EXPERIMENTAL

II EXPERIMENTAL

II. 1. General :

(i) Reagents and solvents :

All reagents and solvents used were of C.P.grade or better unless otherwise stated.

(ii) Analyses of new products :

Analyses of new products were obtained for metal, nitrogen, carbon and hydrogen as required, by known micromethods.

(iii) Melting points :

All melting points recorded herein are uncorrected.

(iv) UV Spectra :

Ultraviolet absorption spectra of a few compounds in suitable solvents were obtained from the readings of the Beckman Spectrophotometer Model DU using 10 mm. matched quartz cells.

(v) IR Spectra :

IR absorption spectra of a few compounds in KBr pellet form were obtained on Infra-cord model of Perkin-Elmer Spectrophotometer.

(vi) Magnetic susceptibility :

Magnetic susceptibilities of transition metal compounds were determined on Gouy's magnetic balance at room temperature using three tubes calibrated with ferrous ammonium sulphate.

(vii) Thermal analyses :

Thermal analyses (D.T.A. and T.G.A.) of some of the complexes were obtained in nitrogen atmosphere using Lenseis model.

(viii) Electrical resistivity :

Electrical resistivity of all substances in the form of pressed pellets were measured on Elico's million megohm-meter Model RM-70.

A pellet, 1.1 cm. in diameter and about 1.5 mm. thick, obtained by pressing the powder at about 6600 psi in a steel mould, was pressed between brass plates and placed in a small tube furnace for measurements of resistivity over a range of temperature.

The observations and results of the various determinations for different compounds are given at appropriate places in the following pages.

II. 2. 2,5-Dihydroxy-p-benzoquinone and its transition metal complexes :

(i) 2,5-Dihydroxy-p-benzoquinone :

It was prepared by the method of Jones and Shonle[235].

A 500 cc. three-necked flask was provided with a dropping funnel, a thermometer and a heavy glass stirrer. In the flask were placed 200 gms. of 50 % sodium hydroxide solution and 27.5 gms. of hydroquinone. This mixture was well stirred while 100 cc. of 27 % hydrogen peroxide were added dropwise from the dropping funnel. As soon as the temperature of the reaction reached 45°C, the flask was surrounded with an ice-bath and the rate of addition of hydrogen peroxide was adjusted so that the temperature was maintained between 45 to 50°C. About thirty minutes were required for the addition. Stirring was continued for two hours. The ice-bath was removed but the temperature was watched closely and kept below 50°C by occasional cooling. The reaction mixture now consisted of a thick paste of red-orange sodium salt of 2,5-dihydroxy-p-benzoquinone. It was stirred into 500 gms. of crushed ice and acidified with a mixture of 225 cc. of 36 % hydrochloric acid and 300 gms. of ice. The resulting yellow precipitates of 2,5-dihydroxy-p-benzoquinone were collected and washed with 200 cc. of ice water.

The product was dried in vacuum over calcium chloride (m.p. 212-14°C). It was recrystallised from ethyl alcohol. It melts at 218°C.

(ii) Thioaniline (4,4'-diaminodiphenyl sulfide):

It was prepared from p-chloronitrobenzene[236] through the intermediate formation of 4-nitro-4'-aminodiphenyl sulfide, by the method of Waiziss et al.[237]

(a) 4-Nitro-4'-aminodiphenyl sulfide:

A mixture of 480 gms. of sodium sulfide dissolved in 2000 cc. of water and 128 gms. of p-chloronitrobenzene was refluxed for 8 hours. 128 gms. of p-chloronitrobenzene was further added and refluxing was continued for 15 hours. The mixture was steam distilled to remove unchanged p-chloronitrobenzene. After cooling the crude orange-yellow crystals were filtered off. It was recrystallised from alcohol. It melts at 146°C.

(b) Thioaniline (4,4'-diaminodiphenyl sulfide):

To a boiling suspension of 200 gms. of 4-nitro-4'-aminodiphenyl sulfide in a mixture of 530 cc. of concentrated hydrochloric acid and 500 cc. of water, 180 gms. of tin turnings were added slowly and after the solution was completed, 40 cc. of concentrated hydrochloric acid and 22 gms. of tin were further added. After 10 minutes of boiling, 2 gms. of charcoal were added and the solution was boiled 15 minutes longer and filtered hot.

After cooling, 40 % of sodium hydroxide solution was added until strongly alkaline. The curdy precipitates were filtered and washed with water until washings were neutral to litmus and drained well.

The material was suspended in 1200 cc. of boiling alcohol, 5 gms. of charcoal were added and the mixture was refluxed for 30 minutes. The hot, almost colorless filtrate was added to 10 litres of cold water with stirring. White precipitates were obtained. These were filtered, dried in vacuum, and recrystallised from 50 % alcohol (m.p. 108°C).

(iii) p-Azoaniline (4,4′-diamino azobenzene):

It was prepared from p-nitroaniline through the intermediate formation of 4,4′-dinitro-azobenzene.

(a) 4,4′-Dinitro-azobenzene :

It was prepared by the method of Cook and Jones[238].

5 gms. of nitroaniline were dissolved in 12.5 cc. of concentrated sulphuric acid diluted to 55 cc. with water and 20 gms. of potassium persulfate were added to it in small portions at 60-70°C. After one hour the brown precipitates were collected. They contained some p-dinitrobenzene, which was removed by steam distillation. The residue was recrystallised from glacial acetic acid and then several times from toluene (m.p.214-16°C).

(b) p-Azoaniline (4,4′-diamino azobenzene) :

It was prepared by the method of Ashley et al.[239]

A mixture of 10 gms. of 4,4'-dinitro azobenzene, 100 gms. of crystalline sodium sulfide, 100 cc. of water and 300 cc. of alcohol was refluxed for half an hour. The precipitated mass was filtered hot. It was recrystallised from alcohol (m.p. 245-46°C).

(iv) Cobalt (II) complex of 2,5-dihydroxy-p-benzoquinone in alcoholic medium :

2.5 gms. of cobalt acetate dissolved in alcohol with few drops of glacial acetic acid were added to 1.4 gms. of 2,5-dihydroxy-p-benzoquinone dissolved in 50 cc. of alcohol, drop by drop, with stirring. Stirring was continued for 3 hours. The brick-red product separated. It was kept overnight and then filtered, washed with alcohol and ether and dried.

It is insoluble in water and all common organic solvents. It is brick-red in colour and does not melt upto 400°C.

Analysis :

Found : % Co : 25.8 ; % C : 30.9;

$C_6H_6O_6Co$ requires : % Co : 25.2 ; % C : 30.9.

Some properties of the polychelate (BQCo) are tabulated together with those of the ammino polychelates.

(v) Cobalt (II) complexes of 2,5-dihydroxy-p-benzoquinone in presence of (a) pyridine or (b) diamine :

Cobalt acetate dissolved in alcohol with a few drops of acetic acid was added drop by drop, with stirring, to the calculated amounts of 2,5-dihydroxy-p-benzoquinone and pyridine or diamine dissolved in alcohol (salt : ligand: amine:: 1:1:3). Stirring was continued for 2-3 hours. The mixture was then refluxed for 3 hours and left overnight. The precipitates were filtered, washed with alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p. etc. are presented in table-7. The magnetic susceptibility of these polychelates is presented in table-8. The infra-red spectrum of BQCo B is shown in fig. 15 and the thermal analyses (T.G.A. and D.T.A.) of BQCo B and BQCo Py are shown in figs. 16 and 17. The electrical resistivity of the polychelates over a range of temperature is presented in table-9.

When the amine used was not in sufficient excess, the product isolated contained less amount of amine. The analysis of some of these products, their m.p., etc. are presented in table-10. Their electrical resistivity over a range of temperature is presented in table-11.

(vi) Nickel (II) complex of 2,5-dihydroxy-p-benzoquinone in alcoholic medium :

It was prepared by the method of Kanda.[120] 2.38 gms. of nickel chloride dissolved in alcohol were added to 1.4 gms. of 2,5-dihydroxy-p-benzoquinone dissolved in 50 ml. of alcohol, drop by drop, with stirring. Stirring

Table 7

Cobalt chelate polymers with 2,5-dihydroxy-p-benzoquinone and an amine

No.	Complex	Amine used	m.p. (°C)	Colour	Formula	Analysis			
						% Co found	% N found	% Co reqd.	% N reqd.
1.	BQCo Py	Pyridine	> 400	Brick red	$C_{11}H_9NO_5Co$	20.67	4.20	20.05	4.76
2.	BQCo B	Benzidine	> 400	Dark brown	$C_{18}H_{16}N_2O_5Co$	15.18	7.25	14.78	7.02
3.	BQCo A	Azoaniline	> 400	Brown	$C_{12}H_{18}N_2O_9Co$	14.31	7.63	14.70	7.00

Table 8

Magnetic susceptibility of cobalt chelate polymers

No.	Complex	Temperature ($^{\circ}$C)	Magnetic susceptibility $\chi_g \times 10^6$	Diamagnetic correction (per cobalt atom) $\times 10^6$
1.	BQCo	32.0	(a) 46.90	- 80.6
2.	BQCo Py	31.5	32.3	-119.4
3.	BQCo B	31.0	27.70	-191.2
4.	BQCo A	33.7	27.20	-178.1
5.	BQCo $B_{(f)}$	32.0	(b) 30.90	-153.2
6.	BQCo P	32.0	29.70	-138.1

