EXPERIMENTAL

II EXPERIMENTAL

II 1. General :

(i) Reagents and solvents.

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

(ii) Analyses of New Products :

Analyses of new products were carried out for metal, nitrogen, carbon and hydrogen as required, by known micro methods.

(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) Visible spectra :

Absorption spectra in the visible range (400-800 mμ) were obtained for a few compounds in suitable solvents from the readings of a spekol spectrophotometer.

(vi) IR Spectra :

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

(vii) Electrical resistivity :

Electrical resistivity of a few substances in the form of pressed pellet was measured on Elico's Million megohmmeter Model RM-70.

(viii) Magnetic susceptibility :

Magnetic susceptibility of transition metal complexes was determined on Gouy's magnetic balance at room temperature.

(ix) Thermal analyses :

Thermal analyses (D.T.A. and T.G.A.) of a few compounds were carried out in nitrogen atmosphere using Lenseis Model.

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

II.2 Bis-azo disalicylaldehyde and its transition metal complexes :

(i) 4,4′ Bis (m-formyl p-hydroxy-phenylazo) biphenyl.(BASA)

It was prepared by the method of Sen and Ghosh.[140]

A tetrazotised solution of benzidine (9.2 g.) was poured into a cold solution of salicylaldehyde (6.5 g.) and sodium carbonate (23.0 g.) in water and the mixture was stirred for 3 to 4 hours. When the coupling with salicylaldehyde was complete, salicylaldehyde (6.5 g.) dissolved in minimum quantity of sodium hydroxide solution was further added to it. Stirring was continued until the reaction was complete. The precipitated bis-azo compound was filtered, washed with water and dried. It was obtained as a microcrystalline yellow powder by recrystallisation from hot nitrobenzene. It is insoluble in water and all common organic solvents except nitrobenzene, pyridine and dimethylformamide. It does not melt upto 300°C.

(ii) Cu(II), Ni(II) and Co(II) complexes of 4,4′ bis (m-formyl-p-hydroxy-phenylazo) biphenyl. (in pyridine)

4,4′ bis (m-formyl-p-hydroxy-phenylazo) biphenyl (1.2 g.) dissolved in pyridine was mixed with calculated amount of metal acetate in pyridine (salt : ligand :: 1 : 1). The mixture became turbid, gradually forming slimy precipitates and was left overnight. The precipitates were carefully filtered, washed with alcohol and little pyridine and dried. They are insoluble in water and all common organic solvents except pyridine and dimethylformamide in which they are sparingly soluble. The colour, m.p., analysis, etc., of these complexes are presented in Table E-1. The mass magnetic susceptibilities and dimagnetic corrections of these complexes are given in

Table E-1

Transition metal complexes of 4,4'-bis(m-formyl-p-hydroxy-phenylazo)biphenyl (BASA)

No.	Complex	Colour	m.p. (°C)	Formula	Analysis			
					%M Found	%N Found	%M reqd.	%N reqd.
(a)	**In pyridine**							
(1)	BASA-Cu(P)	Brickred	300	$C_{186}H_{152}N_{29}O_{39}Cu_5$	8.54	10.62	8.51	10.80
(2)	BASA-Ni(P)	Orangered	300	$C_{57}H_{47}N_9O_{12}Ni$	5.42	11.52	5.34	11.47
(3)	BASA-Co(P)	Darkred	300	$C_{57}H_{53}O_{16}N_9CO_2$	9.32	10.34	9.53	10.20
(b)	**In dimethylformamide**							
(4)	BASA-Cu(D)	Brickred	300	$C_{286}H_{238}N_{44}O_{74}Cu_{10}$	11.20	9.73	10.40	10.09
(5)	BASA-Co(D)	Red	300	$C_{182}H_{156}N_{28}O_{40}CO_4$	6.63	10.72	6.53	10.87

Table E-2.

Optical density of the compounds in dimethylformamide in the visible region of the spectrum is presented in Table E-3 and optical density of the compound in dimethylformamide in the ultraviolet region of the spectrum are presented in Table E-4. The infrared spectra of the compounds are presented in fig. E-1.

Wt. loss (ΔW) in mg. per 50 mg. sample and temperature difference (ΔT) at a few selected temperatures observed in thermal analyses (D.T.A. and T.G.A.) of the complexes are presented in Table E-5.

