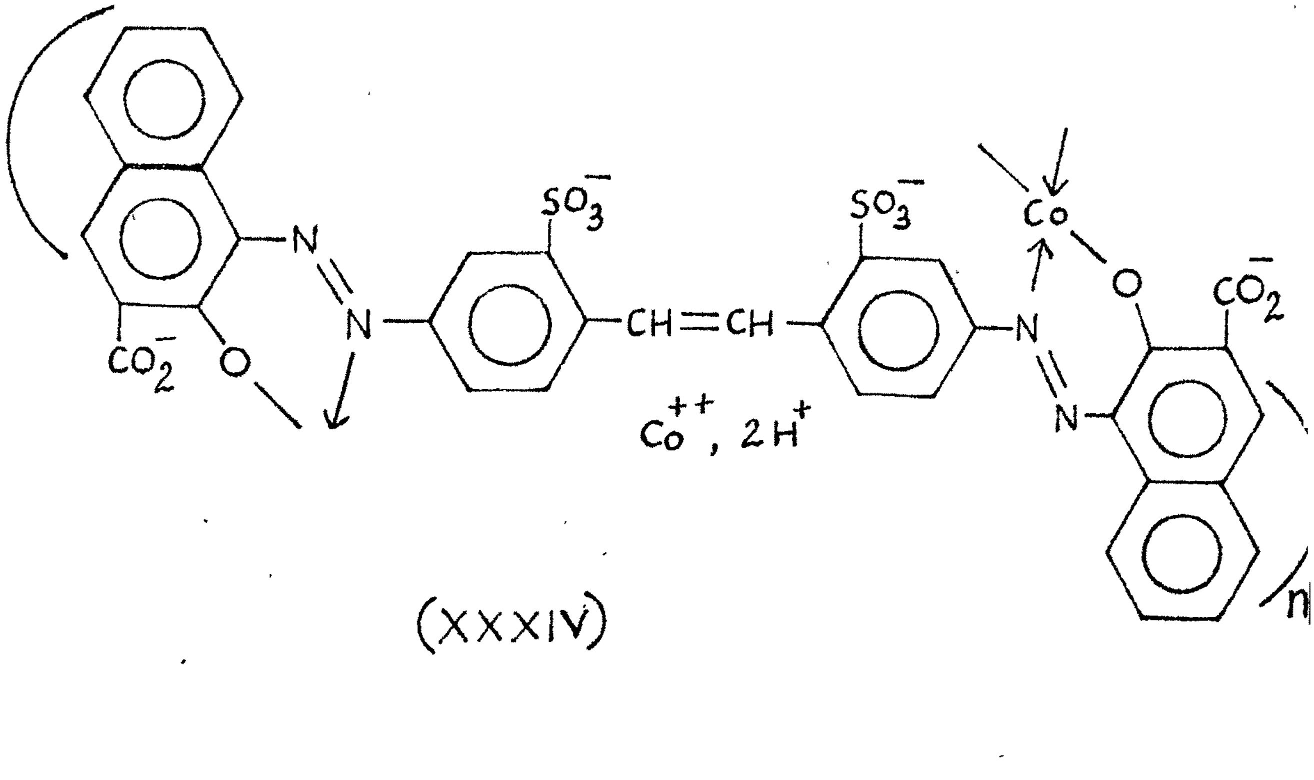
TG weight loss of the Polychelates of BAN and SAN

No	Polychelate	Temperature range	% weight loss
1	CoBAN	165-340	3
		* 340-420	76
2	CuBAN	150-275	10
		*275-305	79
3	CoSAN	180-185	2
		225-325	10
		340-470	28
		480-500	25
4	NiSAN	165-250	8
		250-425	40
		*450-500	42
5	CuSAN	175-300	7
		*320-360	58