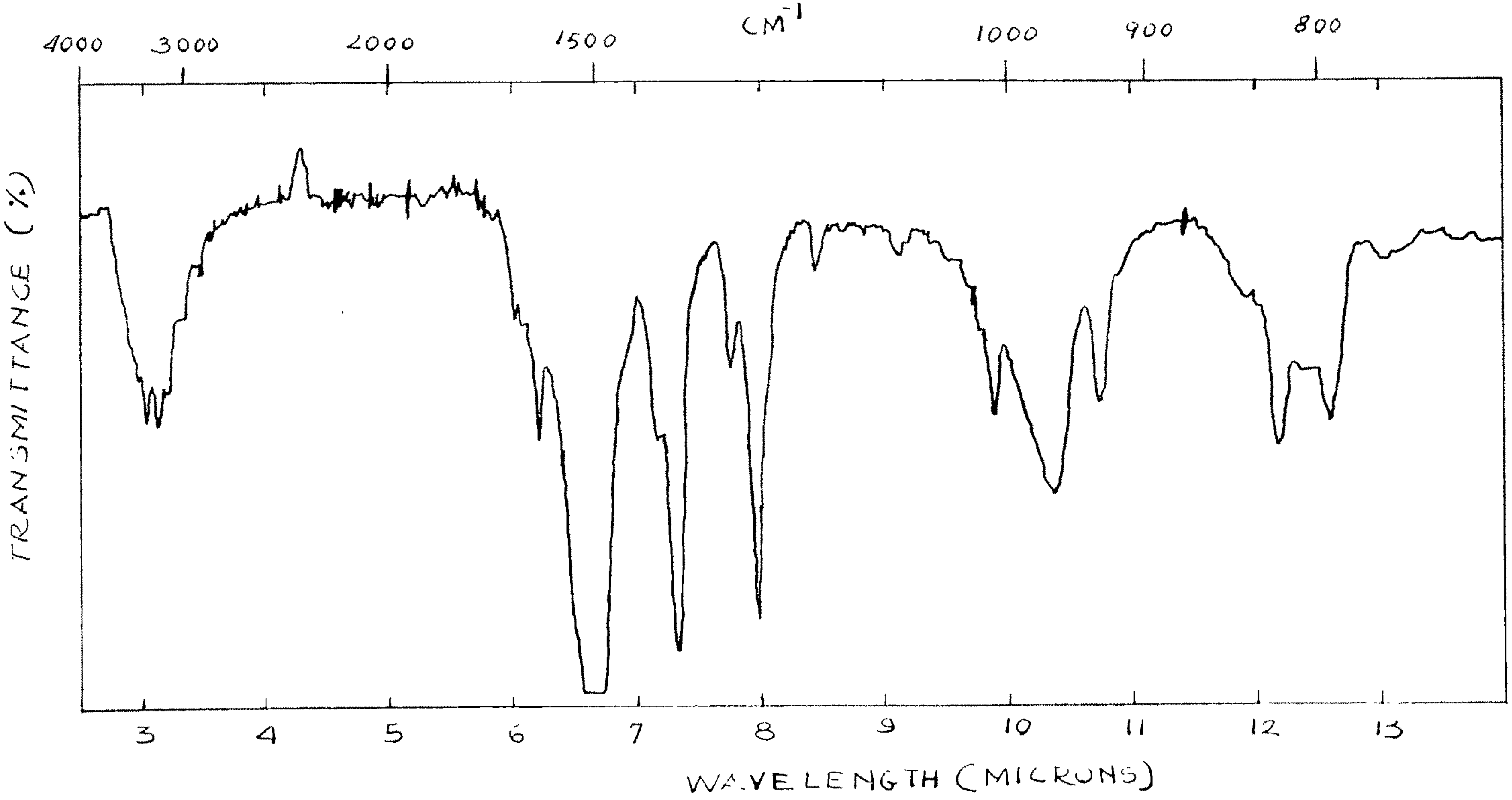

FIG. 15: IR SPECTRUM OF BQCo B

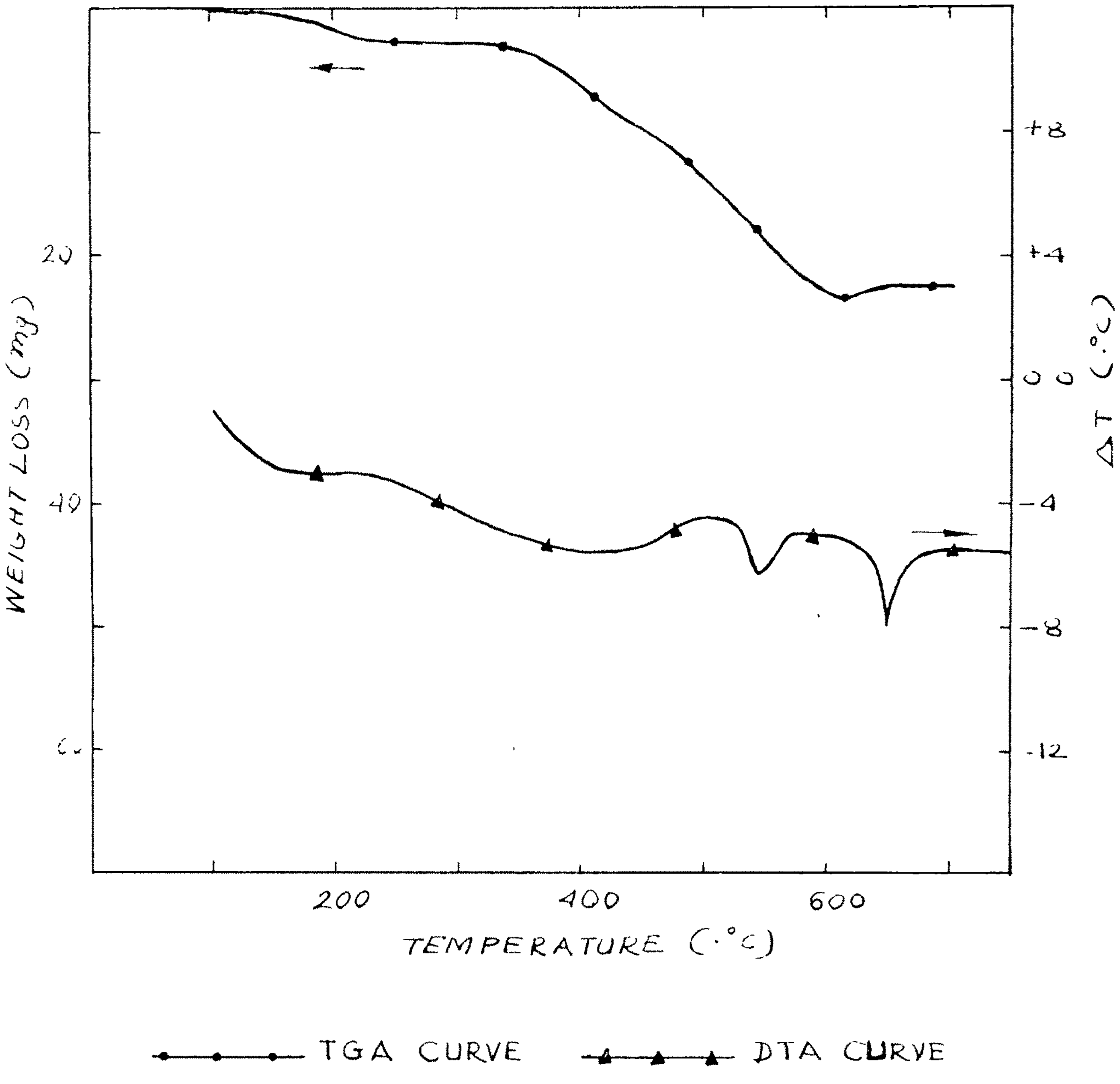

FIG 16: TGA AND DTA OF BQCo B

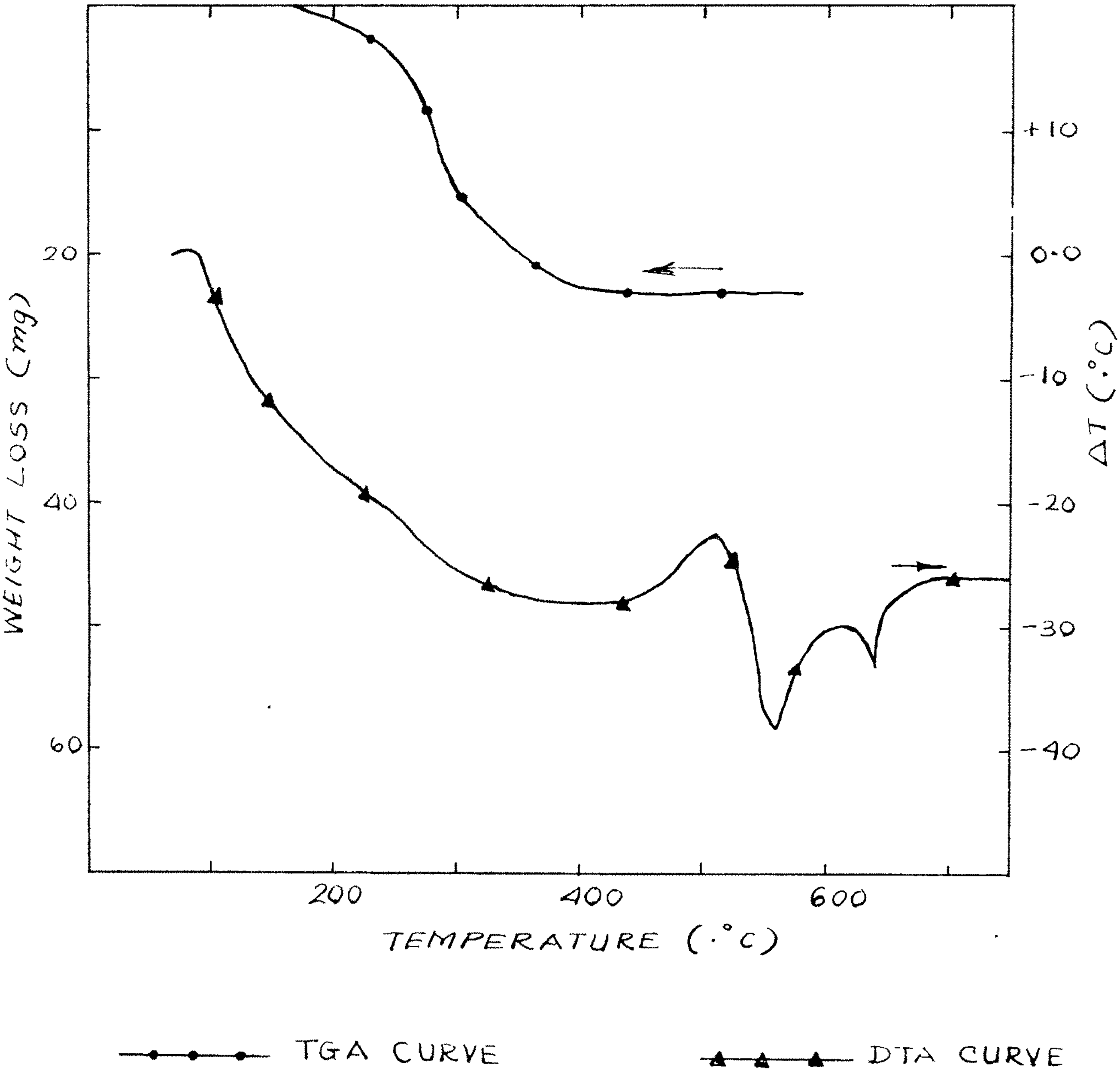

FIG. 17: TGA AND DTA OF BQCo Py

Table 9

Electrical resistivity of cobalt chelate polymers at different temperatures.

(a) BQCo

Temp. (°C)	Resistivity (ρ x 10^{-13} ohm cm.)
62	6.4
75	5.1
101	3.2
118	2.6
120	2.5
100	3.2
82	4.6
60	10.3

(b) BQCo B

Temp. (°C)	Resistivity (ρ x 10^{-12} ohm cm.)
83	61.1
92	24.5
101	16.5
110	9.8
117	6.1
109	9.8
100	18.3
94	27.5
85	53.2

(c) BQCo A

Temp. (°C)	Resistivity (ρ x10^{-12} ohm cm.)	Temp. (°C)	Resistivity (ρ x 10^{-12} ohm cm.)
93	69.4	135	1.2
114	6.4	120	4.5
130	1.8	100	37.2
152	0.25		

Table 10

Cobalt chelate polymers with 2,5-dihydroxy-p-benzoquinone and an amine

No.	Complex	Amine used	m.p. (°C)	Colour	Formula	Analysis % Co found	 % N found	 % Co reqd.	 % N reqd.
1.	BQCo $B_{(f)}$	Benzidine	> 400	Black	$C_{66}H_{66}N_6O_{30}Co_5$	16.80	5.00	17.13	4.89
2.	BQCo P	p-Phenylene diamine	> 400	Black	$C_{54}H_{62}N_8O_{30}Co_5$	18.32	7.35	18.45	7.02
3.	BQCo T	Thioaniline	> 400	Brown	$C_{42}H_{32}N_2O_{25}SCo_5$	22.82	2.13	22.82	2.17

Table 11

Electrical resistivity of cobalt chelate polymers at different temperatures.