Tests were carried out to detect acetate in the complexes; the results were negative. Further, precipitates of sulphides were not obtained when the complexes in dimethylformamide were treated with hydrogen sulphide.

(iii) Cu(II) and Co(II) complexes of 4,4' bis (m-formyl-p-hydroxy-phenylazo) biphenyl. (in dimethylformamide)

4,4' bis (m-formyl-p-hydroxy-phenylazo) biphenyl (1.2 g.) dissolved in dimethylformamide was mixed with calculated amount of metal acetate in dimethylformamide (salt : ligand : : 1 : 1). The mixture was refluxed on sand bath for three hours and left overnight. The precipitates were filtered, washed with little dimethylformamide, water and alcohol and dried. They are insoluble in water and all common organic solvents. The colour, m.p., analysis, etc. of these complexes are presented in Table E-1. Their mass magnetic suspectibilities and dimagnetic corrections are given in Table E-2.

Table E-2

Magnetic susceptibility of the complexes

No	Complex	Mass Magnetic Susceptibility	temp.	Diamagnetic correction (per metal atom)
		$X_g \times 10^6$	(°C)	$\chi \times 10^6$
(1)	BASA-Cu(P)	2.58	32	- 346
(2)	BASA-Ni(P)	2.83	29	- 515
(3)	BASA-Co(P)	13.8	32.5	- 324
(4)	BASA-Co(D)	1.25	30	- 278
(5)	BASA-Co(D)	10.69	31	- 583

Table E-3

Optical density of the compounds in dimethylformamide in the visible region (400-800 mμ).

Wavelength	Optical Density			
(mμ)	BASA	BASA-Cu(P)	BASA-Ni(P)	BASA-Co(P)
800	0.005	0.032	0.008	0.008
780	0.005	0.031	0.008	0.005
760	0.004	0.027	0.004	0.004
740	0.004	0.022	0.004	0.004
720	0.004	0.018	0.004	0.009
700	0.004	0.018	0.004	0.009
680	0.004	0.018	0.004	0.013
660	0.004	0.027	0.009	0.018
640	0.004	0.032	0.018	0.027
620	0.013	0.041	0.024	0.046
600	0.022	0.056	0.032	0.081
580	0.061	0.092	0.071	0.125
560	0.143	0.137	0.143	0.169
540	0.310	0.244	0.319	0.284
520	0.469	0.409	0.482	0.585
500	0.469	0.602	0.538	1.046
480	0.398	0.796	0.469	1.523
460	0.292	1.000	0.387	1.699
440	0.268	1.222	0.357	1.699
420	0.292	1.523	0.369	1.699
400	0.276	1.875	0.359	1.562

Table E-3 (contd.)

Wavelength (mμ)	Optical density	
	BASA-Cu (D)	BASA-Co (D)
800	0.008	0.009
780	0.005	0.005
760	0.004	0.004
740	0.004	0.004
720	0.004	0.004
700	0.004	0.004
680	0.004	0.004
660	0.004	0.004
640	0.004	0.004
620	0.004	0.004
600	0.013	0.004
580	0.032	0.013
560	0.051	0.018
540	0.102	0.056
520	0.201	0.125
500	0.292	0.260
480	0.367	0.440
460	0.398	0.699
440	0.409	0.659
420	0.434	1.140
400	0.442	1.176

Table E-4

Optical density of the compound in dimethylformamide in the ultraviolet region (360-220 mμ).

Wavelength	Optical Density			
(mμ)	BASA	BASA-Cu(P)	BASA-Ni(P)	BASA-Co(P)
360	0.760	0.223	0.142	0.255
356	0.710	0.214	0.138	0.245
352	0.665	0.206	0.132	0.237
348	0.620	0.197	0.127	0.230
344	0.590	0.191	0.123	0.225
340	0.560	0.185	0.120	0.220
336	0.540	0.183	0.114	0.220
332	0.520	0.180	0.110	0.220
328	0.505	0.185	0.108	0.220
324	0.495	0.187	0.105	0.220
320	0.490	0.195	0.103	0.222
316	0.480	0.200	0.101	0.225
312	0.480	0.205	0.103	0.232
308	0.480	0.217	0.103	0.245
304	0.485	0.225	0.103	0.260
300	0.487	0.237	0.103	0.282
296	0.495	0.248	0.104	0.300
292	0.510	0.261	0.105	0.322
288	0.540	0.275	0.108	0.345
284	0.580	0.292	0.113	0.370
280	0.640	0.310	0.122	0.405
276	0.730	0.327	0.134	0.445
272	0.800	0.352	0.144	0.500