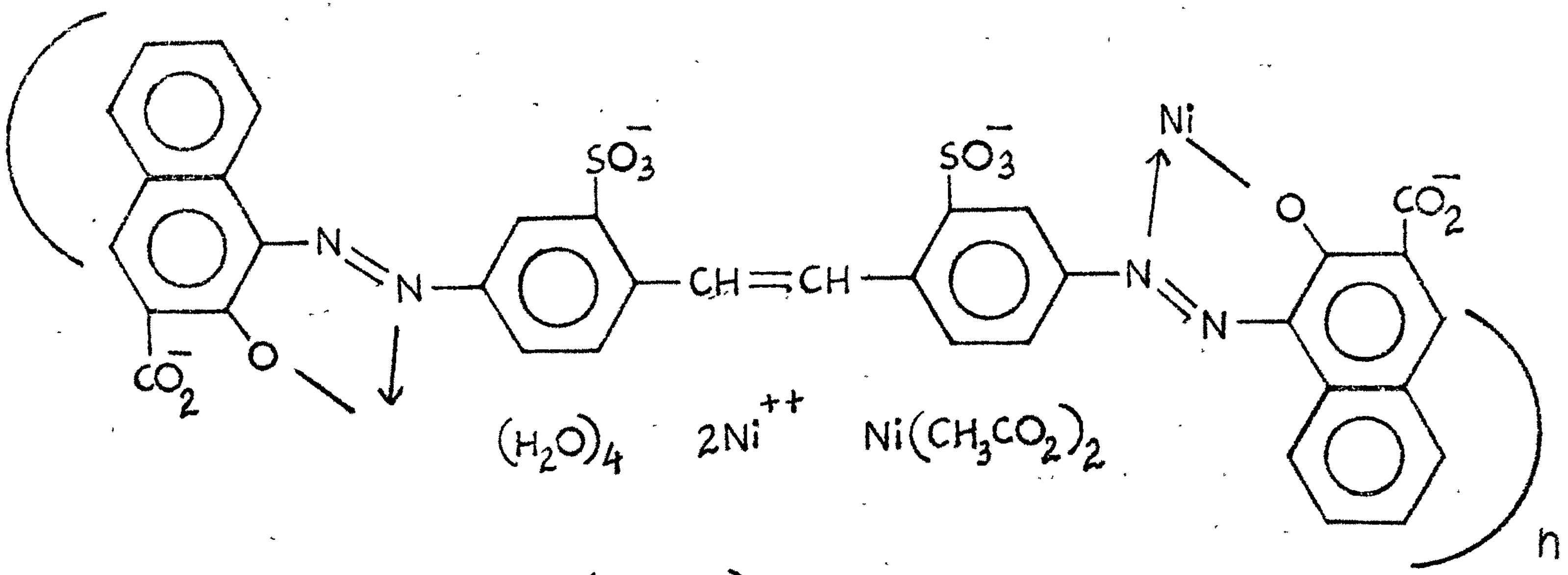


(XXXIII)

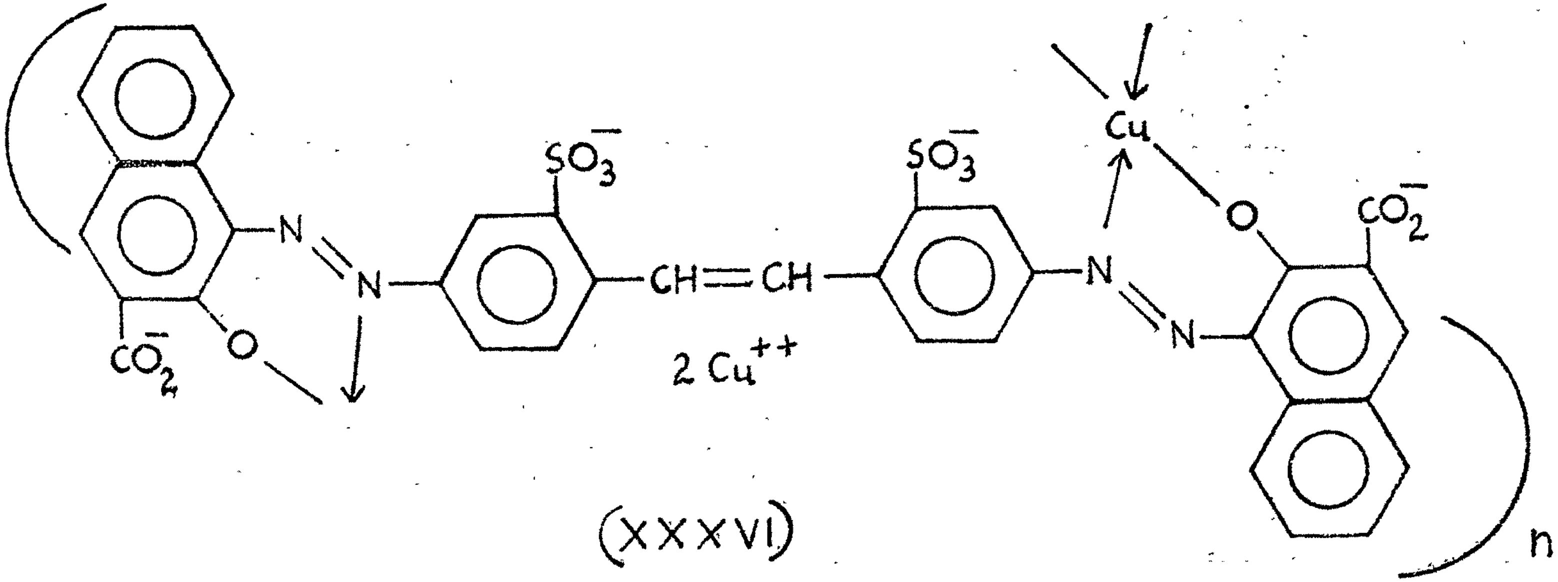
M = Co, Cu



(XXXIV)