(a) BQCo $B_{(f)}$

Temp. (°C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
40	70.9
50	41.9
60	25.8
70	15.5
80	9.7
70	15.5
60	25.1
50	41.9
40	70.9

(b) BQCo P

Temp. (°C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
99	21.9
109	9.7
132	1.9
149	0.68
130	2.3
115	7.3
101	19.5

(c) BQCo T

Temp. (°C)	Resistivity ($\rho \times 10^{-12}$ ohm cm.)	Temp. (°C)	Resistivity ($\rho \times 10^{-12}$ ohm cm.)
90	18.3	135	0.49
104	4.9	121	1.2
117	1.7	109	3.1
131	0.52	93	13.5
142	0.26		

was continued for 3 hours. The mixture was then refluxed for 3 hours. The light pink product separated. It was kept overnight and then filtered, washed with alcohol and ether and dried.

It is insoluble in water and all common organic solvents. It does not melt upto 400 °C.

Analysis :

	Found	: % Ni : 23.5 ; % C : 29.7 ;
$C_6H_8O_7Ni$	requires	: % Ni : 23.4 ; % C : 28.7 .

Kanda found that the complex is a linear polymer with nickel: ligand ratio of 1:1 .

Some properties of the polychelate (BQNi) are tabulated together with those of the ammino polychelates.

(vii) Nickel (II) complexes of 2,5-dihydroxy-p-benzoquinone in presence of (a) pyridine or (b) diamine :

Nickel chloride dissolved in alcohol was added, drop by drop, with stirring, to the calculated amounts of 2,5-dihydroxy-p-benzoquinone and pyridine or diamine dissolved in alcohol (salt : ligand : amine :: 1:1:3). Stirring was continued for 2-3 hours. The mixture was then refluxed for 3 hours and left overnight. The precipitates were filtered,washed with alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p. etc. are presented in table-12. The magnetic susceptibility of these polychelates are presented in table-13. The infra-red

Table 12

Nickel chelate polymers with 2,5-dihydroxy-p-benzoquinone and an amine

No.	Complex	Amine used	m.p. (°C)	Colour	Formula	Analysis			
						% Ni found	% N found	%Ni reqd.	% N reqd.
1.	BQNi Py	Pyridine	> 400	Orange red	$C_{16}H_{12}N_2O_4Ni$	16.69	7.38	16.55	7.89
2.	BQNi P	p-Phenylene diamine	> 400	Ash-green	$C_{12}H_{10}N_2O_4Ni$	18.35	9.30	19.26	9.19
3.	BQNi T	Thio-aniline	> 400	Grey	$C_{144}H_{204}N_{14}O_{90}S_7Ni_{10}$	13.55	4.30	13.41	4.48
4.	BQNi A	Azo-aniline	> 400	Grey	$C_{18}H_{30}N_4O_{12}Ni$	10.83	10.25	10.60	10.10

Table 13

Magnetic susceptibility of nickel chelate polymers

No.	Complex	Temperature (. $^{\circ}$C)	Magnetic susceptibility $\chi_g \times 10^6$	Diamagnetic correction (per nickel atom) $\times 10^6$
1.	BQNi	33.0	17.7	- 91.0
2.	BQNi Py	33.9	11.0	- 158.2
3.	BQNi P	33.5	13.0	- 131.6
4.	BQNi T	34.5	9.4	- 210.4
5.	BQNi A	34.5	8.2	- 265.1

spectrum of BQNi is shown in fig. 18. The electrical resistivity of these polychelates over a range of temperature is presented in table-14.

(viii) a Copper (II) complex of 2,5-dihydroxy-p-benzoquinone in alcoholic medium :

It was prepared by the method of Kanda and Saito[240].

2.0 gms. of copper acetate dissolved in alcohol with few drops of glacial acetic acid were added to 1.4 gms. of 2,5-dihydroxy-p-benzoquinone dissolved in 50 ml. of alcohol, drop by drop, with stirring. Stirring was continued for 2-3 hours after the addition was completed. The mixture was then refluxed for 3 hours. The brown product separated. It was kept overnight and then filtered, washed with alcohol and ether and dried.

It is insoluble in water and all common organic solvents. It is dark brown in colour and decomposes at 360°C.

Analysis :

	Found	: % Cu : 29.5 ; % C : 34.8 ;
(Kanda and Saito)	Found	: % Cu : 30.0 ; % C : 35.5 ;
$C_{12}H_6O_9Cu_2$	requires	: % Cu : 30.2 ; % C : 34.3.

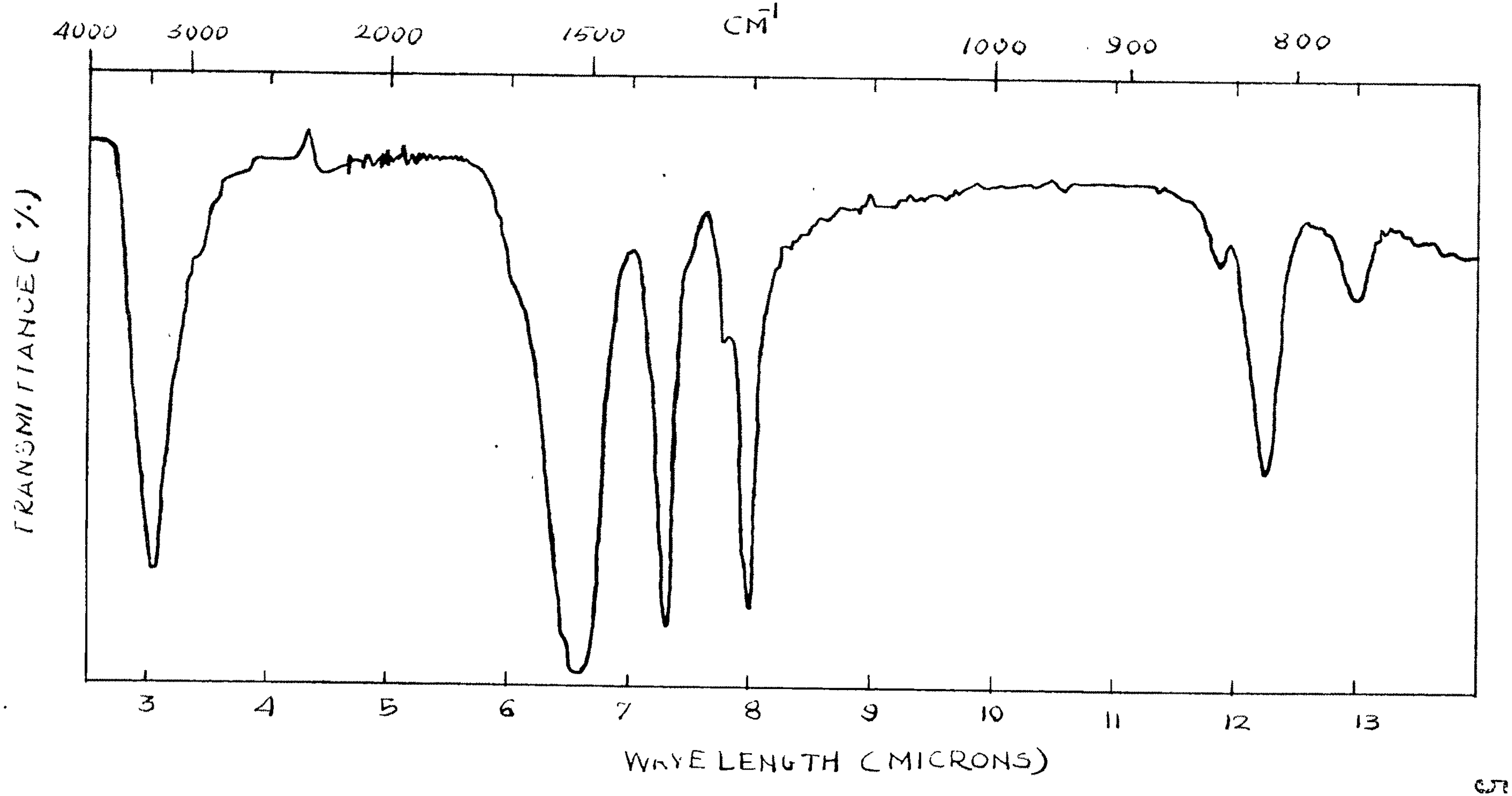

FIG. 18: IR SPECTRUM OF BQNi

Table 14

Electrical resistivity of nickel chelate polymers at different temperatures.

(a) BQNi

Temp. (. °C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
120	84.5
130	39.7
140	14.9
150	5.5
155	3.8
145	9.4
135	25.8
125	61.6

(b) BQNi Py

Temp. (. °C)	Resistivity ($\rho \times 10^{-12}$ ohm cm.)
121	17.6
128	11.4
133	7.4
138	4.0
145	1.9
140	3.5
131	7.7
127	10.9
122	17.6

(c) BQNi P

Temp. (. °C)	Resistivity ($\rho \times 10^{-12}$ ohm cm.)	Temp. (. °C)	Resistivity ($\rho \times 10^{-12}$ ohm cm.)
100	17.6	133	2.4
110	8.7	121	4.6
117	5.3	109	9.7
135	2.4	98	19.4
145	1.3		

Table 14 (Contd.)

Electrical resistivity of nickel chelate polymers at different temperatures.

(d) BQNi T		(e) BQNi A	
Temp. (. ^{o}C)	Resistivity (ρ x 10^{-11} ohm cm.)	Temp. (. ^{o}C)	Resistivity (ρ x 10^{-11} ohm cm.)
105	39.6	94	25.8
115	16.8	105	11.0
125	6.0	119	2.6
135	3.0	129	1.1
144	1.3	137	0.56
136	2.7	126	1.4
122	7.8	117	3.8
114	15.0	108	7.0
98	72.0	96	23.4

(viii) b Copper (II) complex of 2,5-dihydroxy-p-benzoquinone from diammonium salt of 2,5-dihydroxy-p-benzoquinone :

It was prepared by the method of Frank, Clerk and Coker[241].

1.4 gms. of 2,5-dihydroxy-p-benzoquinone were dissolved in alcohol and alcoholic ammonia was added dropwise to it, to precipitate the red diammonium salt. The product was filtered washed with alcohol, and ether and dried.

1.7 gms. of copper chloride dissolved in 20 cc. of water were added to 1.74 gms. of diammonium salt of 2,5-dihydroxy-p-benzoquinone dissolved in 50 cc. of water, drop by drop, with stirring. Stirring was continued for 3 hours. The dirty green product separated. It was kept overnight and filtered, washed with water, alcohol and ether and dried.