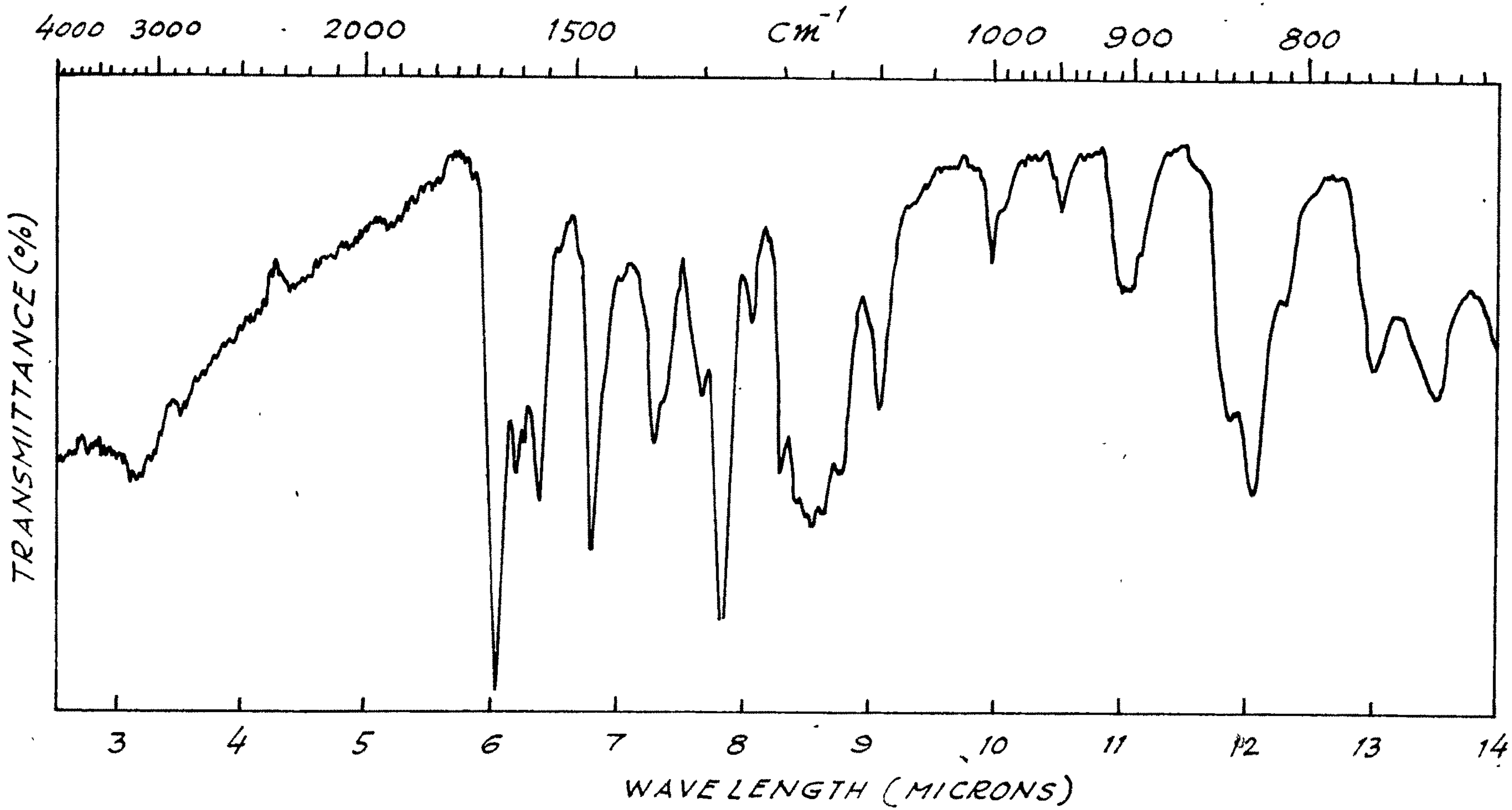

FIG. E-1(a) : IR SPECTRUM OF BASA

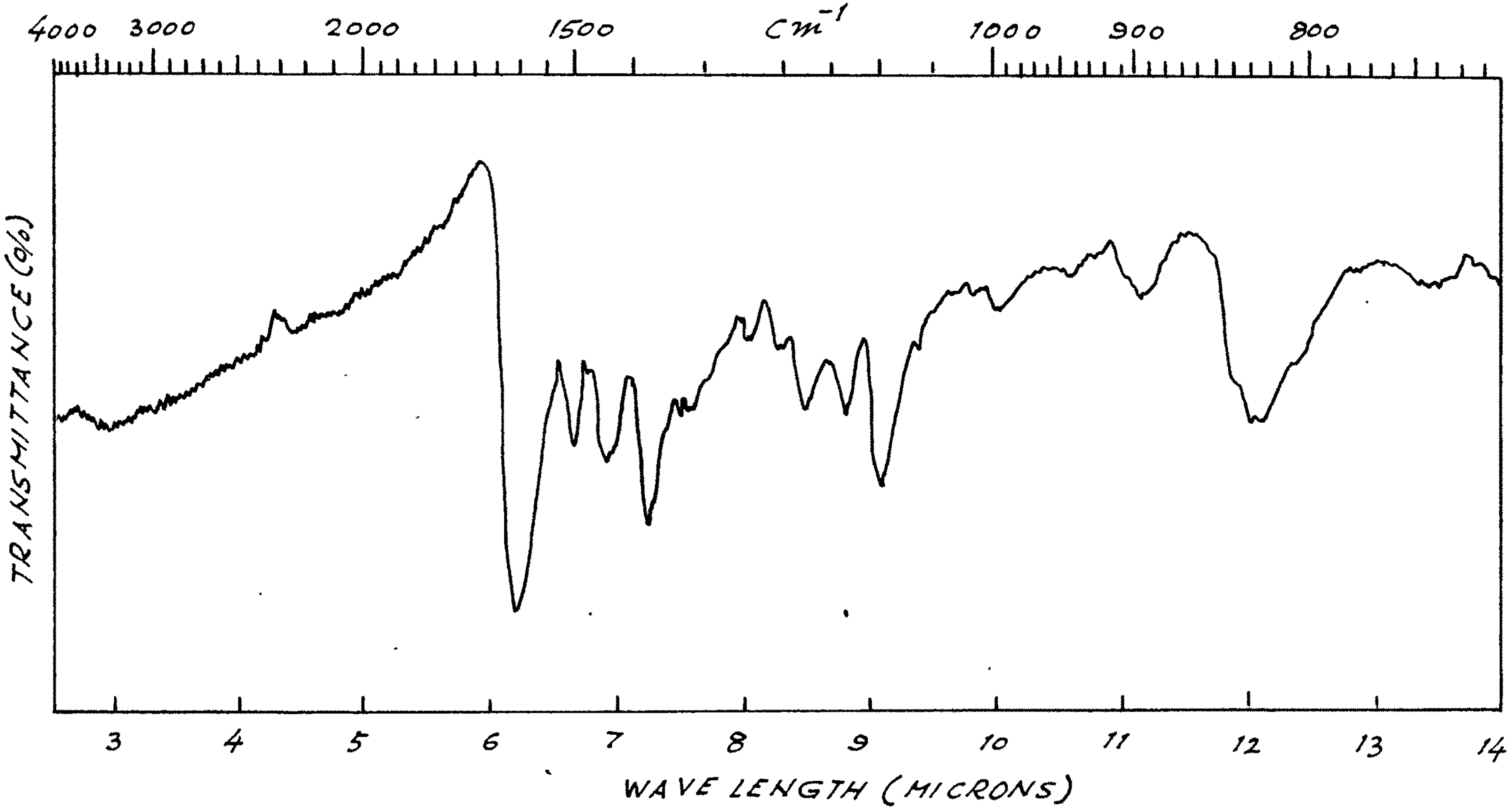

FIG. E-1(b) : IR SPECTRUM OF BASA-Co

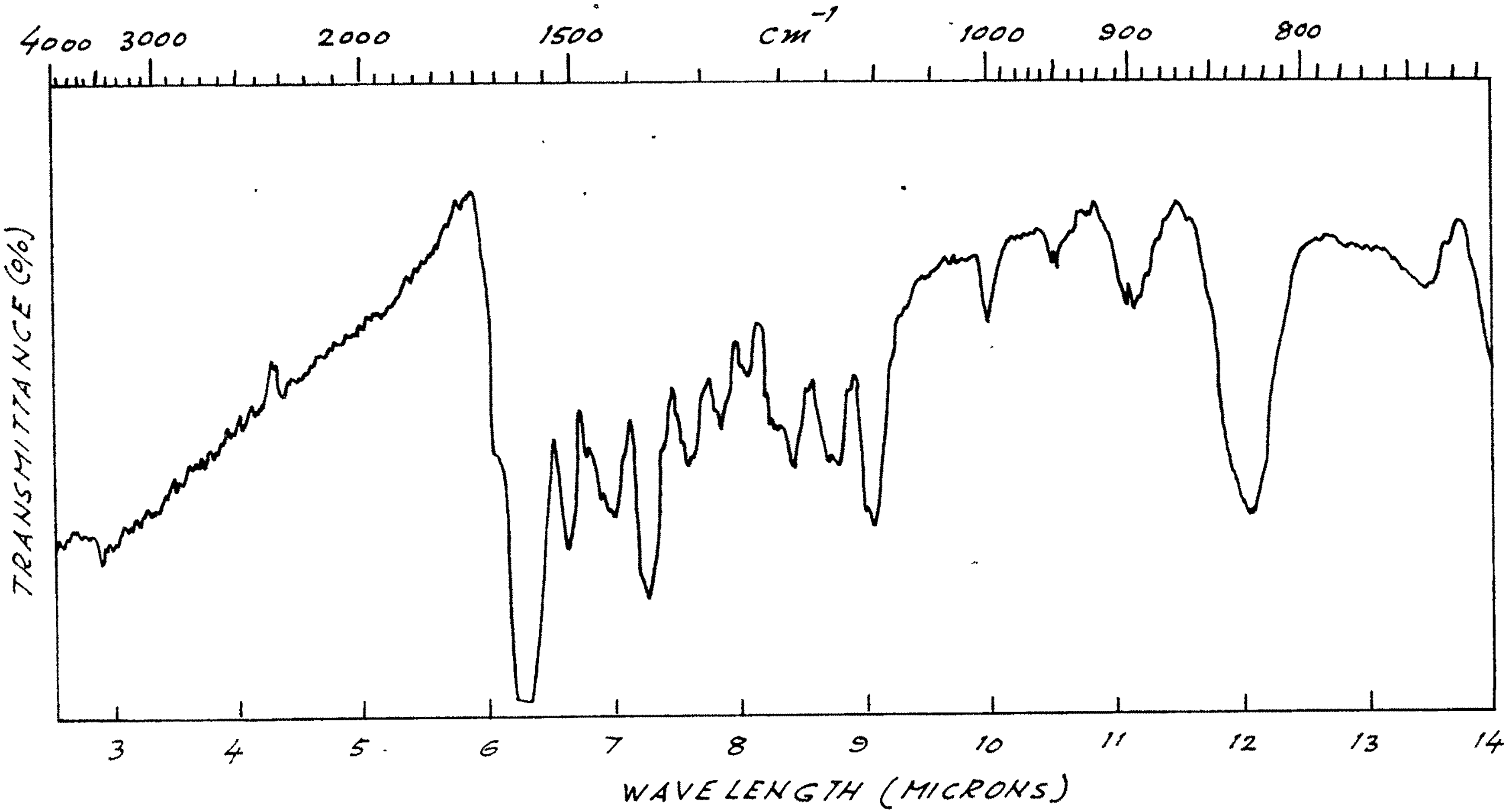