SO$_3^-$
SO$_3^-$
Ni
CO$_2^-$
N
N
CH═CH
CO$_2^-$
O
(H$_2$O)$_4$ 2Ni^{++} Ni(CH$_3$CO$_2$)$_2$
n

(XXXV)


Cu
SO$_3^-$
SO$_3^-$
CO$_2^-$
O
N
N
CH═CH
CO$_2^-$
2 Cu^{++}
n

(XXXVI)

and is represented as (XXXVI).

(A) CoBAN :

Its magnetic moment is calculated as 6.1 B.M. per metal atom. The ligand is sixadentate and the metal ion is considered 6-covalent with octahedral crystal field surrounding the ion. The magnetic moment is much higher and may be related to ferromagnetic interactions of cobalt atoms.

The endothermic DTA peak are 160°C is a second order change and is indicative of glass-transition temperature. Endothermic DTA peak at 270°C is broad and indicates slow decomposition reaction. Exothermic peak at 335°C is attributed to decomposition reaction. TG weight losses indicate slow degradation evolving carbon dioxide + nitrogen upto 330°C and oxidative degradation upto 420°C leaving a residue possibly of cobalt carbonate.

(b) CuBAN :

Its magnetic moment is calculated as 2.4 B.M. per metal atom.

Endothermic DTA peaks at 170°C and 270°C and exothermic peak at 355°C indicate decomposition reactions in steps. TG weight losses indicate loss of carbon dioxide upto 275°C and oxidative degradation upto 305°C leaving a residue of copper oxide.

(c) CoSAN:

Its magnetic moment is calculated as 5.3 B.M. per metal atom. The metal ion is considered 6-covalent with octahedral crystal field surrounding it.

Endothermic peaks at 160°C and 305°C and exothermic peak at 450°C may be related to degradation reactions. TG weight losses indicate loss of carbon dioxide and nitrogen in steps upto 325°C and oxidative degradation at higher temperatures.

(d) NiSAN:

Its mangetic moment is calculated as 3.4 B.M. per metal atom. The polychelate contains ionic and chelated nickel.

Endothermic peak at 130°C is related to phase transition and endothermic peak at 390°C and exothermic peak at 460°C are attributed to degradation reactions. TG weight losses indicate loss of carbon dioxide + nitrogen upto 250°C and degradation at higher temperature.

(e) CuSAN:

Its magnetic moment is calculated as 1.9 B.M. per metal atom.

Endothermic peak at 160° and exothermic peak at 295° indicate degradation reactions. TG weight losses indicate loss of carbon dioxide + nitrogen upto 300°C and oxidative degradation at higher temperatures.

(f) General Considerations:

BAN forms one type (1:1) of the polychelates whereas SAN forms three types (2:1, 3:1 and 4:1) of the polychelates.

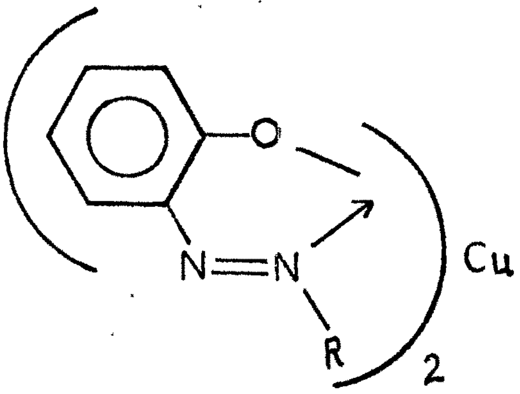
Drew and Landquist (242) studied copper chelates of o-hydroxy, o-carboxy, o-o'-dihydroxy and o-hydroxy-o'-carboxy azo compounds of benzene and naphthalene series and suggested their structures as (XXXVII-a), (XXXVII-b), (XXXVII-c) and (XXXVII-d). Beech and Drew (245) represented a (3:2) copper chelate of o-o'-dihydroxy azo ligand as (XXXVIII-a). It is also represented as a chelate of o-hydroxy, o'-quinone hydrazone (XXXVIII-b). In the present studies the structures are assigned on the basis of azo structure and the assumption of stability of 6-membered chelate ring.