It is insoluble in water and all common organic solvents. It is dirty green in colour and decomposes at 350°C.

Analysis :

	Found	: % Cu: 27.4 ;	% C : 31.7 ;
(Frank, et al)	Found	: % Cu: 27.1 ;	% C : 31.9 ;
$C_{12}H_{10}O_{11}Cu_2$	requires	: % Cu: 27.6 ;	% C : 31.7 .

(ix) Copper (II) complexes of 2,5-dihydroxy-p-benzoquinone in presence of (a) pyridine or (b) diamine :

Copper acetate dissolved in alcohol with a few drops of acetic acid was added, drop by drop, with stirring, to the calculated amounts of 2,5-dihydroxy-p-benzoquinone and pyridine or diamine dissolved in alcohol (salt : ligand:amine:: 1:1:2). Stirring was continued for 2-3 hours. The mixture was then refluxed for 3 hours and left overnight. The precipitates were filtered, washed with alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p., etc. are presented in table 15. The magnetic susceptibility of these compounds is presented in table 16. The infra-red spectrum of BQCu A is shown in fig. 19. The electrical resistivity of the compounds over a range of temperature is given in table 17.

(x) <u>Iron(II) complex of 2,5-dihydroxy-p-benzoquinone in aqueous alcoholic medium</u> :

2.78 gms. of ferrous sulphate dissolved in 25 % alcohol were added to 1.4 gms. of 2,5-dihydroxy-p-benzoquinone dissolved in 100 cc. 25 % alcohol, drop by drop, with stirring. Stirring was continued for 2-3 hours. The dark brown product separated. It was left overnight and then filtered, washed with water, alcohol and ether and dried.

It is insoluble in water and all common organic solvents. It is dark brown in colour and does not decompose upto 400 °C.

Table 15

Copper chelate polymers with 2,5-dihydroxy-p-benzoquinone and an amine

No.	Complex	Amine used	m.p. (°C)	Colour	Formula	Analysis			
						% Cu found	% N found	% Cu reqd.	% N reqd.
1.	BQCu Py	Pyridine	320(d)	Brick red	$C_{39}H_{31}N_3O_{20}Cu_4$	23.07	3.60	22.78	3.77
2.	BQCu B	Benzidine	> 400	Red brown	$C_{42}H_{36}N_4O_{15}Cu_3$	18.79	5.30	18.59	5.46
3.	BQCu T	Thio-aniline	> 400	Black	$C_{60}H_{62}N_6O_{25}S_3Cu_4$	15.15	5.32	15.73	5.20
4.	BQCu A	Azo-aniline	> 400	Black	$C_{18}H_{20}N_4O_7Cu$	13.65	11.50	13.60	11.98

Table 16

Magnetic susceptibility of copper chelate polymers

No.	Complex	Temperature (. ^{o}C)	Magnetic susceptibility $\chi_g \times 10^6$	Diamagnetic correction (per copper atom) $\times 10^6$
1.	BQCu	30.5	6.4	- 75.3
2.	BQCu Py	30.3	6.3	-107.0
3.	BQCu B	34.5	4.6	-150.8
4.	BQCu T	33.8	3.1	-185.2
5.	BQCu A	33.9	4.0	-223.2

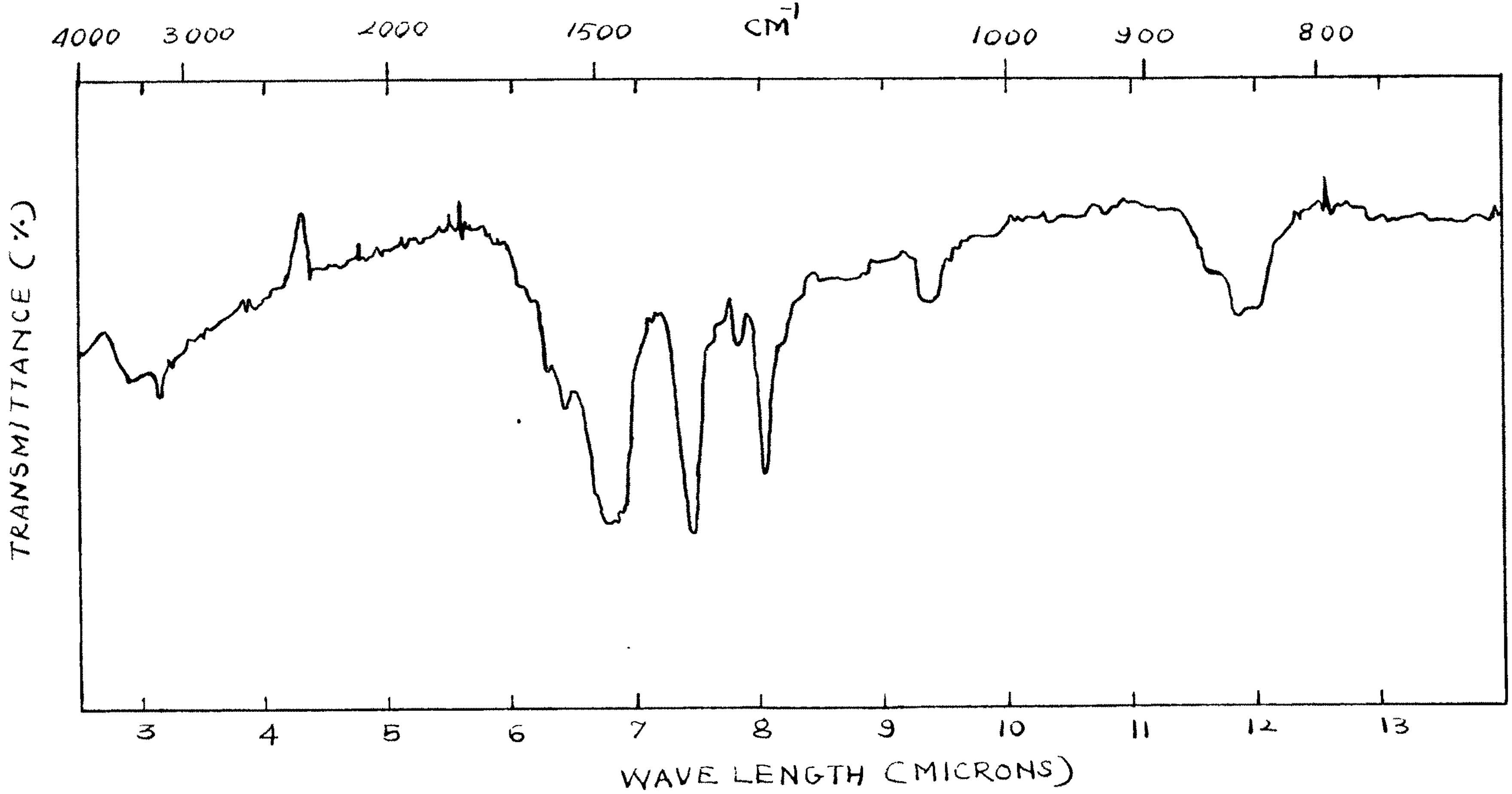

FIG. 19: IR SPECTRUM OF BQCu A

Table 17

Electrical resistivity of copper chelate polymers at different temperatures.

(a) BQCu

Temp. (°C)	Resistivity (ρ X 10^{-9} ohm cm.)
40	52.8
60	26.4
80	17.6
95	12.3
115	8.4
120	7.9
105	10.6
90	14.1
70	22.0
50	39.6

(b) BQCu Py

Temp. (°C)	Resistivity (ρ X 10^{-10} ohm cm.)
40	26.4
50	16.1
60	12.8
70	5.3
80	4.0
90	3.6
80	4.4
70	7.3
60	11.5
50	17.5
40	27.6

(c) BQCu B

Temp. (°C)	Resistivity (ρ X 10^{-10} ohm cm.)	Temp. (°C)	Resistivity (ρ X 10^{-10} ohm cm.)
79	117.4	131	2.2
99	26.4	110	10.0
120	4.8	89	58.7
143	1.0	70	352.2

Table 17 (Contd.)

Electrical resistivity of copper chelate polymers at different temperatures.

(d) BQCu T		(e) BQCu A	
Temp. ($^{\circ}$C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)	Temp. ($^{\circ}$C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
87	46.6	100	35.5
97	18.6	110	17.0
112	4.7	120	7.5
125	1.5	130	3.1
137	0.8	140	1.5
149	0.31	150	0.56
140	0.59	135	2.4
130	1.2	125	4.9
115	4.0	115	9.4
100	14.3	105	24.5

Iron to ligand ratio is found to be 1:0.93 on analysis, (Found: Fe : 21.18 % ; C: 25.60 %).

Some properties of the above complex (BQFe) are tabulated together with those of the ammino complexes.

(xi) Iron (II) complexes of 2,5-dihydroxy-p-benzoquinone in presence of (a) pyridine or (b) diamine :

Ferrous sulphate dissolved in 50 % alcohol was added, drop by drop, with stirring, to the calculated amounts of 2,5-dihydroxy-p-benzoquinone and pyridine or diamine dissolved in alcohol (salt : ligand : amine :: 1 : 1 : 2). Stirring was continued for 2-3 hours. The mixture was then refluxed for 3 hours, and left overnight. The precipitates were filtered, washed with water, alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p., etc. are presented in table 18. The magnetic susceptibility of these compounds is presented in table 19. The infra-red spectra of BQFe is shown in fig. 20. The electrical resistivity of the compounds over a range of temperature is given in table 20.

(xii) Addition products of 2,5-dihydroxy-p-benzoquinone and diamine :

The diamine dissolved in alcohol was added, drop by drop, with stirring, to the calculated amount of 2,5-dihydroxy-p-benzoquinone dissolved in alcohol (ligand: amine :: 1:1). Stirring was continued for two hours.