FIG. E-1(c) : IR SPECTRUM OF BASA-Cu

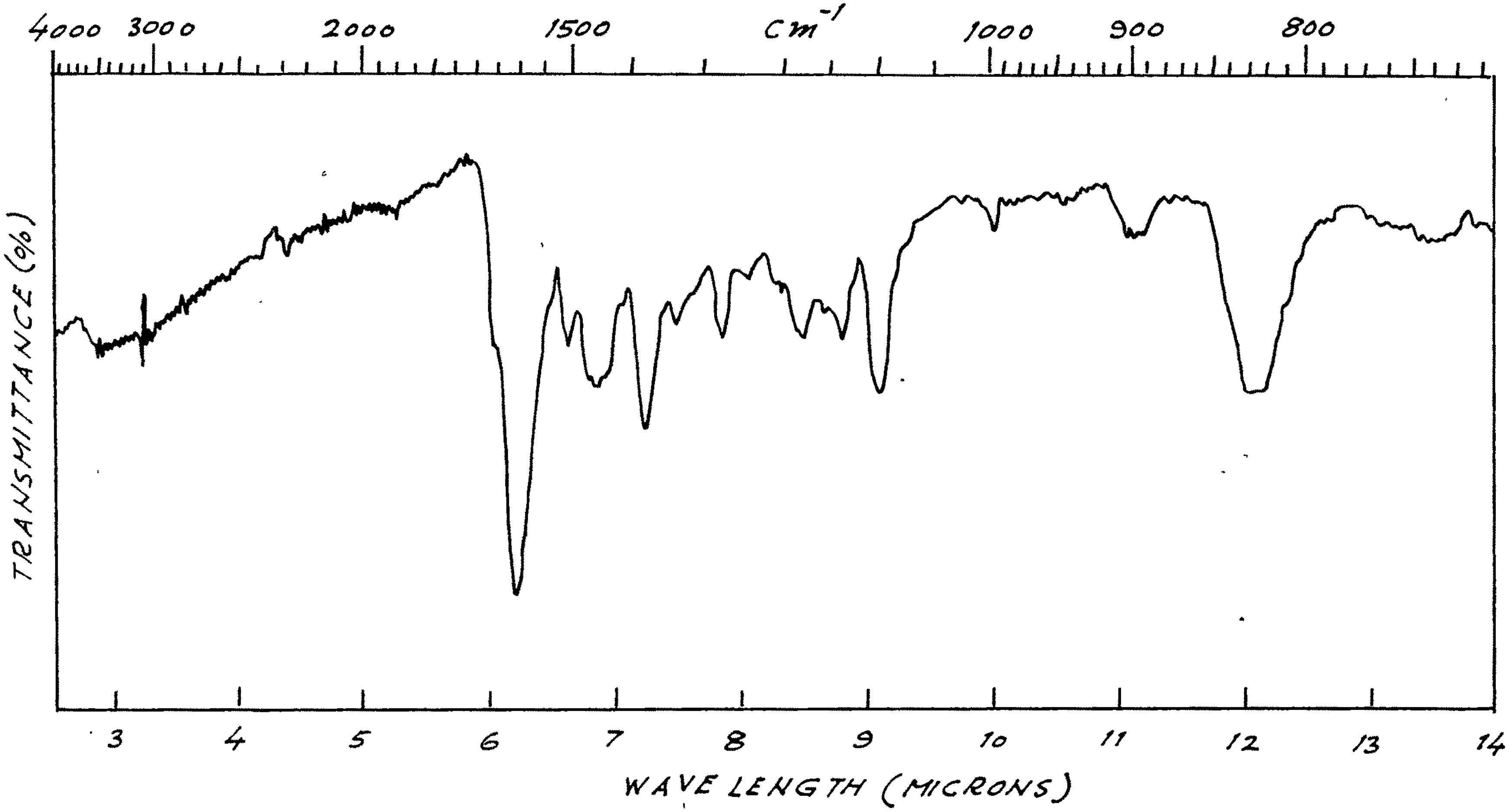

FIG. E-1(d): IR SPECTRUM OF BASA-Ni

Table E-5

Thermal analysis of the complexes

Temp. (°C)	BASA-Cu(P) ΔW(mg)	BASA-Ni(P) ΔW(mg)	BASA-Co(P) ΔW(mg)	ΔT(°C)
100	0.0	3.0	1.0	- 5.0
150	1.0	3.5	1.5	- 5.0
210	1.5	5.0	1.5	- 3.0
255	1.7	5.0	1.5	- 2.5
305	4.0	5.0	1.5	- 0.0
355	8.0	5.0	1.5	+ 1.0
400	10.0	5.0	1.5	- 1.5
450	13.5	5.0	1.5	- 6.0
500	16.0	7.0	1.5	-11.0
550	18.0	7.0	4.5	- 8.0
600	20.5	7.0	5.5	- 3.0
650	23.0	-	5.5	- 5.0
700	25.0	-	5.5	+ 3.0
750	26.5	-	5.5	+ 3.0