From the weight losses observed in TGA studies, we consider the relative stability of the polychelates decreasing in the order

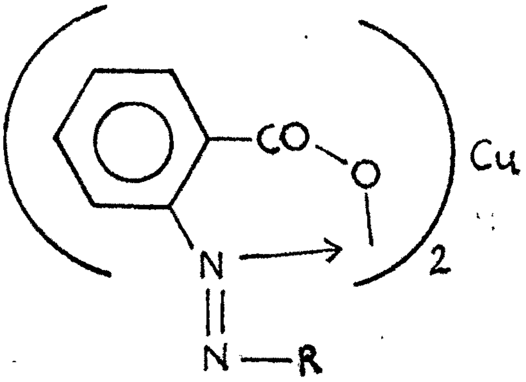
CoBAN > CuBAN

CoSAN > CuSAN > NiSAN

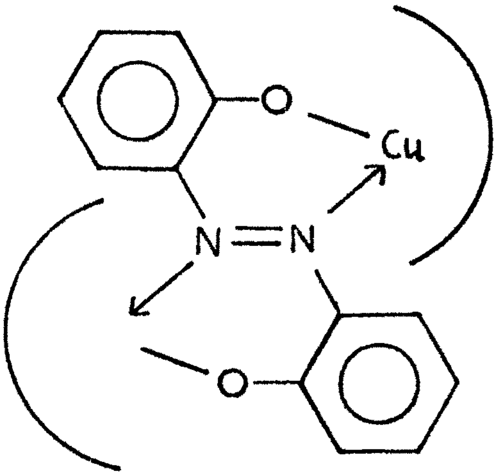
CoBAN, CuBAN and CuSAN decompose gradually over a temperature range of 100°C or more, evolving carbon dioxide and nitrogen. Further decomposition/oxidative degradation



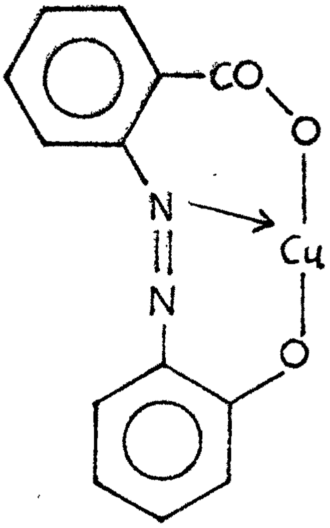
(XXXVII-a)



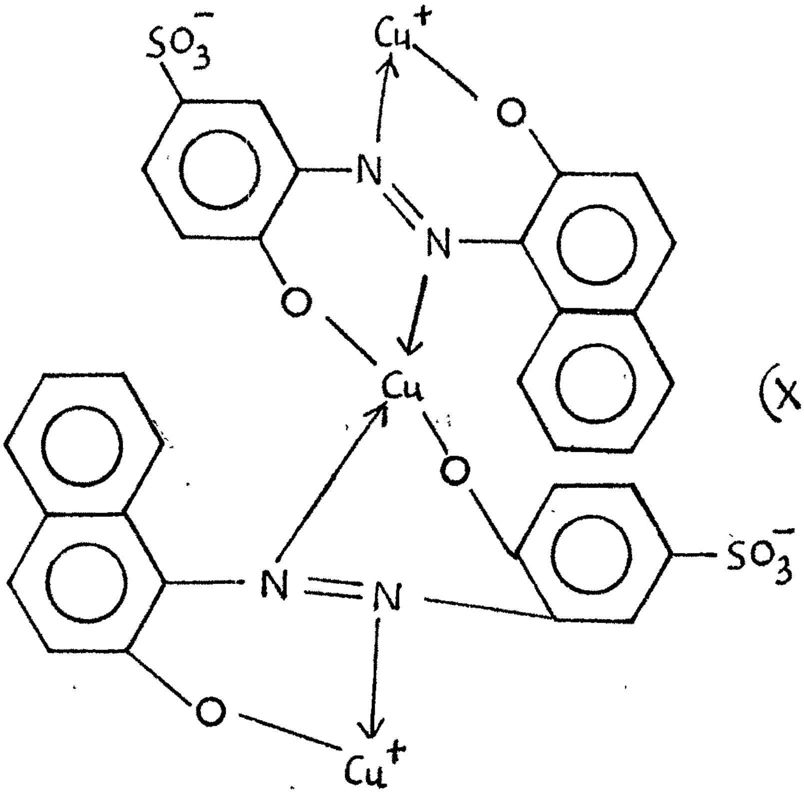
(XXXVII-b)