Table 18

Iron chelate polymers with 2,5-dihydroxy-p-benzoquinone and an amine

No.	Complex	Amine used	m.p. (°C)	Colour	Formula	Analysis			
						% Fe found	% N found	% Fe reqd.	% N reqd.
1.	BQFe Py	Pyridine	> 400	Dark brown	$C_{13}H_{25}NO_{16}Fe_2$	17.97	2.61	18.29	2.29
2.	BQFe T	Thioaniline	> 400	Black	$C_{60}H_{108}N_6O_{48}S_3Fe_4$	11.47	4.0	11.18	4.20
3.	BQFe A	Azoaniline	> 400	Black	$C_{78}H_{128}N_{16}O_{55}Fe_5$	11.41	9.4	11.41	9.15

Table 19

Magnetic susceptibility of iron chelate polymers

No.	Complex	Temperature (. ^{o}C)	Magnetic susceptibility $\chi_g \times 10^{6}$	Diamagnetic correction (per iron atom) $\times 10^{6}$
1.	BQFe	34.0	41.4	- 137.5
2.	BQFe Py	28.0	41.4	- 126.1
3.	BQFe T	33.0	21.1	- 245.4
4.	BQFe A	33.8	21.9	- 239.9

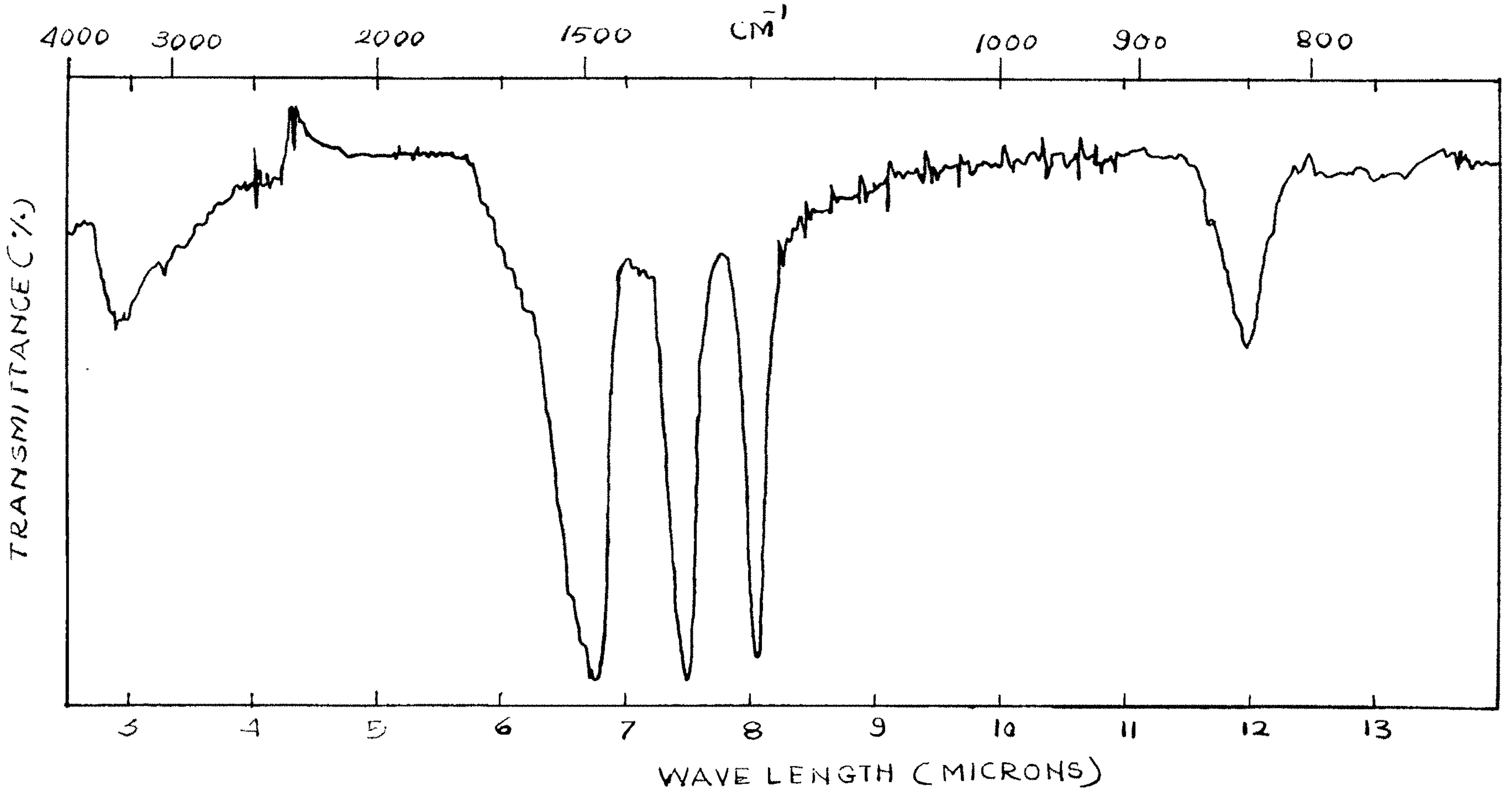

FIG. 20: IR SPECTRUM OF BQFe.

Table 20

Electrical resistivity of iron chelate polymers at different temperatures.

(a) BQFe		(b) BQFe Py	
Temp. (°C)	Resistivity ($\rho \times 10^{-10}$ ohm cm.)	Temp. (°C)	Resistivity ($\rho \times 10^{-8}$ ohm cm.)
40	44.1	40	14.2
62	10.0	59	5.5
80	3.2	75	2.4
98	1.3	96	1.0
118	0.48	98	0.9
100	1.1	82	1.8
80	3.6	64	4.1
60	11.2	40	14.2
40	44.1		

Table 20 (Contd.)

Electrical resistivity of iron chelate polymers at different temperatures.

(c) BQFe T Temp. (.°C)	Resistivity (ρ x 10^{-8} ohm cm.)	(d) BQFe A Temp. (.°C)	Resistivity (ρ x 10^{-8} ohm cm.)
38	24.0	38	48.4
62	6.2	60	13.6
85	2.0	81	4.8
106	0.8	102	2.0
101	1.0	120	1.0
81	2.4	102	1.8
60	6.7	81	5.7
38	24.0	59	17.4
		38	48.4

The mixture was then refluxed for 3 hours and left overnight. The reddish product separated. It was filtered, washed with alcohol and ether and dried. They are insoluble in water,alcohol,acetone,ether,petroleum ether and benzene and soluble in dimethylformamide and pyridine.

The analysis of the products, their m.p.,etc.are presented in table 21. The optical densities of their solutions are presented in table 22 and their electrical resistivity over a range of temperature is given in table 23.

II.3 Naphthazarin and its transition metal complexes :

(i) Naphthazarin (5,8-dihydroxy-1,4-naphthaquinone) :

It was prepared by the method of Zahn and Ochwat[242].

A mixture of 100 gms. of anhydrous aluminium chloride,11 gms. of hydroquinone,20 gms. of sodium chloride and 10 gms. of maleic anhydride was ground and placed in a reaction flask. The flask was kept in an oil bath at a temperature of 200-20 °C for fifteen minutes. The colour changed to red first and to dark violet later. The flask was removed from the oil bath and kept cool. Aluninium chloride was decomposed by dilute hydrochloric acid and the solution was filtered. The residue was extracted with acetic acid and precipitated with water. The precipitates were filtered,dried and recrystallised from alcohol. It is reddish brown in colour and decomposes on heating at ordinary pressure.

It is soluble in acetic acid.It gives blue colour

Table 21

Addition products of 2,5-dihydroxy-p-benzoquinone and diamine

No.	Addition product	Amine used	m.p. (°C)	Colour	Formula	Analysis	
						% N found	% N required
1.	BQ B	Benzidine	> 390	Brick red	$C_{18}H_{18}N_2O_5$	8.09	8.20
2.	BQ P	p-Phenylene diamine	> 390	Brick red	$C_{12}H_{14}N_2O_5$	10.2	10.53
3.	BQ A	Azoaniline	> 390	Brown red	$C_{18}H_{18}N_4O_5$	15.57	15.13

Table 22

Optical densities of the addition products in UV region.

Wave length (mμ)	Optical densities		
	BQ B	BQ P	BQ A
360	0.06	0.06	0.279
352	0.095	0.085	0.219
344	0.150	0.133	0.175
336	0.285	0.325	0.186
328	0.60	0.76	0.275
320	0.72	0.886	0.306
312	0.78	0.892	0.310
304	0.73	0.69	0.255
298	0.70	0.530	0.215
292	0.66	0.370	0.166
286	0.63	0.252	0.136
280	0.59	0.180	0.126
274	0.538	0.144	0.147
268	0.451	0.143	0.185
262	0.355	0.166	0.220
256	0.272	0.232	0.245
250	0.225	0.335	0.255
244	0.226	0.45	0.265
238	0.25	0.52	0.264

Table 23

Electrical resistivity of addition products at different temperatures.

(a) BQ B

Temp. (. ^{o}C)	Resistivity (ρ X 10^{-12} ohm cm.)
105	16.9
115	9.4
125	5.0
135	2.8
145	1.6
140	2.0
130	3.8
120	6.4
110	12.9

(b) BQ P

Temp. (. ^{o}C)	Resistivity (ρ X 10^{-12} ohm cm.)
115	19.8
125	9.2
135	4.6
145	2.6
155	1.2
150	1.7
140	3.7
130	6.6
120	13.2

(c) BQ A

Temp. (. ^{o}C)	Resistivity (ρ X 10^{-11} ohm cm.)	Temp. (. ^{o}C)	Resistivity (ρ X 10^{-11} ohm cm.)
60	38.4	115	0.17
70	12.0	100	0.77
90	1.4	80	4.3
110	0.24	65	21.6
120	0.11		

in alkali and magenta colour in sulphuric acid. It is sparingly soluble in water, alcohol and ether.

(ii) Transition metal complexes of naphthazarin :

Metal acetate dissolved in alcohol with a few drops of acetic acid was added, drop by drop, with stirring, to the calculated amount of naphthazarin dissolved in alcohol (salt : ligand :: 1:1). Stirring was continued for 2-3 hours. The mixture was then refluxed for 3 hours and left overnight. The precipitates were filtered, washed with alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p., etc. are presented in table 24. The magnetic susceptibility of these complexes is presented in table 25. Their electrical resistivity over a range of temperature is given in table 26.

II. 4 Dihydroxy anthraquinones and their transition metal complexes :

(i) Quinizarin (1,4-dihydroxy anthraquinone) :

Quinizarin was prepared by the condensation of phthalic anhydride with hydroquinone[243].

A mixture of 5 gms. of pure hydroquinone and 20 gms. of phthalic anhydride was heated in an open flask with a mixture of 100 gms. of pure sulphuric acid and 10 gms. of water for 3 hours in an oil bath at 170-80 °C and finally for one hour at 190-200 °C. The hot solution was poured into about 400 cc. of water in a porcelain disk with stirring,

Table 24

Transition metal complexes of Naphthazarin

No.	complex	Metal used	m.p. (. ^{o}C)	Colour	Formula	Analysis					
						%C found	%H found	%M found	%C reqd.	%H reqd.	%M reqd.
1.	NQ Cu	Copper	340 (d)	Violet	$C_{10}H_8O_6Cu$	39.45	2.24	23.43	41.74	2.78	22.11
2.	NQ Co	Cobalt	>400	Black	$C_{10}H_{10}O_7Co$	39.28	3.22	20.27	39.89	3.32	19.57

Table 25

Magnetic susceptibility of complexes of Naphthazarin

No.	Complex	Temperature (. ^{o}C)	Magnetic susceptibility $\chi_g \times 10^6$	Diamagnetic correction **(per metal atom)** $\times 10^6$
1.	NQ Cu	31.7	6.5	**- 111.8**
2.	NQ Co	31.3	34.7	**- 122.3**

Table 26

Electrical resistivity of complexes of Naphthazarin at different temperatures.