II.3. Bis-azo disalicylaldoxime and its Ni(II) complex :

(i) Dioxime of 4,4' bis (m-formyl-p-hydroxy-phenylazo) biphenyl : (BASAO)

The method of Sen and Ghosh[140] was adopted for its preparation.

Concentrated aqueous solution of hydroxylamine-hydrochloride and sodium acetate (0.5 g.) was added to the solution of bis-azo disalicylaldehyde (BASA) (1.2 g.) in pyridine and the mixture was heated on water bath for three to four hours. The precipitates were filtered, washed with little pyridine, water and alcohol and dried. The product was recrystallised from dilute pyridine. It is insoluble in water and all common organic solvents except pyridine and dimethylformamide. It does not melt upto 300°C.

(ii) Ni(II) complex of the dioxime of 4,4' bis (m-formyl-p-hydroxy-phenylazo) biphenyl. (BASAO-Ni)

When a solution of nickel acetate (0.8 g.) in pyridine was mixed with solution of bis-azo disalicylaldoxime (BASAO) (0.6 g.) in pyridine, the mixture became turbid, slowly forming slimy precipitates and was left overnight. The precipitates were carefully filtered, washed with little pyridine and alcohol and dried. It is insoluble in water and all common organic solvents except dimethylformamide and pyridine in which it is sparingly soluble.

II.4. Bis-azo(diacetylacetone)and its transition metal complexes.

(i) 3,3 (4,4'biphenylene bis-azo) di(2,4 pentanedione).(BAAC)

It was prepared according to the method of Bulow and Schlotterbeck.[141]

Cold saturated solution of sodium acetate (42.0 g.) was added to acetylacetone (8.0 g.) dissolved in water. To this mixture was added a tetrazotised solution obtained from benzidine (7.4 g.), hydrochloric acid (25 ml.) and sodium nitrite (6.2 g.). The mixture was stirred vigorously and left overnight. The precipitates were filtered, washed with alcohol and dried. The product was recrystallised from acetic acid. It is orange yellow in colour and melts at 258-60°C. It is insoluble in water and all common organic solvents except pyridine and dimethylformamide.

(ii) Cu(II) complex of bis-azo(diacetylacetone): (BAAC-Cu)

Bis-azo diacetylacetone (0.5 g.) dissolved in dimethylformamide by slight warming was mixed with warm solution of copper acetate (0.25 g.) in dimethylformamide. The mixture was refluxed on sand bath for about three to four hours and left overnight. The precipitates were filtered, washed with little dimethylformamide, alcohol and ether and dried. The product is insoluble in water and all common organic solvents.

(iii) Co(II) and Ni(II) complexes of bis-azo(diacetylacetone):

Attempts to prepare Co(II) and Ni(II) complexes of the ligand by different methods were unsuccessful.

II.5. Azo acetylacetone and its transition metal complexes :

(i) 3, (phenylazo) 2,4 pentanedione : (AAC)

It was prepared according to the method of Bulow and Schlotterbeck.[141]

Cold saturated solution of sodium acetate (21.0 g.) was added to acetylacetone (4.0 g.) dissolved in water. To this mixture was added a diazotized solution obtained from aniline (3.7 g.), hydrochloric acid (11.5 g.) and sodium nitrite (3.1 g.). The mixture was stirred and kept overnight. The precipitates were filtered, washed with little water and dried. The product was recrystallised from dilute alcohol in the form of yellow needles. It melts at 98 °C. It is soluble in alcohol, acetone, petroleum ether, chloroform, pyridine, dimethylformamide, nitrobenzene, etc.