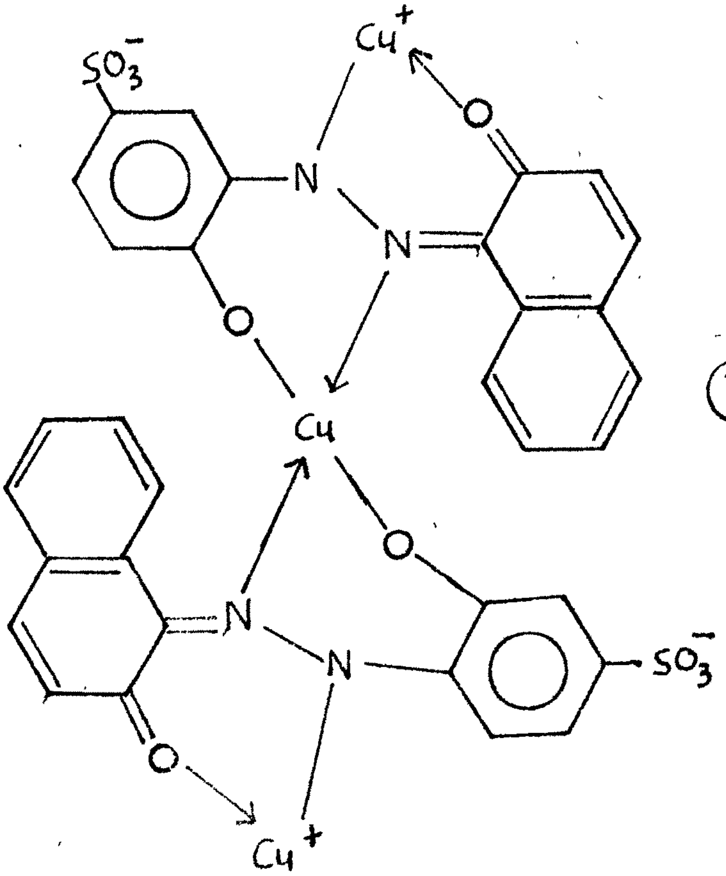
(XXXVII-c)



(XXXVII-d)



(XXXVIII–a)



(XXXVIII–b)

is over a temperature range of 30°C to 80°C and may involve 60 to 80% weight loss. CoSAN undergoes degradation in four steps and total % weight loss is 65%.

The relative thermal stability on the basis of onset temperature for first phase of degradation, is decreasing in order,

$$\text{CuBAN} > \text{CoBAN}$$

$$\text{NiSAN} > \text{CoSAN} \sim \text{CuSAN}$$

(iii) Pyrolyzed Polychelates of BAN and SAN:

The polychelates of BAN and SAN were pyrolyzed at 310-30°C under continuous evacuation. The magnetic moments and IR spectral bands of some of the pyrolyzed products are presented in tables III.5(f) and (g). Solid state electrical conductivity of these products could not be determined as they could not be pelletized.

On the basis of analysis (i) CoBAN(P) and CuBAN(P) are found to have metal-to-ligand (C_{33}) ratio as one-to-one and are represented as (XXXIX), (ii) CoSAN(P) is found to have metal-to-ligand (C_{35}) ratio as two-to-one and is represented as (XXXX-a), (iii) NiSAN(P) is found to have metal-to-ligand (C_{35}) ratio as four-to-one and is represented as (XXXX-b) and (iv) CuSAN(P) is found to have metal-to-ligand (C_{35}) ratio as three-to-one and is represented as (XXXX-c).

TABLE III.5(f)

Magnetic Moments of Pyrolyzed Polychelates

No	Polychelate	Molar magnetic susceptibility (per metal ion) $X_M \times 10^6$	Corrected molar magnetic susceptibility (per metal ion) $X'_M \times 10^6$	Magnetic moment (per metal ion) B.M.
	(i) Pyrolyzed Polychelates of BAN			
1	*CoBAN(P)	-	-	-
2	CuBAN(P)	2229	2557	2.5
	(ii) Pyrolyzed Polychelates of SAN			
3	*CoSAN(P)	-	-	-
4	NiSAN(P)	-	-	-
5	CuSAN(P)	1434	1572	2.0

TABLE III.5(g)