(a) NQCu

Temp. (.°C)	Resistivity (ρ X 10^{-12} ohm cm.)
40	32.5
50	18.7
60	11.4
70	6.8
80	4.4
70	7.1
60	11.4
50	19.5
40	32.5

(b) NQCo

Temp. (.°C)	Resistivity (ρ X 10^{-11} ohm cm.)
40	78.5
50	35.9
60	17.9
70	7.8
80	3.9
70	7.8
60	15.7
50	34.8
40	78.5

heated to boiling and filtered hot with Buchner funnel. The residue was again boiled with water and filtered hot. The precipitates were boiled with 200 cc. of glacial acetic acid and filtered hot with suction. The filtrate was poured into a beaker and treated with its own volume of hot water. The residue remaining on the filter was again boiled up with 100 cc. of glacial acetic acid and after filtration was treated as above. On cooling the crude quinizarin separated. It was filtered, washed with water and dried on a water bath and finally in an air oven at 120°C. After drying it was distilled from a small retort and collected in a beaker. It was recrystallised from glacial acetic acid in the form of large orange yellow leaves. It melts at 202°C.

(ii) <u>Anthrarufin (1,5-dihydroxy anthraquinone)</u> :

It was prepared from 1,5-diamino-anthraquinone[244].

1.2 gms. of 1,5-diamino anthraquinone were dissolved in 6 cc. of con.sulphuric acid. The colour changed from red to yellow to colourless. The mixture was cooled in an ice bath at 0-5°C and gradually 1.0 gm. of sodium nitrite powder added with stirring and the mixture was kept in an oil bath at 90°C for half an hour. The reaction mixture was allowed to cool and water was added to precipitate anthrarufin. The mixture was then boiled for one hour and cooled. The precipitates were filtered, washed and dried. The product was recrystallised from glacial acetic acid in the form of pale yellow plates. It melts at 280°C.

It is soluble in benzene,nitrobenzene,potassium hydroxide, etc. and gives crimson colour with concentrated sulphuric acid. It is sparingly soluble in alcohol and acetic acid and practically insoluble in carbonates and ammonia.

(iii) Transition metal complexes of quinizarin(1,4-dihydroxy anthraquinone) :

(a) Metal acetate dissolved in dilute ammonia was added, drop by drop, with stirring, to the calculated amount of quinizarin dissolved in dilute sodium hydroxide solution (salt:ligand:: 1:1).Stirring was continued for 3 hours. It was then left overnight. The product was filtered, washed with water, alcohol and ether and dried.

(b) Metal acetate dissolved in alcohol with a few drops of acetic acid was added, drop by drop, with stirring, to the calculated amount of quinizarin dissolved in alcohol (salt:ligand:: 1:1). Stirring was continued for 2-3 hours. The mixture was then refluxed for 3 hours and left overnight. The product was filtered,washed with alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p. etc., are presented in table 27. The magnetic susceptibility of these complexes is presented in table 28 and their electrical resistivity over a range of temperature is given in table 29.

Table 27

Transition metal complexes of Quinizarin

No. Complex	Metal used	m.p. (°C)	Colour	Formula	Analysis					
					%C found	% H found	% M found	% C reqd.	% H reqd.	% M reqd.
a :(Ammonia method)										
1. AQ Cu(Am)	Copper	> 400	Black	$C_{14}H_8O_5Cu$	52.2	2.6	17.75	52.57	2.50	19.89
b : (Acetic acid method)										
2. AQ Cu(Ac)	Copper	> 400	Dark violet	$C_{14}H_8O_5Cu$	52.64	2.19	18.94	52.57	2.50	19.89
3. AQ Co(Ac)	Cobalt	> 400	Dark violet	$C_{14}H_{10}O_6Co$	51.55	2.68	17.19	50.47	3.00	17.70

Table 28

Magnetic susceptibility of chelate polymers of Quinizarin

No.	Complex	Temperature ($^{\circ}$C)	Magnetic susceptibility $\chi_g \times 10^6$	Diamagnetic correction (per metal atom) $\times 10^6$
1.	AQCu (Am)	30.5	6.8	- 132.6
2.	AQCu (Ac)	31.0	6.5	- 132.6
3.	AQCo (Ac)	32.0	29.1	- 143.1

Table 29

Electrical resistivity of chelate polymers of Quinizarin at different temperatures.

(a) AQCu (Am)

Temp. (°C)	Resistivity (ρ x 10^{-11} ohm cm.)
50	23.5
60	9.4
70	4.5
80	2.3
90	1.2
80	2.3
70	4.7
60	9.4
50	23.5

(b) AQCu (Ac)

Temp. (°C)	Resistivity (ρ x 10^{-11} ohm cm.)
65	25.1
80	7.9
95	3.2
115	0.89
135	0.30
120	0.63
110	1.3
85	6.3
70	17.8

(c) AQCo (Ac)

Temp. (°C)	Resistivity (ρ x 10^{-9} ohm cm.)	Temp. (°C)	Resistivity (ρ x 10^{-9} ohm cm.)
40	73.9	80	5.0
50	38.0	70	9.5
60	16.9	60	16.9
70	9.0	50	33.8
80	5.0	40	73.9
90	2.7		

(iv) Transition metal complexes of anthrarufin (1,5-dihydroxyanthraquinone) :

Metal acetate dissolved in dilute ammonia was added, drop by drop, with stirring, to the calculated amount of anthrarufin dissolved in dilute potassium hydroxide solution (salt:ligand :: 1:1). Stirring was continued for 3 hours. It was then left overnight. The product was filtered, washed with water, alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p. etc. are presented in table 30. Their electrical resistivity over a range of temperature is given in table 31.

II.5. Derivatives of 2,6-dihydroxy naphthalene and their transition metal complexes :

(i) Dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene:

(a) 2,6-Diacetoxy naphthalene :

It was prepared by the method of Feiser and Lothrop[245].

16 gms. of 2,6-dihydroxy naphthalene were added to 50 cc. acetic anhydride and refluxed for 4 hours at 105°C. The solution on cooling deposited the diacetyl derivative. It was filtered and extracted with ether to remove impurities. It is a pale yellow compound, melting at 175°C.

Table 30

Transition metal complexes of Anthrarufin

No.	Complex	Metal used	m.p. (°C)	Colour	Formula	Analysis					
						%C found	%H found	%M found	%C reqd.	%H reqd.	%M reqd.
1.	AQR-Cu	Copper	> 400	Red-brown	$C_{14}H_8O_5Cu$	53.46	2.46	20.08	52.57	2.50	19.89
2.	AQR-Co	Cobalt	> 400	Dark-brown	$C_{28}H_{18}O_{12}Co_3$	47.12	2.86	24.85	46.48	2.49	24.46
3.	AQR-Ni	Nickel	> 400	Violet red	$C_{56}H_{36}O_{23}Ni_5$	49.03	2.59	21.9	49.09	2.63	21.44

Table 31

Electrical resistivity of complexes of Anthrarufin at different temperatures.

(a) AQRCu

Temp. (°C)	Resistivity ($\rho \times 10^{-12}$ ohm cm.)
130	27.6
135	19.3
140	13.8
145	9.9
150	7.3
143	11.0
138	15.4
134	20.9
130	27.6

(b) AQRCo

Temp. (°C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
40	92.8
60	29.7
80	11.1
100	4.6
105	3.7
80	11.6
60	27.9
40	92.8

(c) AQRNi

Temp. (°C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)	Temp. (°C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
115	63.4	145	8.8
125	33.4	140	13.2
135	17.6	130	22.9
150	6.2	120	47.5
155	3.7		

(b) 1,5-Diacetyl-2,6-dihydroxynaphthalene :

It was prepared by the method of Feiser and Lothrop[245].

12 gms. of 2,6-Diacetoxy naphthalene, 15.8 gms. of anhydrous aluminium chloride and 100 cc. of carbon disulphide were refluxed for 2 hours and the solvent was then distilled out. The residue was heated at 150°C for 4 hours and decomposed with ice. It was filtered, washed and dried. It was extracted with alkali solution and then neutralized with acid to give 1,5-diacetyl-2,6-dihydroxy naphthalene, melting at 263°C.

(c) Dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene :

It was prepared by the method of Dewar and Talati[246].

1 gm. of diacetyl dihydroxy naphthalene in 10 cc. of alcohol, 1 gm. of hydroxylamine hydrochloride in water and 4 gms. of calcium carbonate were mixed and refluxed for 4 hours. The solution was filtered hot. The filtrate on cooling deposited the dioxime in colourless crystals. It was filtered, washed and dried. It melts at 247-48°C.

(ii) Transition metal complexes of dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene :

Metal acetate dissolved in aqueous ammonia was added drop by drop, with stirring, to the calculated amount of dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene dissolved in aqueous ammonia (salt : ligand : : 1 : 1). Stirring was continued for

2-3 hours. The mixture was then left overnight. The precipitated product was filtered, washed with water, alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p. etc. are presented in table 32. The electrical resistivity of these complexes over a range of temperature is presented in table 33.

(iii) 1,5-Diamino-2,6-dihydroxy naphthalene :

(a) 1,5-Dibromo-2,6-dihydroxy naphthalene :

It was prepared by the method of Chakravati and Pasupati[247].

4 gms. of bromine in 8 cc. of glacial acetic acid were added slowly with stirring to 2 gms. of 2,6-dihydroxy naphthalene dissolved in 60 cc. glacial acetic acid. 1,5-Dibromo-2,6-dihydroxy naphthalene separated. It was filtered, washed, dried and recrystallised from alcohol. It melts at 223°C.

(b) 1,5-Dinitro-2,6-dihydroxy naphthalene :

It was prepared by the method of Heinz and Zimmer[248].

10 gms. of 1,5-dibromo-2,6-dihydroxy naphthalene in 120 cc. boiling dioxane were treated with activated charcoal and filtered. The filtrate was cooled to 0°C, mixed with 4.8 gms. of sodium nitrite powder and 40 cc. of acetic acid were added to it dropwise. The mixture was stirred for 30 minutes. 1,5-Dinitro-2,6-dihydroxy naphthalene precipitated. It was filtered, washed with acetic acid and

Table 32

Transition metal complexes of 2,6-dihydroxynaphthalene derivatives

No.	Complex	Metal used	m.p. (°C)	Colour	Formula	Analysis			
						% M found	% N found	% M reqd.	% N reqd.
(a) dioxime of 1,5-diacetyl-2,6-dihydroxy naphthalene									
1.	ON Cu	Copper	> 400	Black	$C_{14}H_{14}N_2O_5Cu$	17.81	8.34	17.99	7.92
2.	ON Co	Cobalt	> 400	Dark brown	$C_{14}H_{16}N_2O_6Co$	16.03	7.77	16.06	7.63
(b) 1,5-Diamino,2-6-dihydroxy naphthalene									
3.	AN Co	Cobalt	> 400	Grey	$C_{20}H_{36}N_4O_{145}Co_{33}$	23.59	7.12	23.61	7.48

Table 33

Electrical resistivity of transition metal complexes at different temperatures.

(a) ON Cu

Temp. (. °C)	Resistivity (ρ x 10^{-7} ohm cm.)
30	12.1
40	8.1
50	5.7
70	2.8
90	1.6
80	2.2
60	4.1
50	6.1
40	7.7

(b) ON Co

Temp. (. °C)	Resistivity (ρ x 10^{-11} ohm cm.)
40	15.9
50	7.6
60	4.0
70	2.0
90	0.64
80	0.99
60	4.0
50	7.9
40	15.9

(c) AN Co

Temp. (. °C)	Resistivity (ρ x 10^{-9} ohm cm.)	Temp. (. °C)	Resistivity (ρ x 10^{-9} ohm cm.)
40	55.5	90	4.3
60	18.8	70	11.9
80	6.6	50	29.7
100	2.6	40	56.1
110	1.8		

water. A second crop was obtained by adding water to the filtrate. It melts at 212 °C. (decomposition starts at 200 °C).

(c) 1,5-Diamino-2,6-dihydroxy naphthalene :

It was prepared by the method of Heinz and Zimmer[248].

Reducing solution was prepared by dissolving 226 gms. of stannous chloride in 400 cc. of acetic acid and 100 gms. of dry hydrochloric acid. It was diluted to 500 cc. with acetic acid and left for few days. It was then decanted.

5 gms. of 1,5-dinitro-2,6-dihydroxy naphthalene in 50 cc. of the reducing solution were refluxed for 15 minutes. 30 cc. of concentrated hydrochloric acid were added to it and heating was continued for 5 minutes to give the dihydrochloride of 1,5-diamino-2,6-dihydroxy naphthalene. It was recrystallised from dilute hydrochloric acid. The free base was not obtained pure in air.

(iv) Cobalt (II) complex of 1,5-diamino-2,6-dihydroxy naphthalene :

Cobalt acetate dissolved in aqueous ammonia was added, drop by drop, with stirring, to the calculated amount of 1,5-diamino-2,6-dihydroxy naphthalene dihydrochloride dissolved in aqueous ammonia (salt:ligand::1:1). Stirring was continued for 2-3 hours. The mixture was left overnight. The product was filtered, washed with water, alcohol and ether and dried. It is insoluble in water and all common organic solvents.

The analysis of the product its melting point,etc., are presented in table 32. The electrical resistivity of the complex over a range of temperature is presented in table 33.

II.6. Dihydroxy quinoxaline and its transition metal complexes :

(i) 5,8-Dihydroxy quinoxaline :

(a) Hydroquinone dimethyl ether (1,4-dimethoxy benzene) :

It was prepared by the method of Bogert and Howells[249].

105 cc. of dimethyl sulphate were added to a solution of 50 gms. of hydroquinone in 275 cc. of 15 % sodium hydroxide solution with vigorous shaking. The temperature gradually rose to 50 °C during the addition of dimethyl sulphate. Shaking was continued for 10 minutes more after the addition was completed. Excess of dimethyl sulphate was destroyed by adding 50 cc. of 10 % sodium hydroxide solution and heating for an hour at 100 °C. Dimethyl ether crystallised out on cooling. It was filtered, washed,dried and recrystallised from 75 % alcohol in large colourless lustrous flakes of strong ethereal odour. It melts at 56-8 °C.

(b) Dinitro-1,4-dimethoxy benzene :

It was prepared by the method of King,Clark and Davis[250].

20.0 gms. of hydroquinone dimethyl ether dissolved in 50 cc. of glacial acetic acid were treated with 25 cc. of 69 % nitric acid. After vigorous reaction subsided, 25 cc. of 69 % nitric acid were added again. The mixture was heated for 5 minutes at 70-80°C. Yellow crystalline solid was obtained on cooling and dilution with water. It was filtered and washed with water to remove acid. The product was a mixture of 2,3- and 2,5-dinitro-quinol dimethyl ether; it could not be fractionated by any convenient method. This mixture was taken directly for reduction.

(c) Diamino 1,4-dimethoxy benzene :

The dinitro compound was reduced by sodium dithionite.

5 gms. of dinitro quinol dimethyl ether were dissolved in 50 cc. alcohol and 12 cc. water, 30 gms. of sodium dithionite were gradually added with constant shaking to the boiling solution. The mixture was refluxed on water bath for one hour. Excess of alcohol was distilled off. 50 cc. of concentrated hydrochloric acid were added to it and the mixture was refluxed to decompose the dithionite. It was diluted with water and neutralised with concentrated sodium hydroxide solution till red litmus turned blue. 2,5-Diamino-1,4-dimethoxy benzene crystallised out on cooling. It was filtered and discarded. The filtrate was extracted with chloroform and evaporated to dryness. The gummy substance was extracted with hot petroleum ether;

2,3-diamino-1,4-dimethoxy benzene was obtained on evaporating the extract. It was recrystallised from water. It melts at 85-87°C.

(d) 5,8-Dimethoxy quinoxaline :

It was prepared by the method of Adachi[251].

Aqueous solution of 5 gms. of glyoxal sodium bisulphite adduct in 50 cc. of water was added to 5 gms. of 2,3-diamino hydroquinone dimethyl ether with stirring at 50°C. for 30 minutes. A little more glyoxal bisulphite adduct was added. Stirring was continued for additional 15 minutes and the solution was filtered. Concentrated sodium hydroxide solution was added and the solution was allowed to stand. The product was filtered, washed and dried. It melts at 150-51°C. and possesses yellow colour when anhydrous and orange colour when hydrated.

(e) 5,8-Dihydroxy quinoxaline :

It was prepared by the method of King, Clark and Davis[250].

0.5 gms. of 5,8-dimethoxy quinoxaline was refluxed for 16 hours with 1.5 gms. of anhydrous aluminium chloride in 20 cc. of dry benzene. Benzene was decanted off and the solid product was dissolved in warm dilute hydrochloric acid. Solid sodium bicarbonate was added until the solution became cloudly. The liquid became clear with a few drops of acid and excess of saturated copper sulphate solution was added to precipitate the copper complex. It was collected on filter paper, washed and decomposed by passing hydrogen sulphide gas into its aqueous suspension.

After removal of copper sulphide the product was isolated from the filtrate with ether. A considerable quantity of the dihydroxy quinoxaline adsorbed on the copper sulphide was removed from the dried precipitates by sublimation at low pressure. The product was a crystalline orange powder, darkening rapidly at 200°C and melting indistinctly at 230°C.

(ii) Transition metal complexes of 5,8-dihydroxy quinoxaline :

Metal acetate dissolved in dimethylformamide with a few drops of acetic acid was added, drop by drop, with stirring, to the calculated amount of 5,8-dihydroxy quinoxaline dissolved in dimethylformamide (salt : ligand:: 1:1). Stirring was continued for 2-3 hours. The mixture was left overnight. The precipitates were filtered, washed with dimethylformamide, alcohol and ether and dried. They are insoluble in water and all common organic solvents.

The analysis of the products, their m.p. etc., are presented in table 34. The electrical resistivity of these complexes over a range of temperature is presented in table 35.

II.7. 4,6-Diacetyl resorcinol and its cobalt complex :

(i) Resacetophenone :

It was prepared by the methof of Cooper[252].

10 gms. of resorcinol were added to 15 gms. of fused zinc chloride in 15 cc. of hot glacial acetic acid. The mixture was heated on a sand bath at 150°C. When the liquid began to boil vigorously, the flame was removed and

Table 34

Transition metal complexes of 5,8-dihydroxy quinoxaline

No.	Complex	Metal used	m.p. (°C)	Colour	Formula	Analysis			
						% M Found	% N Found	% M reqd.	% N reqd.
1.	Q Cu	Copper	> 400	Black	$C_{40}H_{58}N_{10}O_{28}Cu_4$	18.75	10.38	18.43	10.14
2.	Q Co	Cobalt	> 400	Black	$C_{24}H_{90}N_6O_{46}Co_4$	16.64	5.81	16.44	5.86
3.	Q Ni	Nickel	> 400	Black	$C_8H_{16}N_2O_8Ni$	17.52	8.85	17.97	8.57

Table 35

Electrical resitivity of transition metal complexes of 5,8-dihydroxy quinoxaline at different temperatures.

(a) Q Cu

Temp. (. $^\circ$C)	Resistivity ($\rho \times 10^{-9}$ ohm cm.)
70	10.6
90	3.0
105	1.2
132	0.31
153	0.12
140	0.21
122	0.50
100	1.6
80	5.5

(b) Q Co

Temp. (. $^\circ$C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
110	79.2
120	40.1
130	19.0
140	8.3
150	4.2
145	5.8
135	13.7
125	26.4
115	54.9

(c) Q Ni

Temp. (. $^\circ$C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)	Temp. (. $^\circ$C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
80	8.8	130	0.47
100	2.4	110	2.1
120	0.83	90	4.7
140	0.26	70	18.9
149	0.17		

the mixture was left to complete the reaction. The reaction mixture became light red in colour. After cooling the mass was poured in 100 cc. of 1:1 hydrochloric acid with constant stirring to dissolve zinc chloride. It was filtered,dried and recrystallised from hot water. It melts at 142°C.

(ii) <u>4.6-Diacetyl resorcinol</u> :

It was prepared by the method of Trivedi and Sethna[253].

A solution of 13.4 gms. of aluminium chloride in 60 cc. of nitrobenzene was added gradually with shaking to 7.5 gms. of resacetophenone and 5.1 gms. of acetic anhydride dissolved in 20 cc. of nitrobenzene. The reaction was vigorous and considerable heat evolved. The mixture was heated on a steam bath for four hours. After cooling the reaction mixture was treated with cold dilute hydrochloric acid and steam distilled. The distillate contained nitrobenzene and 2,4-diacetyl resorcinol.

Dark-brown residue remaining in the flask was crystallised from rectified spirit. On further recrystallisation from benzene, 4,6-diacetyl resorcinol melting at 182°C was obtained.

(iii) <u>Cobalt complex of 4.6-diacetyl resorcinol</u> :

2.5 gms. of cobalt acetate dissolved in 25 cc. of water were added, drop by drop, with stirring,to 1.94 gms. of diacetyl resorcinol dissolved in 50 cc. of alcohol. The mixture was kept on water bath for digestion. The precipitates were filtered,washed with alcohol and ether and dried. The product is insoluble in water and all common organic solvents. It does not decompose upto 400 °C.

<u>Analysis</u> : Found : % Co : 12.43 ; % C :49.5 ; % H : 4.4

$C_{20}H_{22}O_{10}Co$ requires : % Co : 12.26 ; % C :49.9 ; % H : 4.57.

The electrical resistivity of the complex over a range of temperature is presented in table 36.

II.8. Oxalyl bis(salicylidene hydrazide) and its nickel complex :

They were prepared by the methof of Sacconi[254].

(i) Oxalic acid, dihydrazide :

14.6 gms. of Diethyl oxalate dissolved in 25 cc. of alcohol were added, drop by drop, with stirring, to 100 cc. of hydrazine hydrate dissolved in alcohol. Stirring was continued for 3 hours. The mixture was then left overnight. The crystalline product was filtered,washed with alcohol and dried. It melts at 245 °C.

(ii) Oxalyl bis(salicylidene hydrazide) :

1.18 gms. of dihydrazide dissolved in aqueous alcohol were added,drop by drop, with stirring,to 2.12 gms. of salicylaldehyde dissolved in alcohol. Stirring was continued for 2-3 hours. The mixture was kept on water bath for one hour. The product separated in fine white needles. It was filtered,washed with alcohol and dried. It melts at 310 °C. It is sparingly soluble in aqueous alcoholic ammonia or sodium hydroxide solution.