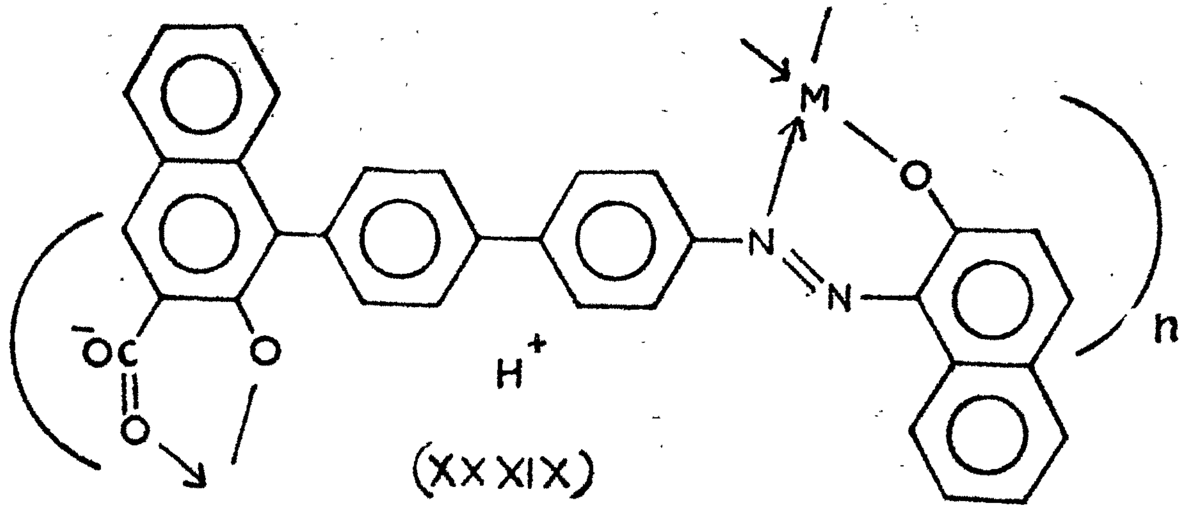
Some Characteristic IR Frequencies (cm^{-1}) of CoBAN(P) and CoSAN(P)

(i) CoBAN(P)

2375 m	2150 w	1550 m(b)	1240 w
1140 w	1100 (sh)	810 m	760 m
680 w	640 w		

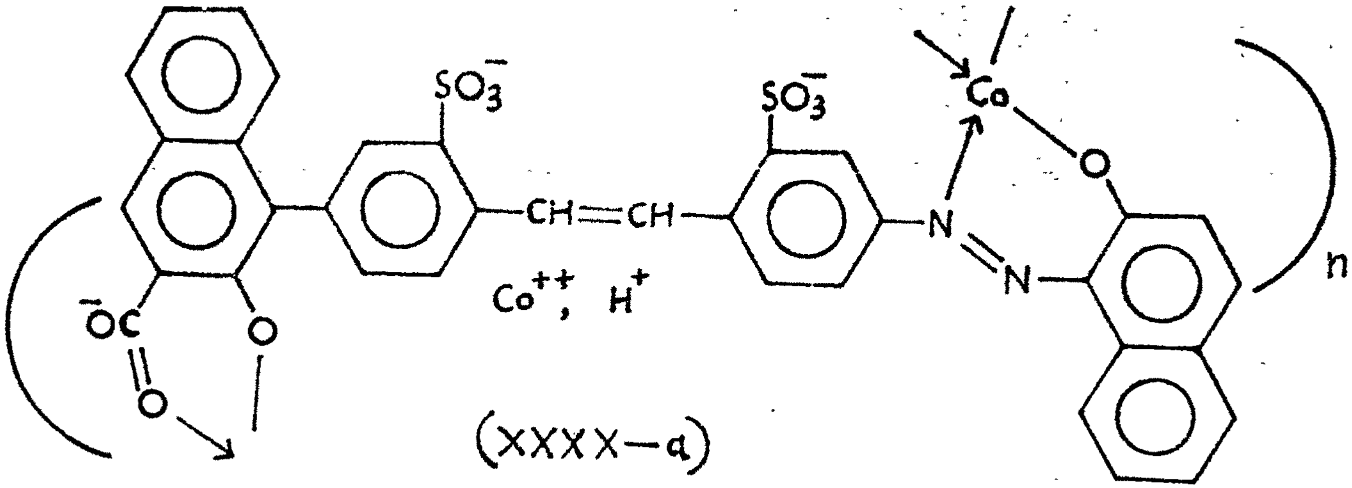
(ii) CoSAN(P)

3350 s(b)	3050 s(b)	2850 s	1560 s(b)
1360 s(b)	1140 s	1080 m(b)	1020 m(b)

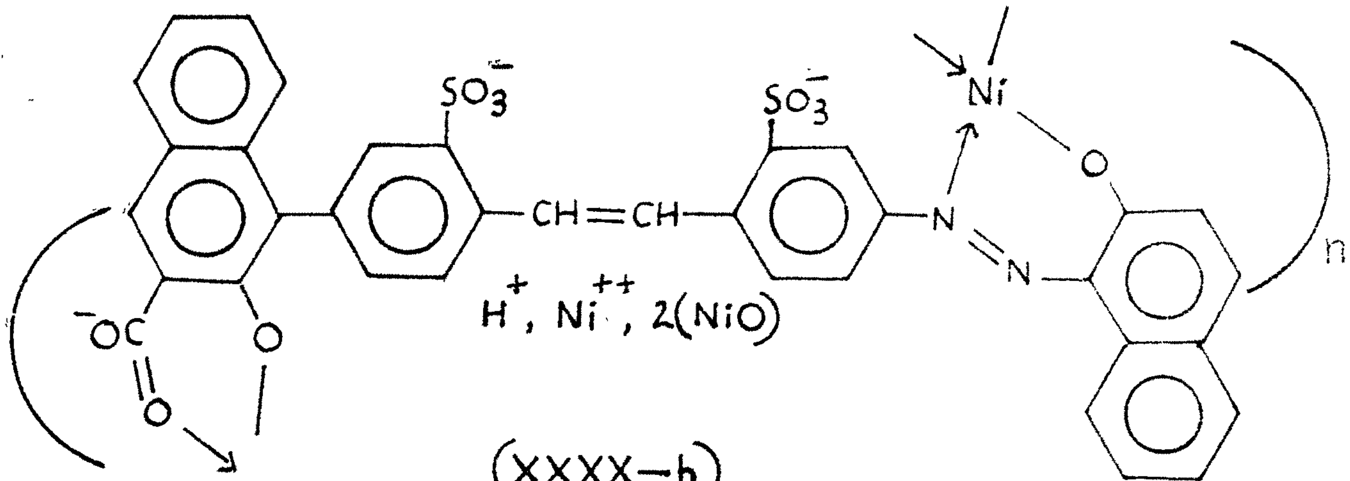


(XXXIX)

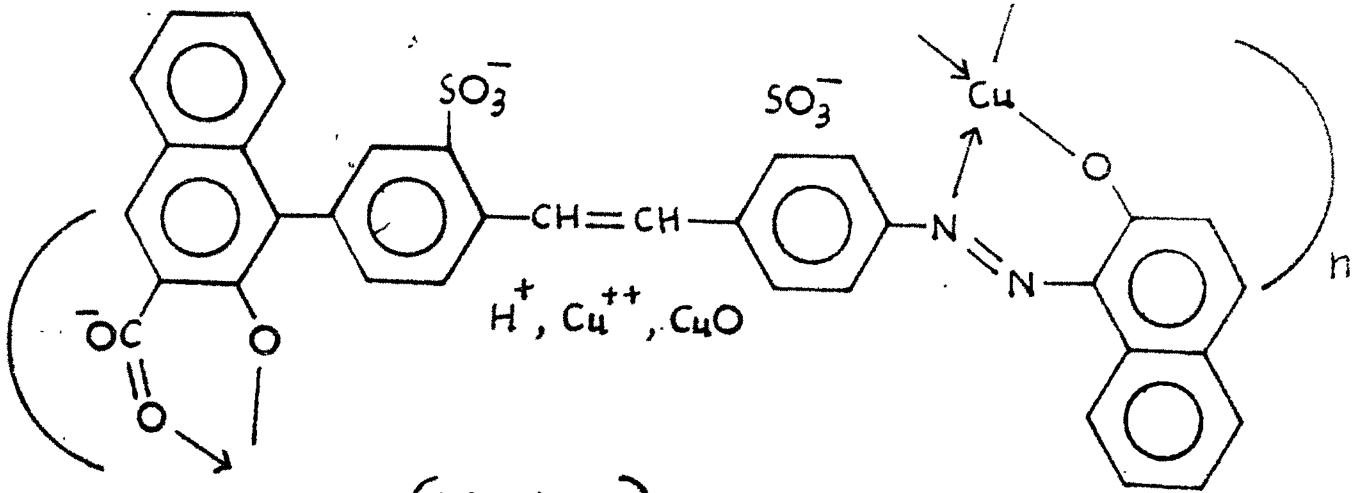
M = Co, Cu



(XXXX—a)


SO_3^-
SO_3^-
Ni
O
CH=CH
N
N
n
^-OC
O
O
H^+, Ni^{++}, 2(NiO)

(XXXX—b)


SO_3^-
SO_3^-
Cu
O
CH=CH
N
N
n
^-OC
O
O
H^+, Cu^{++}, CuO

(XXXX—c)

The magnetic moments of CoBAN(P), CoSAN(P) and NiSAN(P) are not presented as the compounds exhibit ferromagnetic behaviour. CuBAN(P) and CuSAN(P) have magnetic moment of 2.5 B.M. per metal atom and 2.0 B.M. per metal atom respectively.