Table 36

Electrical resistivity of transition metal complexes at different temperatures.

(a) DAR Co		(b) OSH Ni	
Temp. (.°C)	Resistivity ($\rho \times 10^{-12}$ ohm cm.)	Temp. (.°C)	Resistivity ($\rho \times 10^{-11}$ ohm cm.)
105	13.7	115	60.4
115	6.6	125	27.9
125	2.9	135	13.6
135	1.5	145	5.3
145	0.69	155	3.4
140	0.95	150	4.1
130	2.1	140	7.5
120	4.4	130	18.1
110	9.5	120	45.3

(iii) Nickel (II) complex of oxalyl bis(salicylidene hydrazide) :

6.25 gms. of nickel acetate dissolved in aqueous ammonia were added, drop by drop, with stirring, to 2.94 gms. of oxalyl bis(salicylidene hydrazide) suspended in alcohol. The mixture was heated on water bath for one hour. The red-brown product separated on cooling. It was filtered,washed with alcohol and ether and dried. The complex is insoluble in water and all common organic solvents. It decomposes at 200°C with liberation of ammonia.

Analysis :

	Found	: % Ni : 23.68 ;	% N : 17.6 ;
(Sacconi)	Found	: % Ni : 24.8 ;	% N : 17.25 ;
$C_{16}H_{16}N_6O_4Ni_2$	requires	: % Ni : 24.8 ;	% N : 17.7 .

The electrical resistivity of the complex over a range of temperature is presented in table 36.

II. 9. Transition metal complexes of glyoximes and their halogen adducts :

(i) α-Benzil dioxime : α-diphenyl glyoxime (DPG) :

It was prepared by the methof of Boyer, et al.[255]

50 gms. of Benzil and 50 gms. of hydroxylamine hydrochloride dissolved in 400 cc. of methanol were refluxed for 3 hours. α-Benzil dioxime separated from the solution on cooling. It was filtered and recrystallised twice from methanol. It melts at 238-40°C.

(ii) 2,3-Dioxobutyranilide dioxime (OO) :

It was prepared by the method of Desai[256].

(a) 2,3-Dioxobutyranilide-2-oxime :

10 gms. of Acetoacetanilide and 5.0 gms. of sodium nitrite dissolved in 60 cc. of 2 normal sodium hydroxide solution were added, drop by drop, with stirring, to 600 cc. of 2 normal sulphuric acid below 10 °C. Stirring was continued for 2 hours. The yellow precipitates were filtered, washed with water and dried. It was recrystallised from dilute alcohol. It melts at 99-100 °C.

(b) 2,3-Dioxobutyranilide dioxime :

4 gms. of 2,3-Dioxobutyranilide-2-oxime dissolved in alcohol were treated with 2.0 gms. of hydroxylamine hydrochloride dissolved in water. The mixture was warmed gently to 35-40 °C for a few minutes and then left at room temperature for 2-3 hours. The product was filtered, washed with water and dried. It was recrystallised from dilute alcohol. It melts at 192 °C.

(iii) Transition metal (Co, Ni) complexes of diphenyl glyoxime :

Metal acetate dissolved in aqueous ammonia was added, drop by drop, with stirring, to diphenyl glyoxime dissolved in alcohol (salt : ligand :: 1:2). The precipitates were digested for two hours on sand bath, and then filtered, washed with water and alcohol and dried. Cobalt complex (DPG Co) is brown and nickel complex (DPG Ni) red in colour.

(iv) Nickel complex of dimethyl glyoxime :

2.5 gms. of Nickel acetate dissolved in aqueous ammonia were added,drop by drop,with stirring, to 2.4 gms. of dimethyl glyoxime dissolved in alcohol. The precipitates were digested for 2 hours on sand bath and then filtered, washed with water and alcohol and dried. The complex (DMG Ni) is pinkish red in colour.

(v) Transition metal (Cu,Ni,Co) complexes of 2,3-dioxobutyranilide dioxime :

Metal acetate dissolved in water was added,drop by drop, with stirring,to 2,3-dioxobutyranilide dioxime dissolved in dilute alcohol (salt:ligand:: 1:2). The precipitates were digested for 2 hours on sand bath and then filtered, washed with water and alcohol and dried. Copper complex (OOCu) is light brown, cobalt complex (OO Co) is pinkish red and nickel complex (OO Ni) is yellow in colour.

(vi) Reactions of transition metal complex with halogens in solution :

(a) Reactions of bis(diphenyl glyoximato) cobalt and bis(diphenyl glyoximato)nickel with bromine :

16 gms. of Bromine in carbon tetrachloride were added,drop by drop,with stirring, to 5.39 gms. of bis(diphenyl glyoximato)cobalt (DPG Co) or 5.39 gms. of bis(diphenyl glyoximato) nickel (DPG Ni) suspended in 100 cc. of carbon tetrachloride. Stirring was continued for

3 hours. The product was filtered, washed with carbon tetrachloride and ether and dried.

The product (DPG Co Br) is soluble in alcohol, acetone, pyridine and dimethyl formamide and insoluble in ether, petroleum ether, benzene and carbon tetrachloride.

The product (DPG Ni Br) is insoluble in all common organic solvents except hot nitrobenzene, hot dimethyl formamide and pyridine.

(b) Reaction of bis(diphenyl glyoximato) nickel with iodine :

It was prepared by the method of Edelman[257].

3 gms. of Iodine dissolved in benzyl alcohol was added, drop by drop, with stirring, to 3 gms. of bis(diphenyl glyoximato) nickel (DPG Ni) dissolved in 20 cc. of benzyl alcohol. Stirring was continued for 2 hours. The glistening bronze product separated. It was filtered, washed with benzyl alcohol and ether and dried.

The product (DPG Ni I) is insoluble in all common organic solvents, but soluble in hot dimethyl formamide, nitrobenzene and pyridine. It decomposes at 285°C.

(c) Reactions of Bis(dimethyl glyoximato) nickel (DMG Ni), bis(2,3-dioxobutyranilide dioxime) cobalt (OO Co) and bis(2,3-dioxobutyranilide dioxime) nickel (OO Ni) with bromine :

Bromine in chloroform was added, drop by drop, with stirring, to the large excess of the above complexes suspended in chloroform (bromine:complex :: 10:1) .

Stirring was continued for three hours. The mixture was then left overnight. The product was filtered, washed with chloroform and ether and dried.

The product (DMG Ni Br) is insoluble in all common organic solvents but soluble in hot nitrobenzene and dimethyl formamide.

The product (00 Co Br) and (00 Ni Br) are insoluble in ether, petroleum ether, carbon tetrachloride and benzene but soluble in alcohol, acetone, dimethyl formamide and pyridine.

(d) Reaction of bis(2,3-dioxobutyranilide) dioxime) copper (00 Cu) with bromine :

4 gms. of Bromine in chloroform were added, drop by drop, with stirring, to 2.5 gms. of the above complex (00 Cu) suspended in chloroform. Stirring was continued for 2-3 hours. The solution was filtered and evaporated to dryness. The residue was extracted with acetone and the extract was added to 200 cc. of distilled water. The Yellow precipitates were obtained. These were filtered, washed with water and alcohol and dried.

The product (00 Cu Br) is insoluble in alcohol, benzene, ether, petroleum ether and carbon tetrachloride but soluble in acetone, chloroform, nitrobenzene, dimethyl formamide and pyridine.

(e) Reaction of bis(2,3-dioxobutyranilide dioxime) copper (00 Cu) with iddine :

1.25 gms. of Iodine dissolved in o-dichlorobenzene were added, with stirring, to 2.51 gms. of the above complex (OOCu) suspended in 30 cc. of hot o-dichlorobenzene. Stirring was continued for two hours. The solution was then left overnight. It was filtered and to the filtrate,petroleum ether was added to precipitate the product. The precipitates were filtered,washed with petroleum ether and ether and dried. The product (OOCu I) is insoluble in all common organic solvents except dimethyl formamide,pyridine and o-dichlorobenzene.

The analysis of the above products, their m.p. etc. are presented in table 37. The electrical resistivity of the adducts over a small range of temperature is presented in table-38. The magnetic susceptibilities of some adducts and their diamagnetic corrections are presented in table-39.

Table 37

Halogen products of transition metal complex of dioximes

No.	Product	m.p. (. °C)	Colour	Formula	Analysis % N Found	 % Br/I Found	 % N reqd.	 % Br/I redq.
1.	DPG Co Br	230 (d)	Yellow	$C_{28}H_{22}N_4O_4Br_5Co$	6.68	43.08	5.98	42.74
2.	DMG Ni Br	110 (d)	Black	$C_{16}H_{52}N_8O_{20}Br_{11}Ni_2$	6.48	52.24	6.69	52.60
3.	00 Cu Br	150 (d)	Yellow	$C_{20}H_{28}N_6O_{10}Br_8Cu$	6.56	53.15	6.91	52.64
4.	00 Co Br	190 (d)	Yellowish green	$C_{20}H_{24}N_6O_8Br_6Co$	7.72	49.00	8.28	47.30
5.	00 Ni Br	165 (d)	Yellowish green	$C_{20}H_{28}N_6O_{10}Br_{12}Ni$	5.22	62.61	5.49	62.70
6.	00 Cu I	160 (d)	Snuff	$C_{20}H_{20}N_6O_6ICu$	12.09	21.11	13.32	20.14

Table 38

Electrical resistivity of halogen adducts at different temperatures.

(a) DPG Co Br		(b) DMG Ni Br		(c) OO Cu Br	
Temp. (.°C)	Resistivity ($\rho \times 10^{-3}$ ohm cm.)	Temp. (.°C)	Resistivity ($\rho \times 10^{-4}$ ohm cm.)	Temp. (.°C)	Resistivity ($\rho \times 10^{-7}$ ohm cm.)
37	4.6	37	1.1	37	0.49
20	13.8	20	3.9	20	6.5
5	41.3	5	13.7	5	60.9
18	16.1	18	4.7	18	8.1
35	5.1	35	1.4	35	0.81

Table 38 (contd.)

Electrical resistivity of halogen adducts at different temperatures.

(d) 00 Cu I		(e) 00 Co Br		(f) 00 Ni Br	
Temp. (.°C)	Resistivity (ρ x 10^{-7} ohm cm.)	Temp. (.°C)	Resistivity (ρ x 10^{-6} ohm cm.)	Temp. (.°C)	Resistivity (ρ x 10^{-7} ohm cm.)
37	1.0	37	3.7	37	0.49
20	3.2	20	19.4	24	5.4
5	10.1	6	88.0	15	30.9
18	3.6	18	22.0	25	4.5
35	1.2	35	4.4	35	0.65

Table 39

Magnetic susceptibility of halogen adducts

No.	Halogen adducts	Temperature (^{o}C)	Magnetic susceptibility $\chi_g \times 10^6$	Diamagnetic correction (per metal atom) $\times 10^6$
1.	OOCu Br	33.0	1.70	- 275.5
2.	OOCo Br	32.0	2.0	- 408.0