It is suggested that 1-azo-2-hydroxy 3-naphthoic acid derivatives form chelates wherein azo and hydroxy groups are considered involved in chelation in preference to hydroxy and carboxylic acid groups. On pyrolysis, one of the two azo groups and one of the two carboxylic acid groups are considered involved in degradation releasing nitrogen and carbon dioxide. The pyrolyzed product, then, has structural rearrangements. In this degradation, basic metal compounds (oxide, hydroxide, bridged oxy or hydroxy compounds, etc.) have been found.

III.6 Concluding remarks:

Pyrolysis has been used as a technique for the synthesis of PYRO-CHELATE-POLYMERS and for understanding the changes in chelate polymers.

Korshak et al (266) observed that the concentration of paramagnetic centres in semiconducting N-polymers increased linearly with heat-treatment temperature between 400° and 900°C. Above 500°C, in addition to degradation, the polymer underwent cross-linking accompanied by the formation of bundle of layers of condensed aromatic rings.

The first step in the thermal splitting of a polymer is the free-radical formation and growth of the reaction is accompanied by bond opening and lowering of the molecular mass. Termination reactions may result in the formation of different end-groups in a macromolecule, in a change in molecular mass distribution and in the formation of branched and three-dimensional structures. Like any chain reaction, thermal degradation is accelerated by substances which decompose readily into free-radicals and is slowed down in the presence of substances which are free-radical acceptors.

Thermal degradation also causes depolymerisation. The monomer yield depends not only on the kind of polymer but also on the conditions and mechanism of its synthesis and thermal splitting. If inter-molecular reactions predominate, branched and three-dimensional structures result. When depolymerisation is accelerated by air, the molecular mass decreases, but the monomer may not be obtained. When halo-derivatives of polymers are heated, the chemical nature of the polymer changes before thermal depolymerisation could have set in. When heterochain polymers are heated, very complex processes usually occur, accompanied by a decrease in the molecular mass and evolution of various decomposition products. In some cases, however, the heterochain polymers are depolymerised.

Pyrolysis of the polychelates of chloronilic acid resulted in dehydration and dechlorination followed by cross-polymerisation and "depolymerisation". Pyrolysis of the polychelates of 3,3'-diacetyl 4,4'-dihydroxy diphenyl sulphone led to deammoniation and dehydrogenation followed by cross-polymerisation and cyclization. Pyrolysis of the chelates of 2,4-dinitroso resorcinol under controlled conditions resulted in (i) lowering of molecular mass, (ii) depolymerisation, (iii) weaking of the crystal field around metal ion, and/or (iv) reorientation of crystal field around metal ion. Pyrolysis of the polychelates of bis (4-azo resorcinol) dyes resulted in partial denitrogenation which was not inhibited by the metal ion linked to azo group. Pyrolysis of the polychelates of bis (1-azo-2-hydroxy-3-naphthoic acid) dyes led to the partial denitrogenation and decarboxylation.

Some of the products obtained have high thermal stability and can be considered for high temperature applications.

Pyrolyzed polychelate of lead with chloranilic acid has a magnetic moment of 2.6 B.M. per metal atom. The paramagnetic nature is related to stabilized radical anion. Pyrolyzed polychelates of bis (4-azo resorcinol) dyes with cobalt, nickel and iron exhibited ferromagnetic behaviour whereas that with copper exhibited antiferromagnetic behaviour. Pyrolyzed polychelate of bis (1-azo-2-hydroxy-3-naphthoic acid) dyes with cobalt also exhibited ferromagnetic behaviour. Pyrolyzed polychelate of copper with 2,4-dinitroso resorcinol exhibited diamagnetic behaviour. Thus, some pyrolyzed polychelates exhibited unusual magnetic behaviour as ferromagnetic, antiferromagnetic, paramagnetic and diamagnetic behaviour and can be considered useful for preparing magnetic tapes, ferromagnetic powders, stabilised radicals, etc.

Thermal studies (DTA and TGA) of the polychelates indicate solid-solid phase transitions in the case of (i) copper and iron polychelates of chloranilic acid and (ii) nickel polychelate of bis (1-azo-2-hydroxy-3-naphthoic acid) dye.

When pyrolysis led to the cross-polymerisation forming polynuclear or polycyclic ring compounds, it would bring about ordered orientation of two-dimentional net-works, favouring coplanarity of linked rings. The pyrolysis, then, would increase electrical conductivity through increased conjugation and coplanarity and decrease the energy gap for conduction due to reduced energy barriers (267, 268). Attempts were made to prepare pellets of the pyrolyzed products under different conditions. However, no pellet could be obtained in stable form for the determination of electrical conductivity. It is believed that many of these pyrolyzed polychelates would have high electrical conductivity, exhibit semi-conducting behaviour and find many applications.