(ii) Cu(II) complex of azo acetylacetone : (AAC-Cu)

Azo acetylacetone (2.0 g.) dissolved in dilute alcohol was mixed with warm alcoholic solution of copper acetate (1.0 g.). The mixture was stirred for two hours and left overnight. The precipitates were filtered, washed with water and dilute alcohol and dried. The product was recrystallised from dilute alcohol. It is soluble in methanol, acetone, benzene, petroleum ether, pyridine, dimethylformamide, etc.

BASAO-Ni, BAAC-Cu, AAC-Cu :

The colour, m.p. analysis, etc. of these complexes are presented in Table E-6; the mass magnetic susceptibilities and dimagnetic corrections of these complexes are presented in Table E-7.

Optical densities of the ligands and their above complexes in the visible region of the spectrum are presented in Table E-8 and optical density of these compounds in dimethylformamide in the ultraviolet region of the spectrum is presented in Table E-9. The infrared spectra of the compounds are shown in fig. E-2.

Wt. loss (ΔW) in mg. per 50 mg. sample taken and temperature difference (ΔT) at a few selected temperatures observed in the thermal analyses (T.G.A. and D.T.A.) of these complexes are presented in Table E-10.

Table E-6

Transition metal complexes

No.	Complex	Colour	m.p. (°C)	Formula	Analysis			
					%M Found	%N Found	%M reqd.	%N reqd.
1	BASAO-Ni	Orange	300	$C_{26}H_{20}N_6O_5Ni$	10.31	15.13	10.53	15.15
2	BAAC-Cu	Black	300	$C_{30}H_{36}N_4O_{14}Cu_3$	22.4	6.5	22.0	6.46
3	AAC-Cu	Snuff	196	$C_{22}H_{22}N_4O_4Cu$	12.84	12.1	13.61	12.03

Table E-7

Magnetic susceptibility of the complexes

No.	Complex	Mass magnetic susceptibility $X_g \times 10^6$	temp. (°C.)	Diamagnetic corrections (per metal atom) $X \times 10^6$
1	BASAO-Ni	5.18	29.0	- 285
2	BAAC-Cu	2.37	29.5	- 386
3	AAC-Cu	3.62	29.5	- 221

Table E-8

Optical density of the compounds in dimethylformamide in the visible region (400-800 mμ).

(a) **Ligands:**

Wavelength (mμ)	Optical Density		
	BASAO	BAAC	AAC
800	0.008	0.007	0.008
780	0.005	0.005	0.005
760	0.004	0.004	0.004
740	0.004	0.004	0.004
720	0.004	0.004	0.004
700	0.004	0.009	0.004
680	0.004	0.009	0.004
660	0.009	0.018	0.004
640	0.027	0.022	0.004
620	0.066	0.041	0.009
600	0.155	0.076	0.022
580	0.301	0.109	0.071
560	0.420	0.187	0.114
540	0.523	0.347	0.143
520	0.602	0.721	0.149
500	0.721	2.000	0.137
480	1.000	2.000	0.137
460	1.523	2.000	0.244
440	2.000	2.000	1.222
420	1.658	1.903	1.486
400	1.518	1.812	1.349

Table E-8 (contd.)

(b) Complexes :

Wavelength	Optical Density		
(mμ)	BASAO-Ni	BAAC-Cu	AAC-Cu
800	0.008	0.007	0.050
780	0.005	0.005	0.046
760	0.004	0.004	0.036
740	0.004	0.004	0.036
720	0.004	0.004	0.041
700	0.000	0.004	0.041
680	0.000	0.004	0.046
660	0.000	0.004	0.056
640	0.004	0.004	0.071
620	0.005	0.009	0.076
600	0.009	0.009	0.097
580	0.013	0.013	0.108
560	0.013	0.013	0.114
540	0.032	0.027	0.168
520	0.036	0.056	0.301
500	0.046	0.081	0.602
480	0.051	0.102	1.046
460	0.051	0.149	1.398
440	0.051	0.268	1.523
420	0.063	0.456	1.568
400	0.098	0.699	1.406

Table E-9

Optical density of the compounds in dimethylformamide in the ultraviolet region (360-220 mμ).

(a) Ligands :

Wavelength (mμ)	Optical Density BASAO	 BAAC	 AAC
360	0.387	0.630	1.17
356	0.355	0.560	1.15
352	0.325	0.495	1.10
348	0.295	0.440	1.05
344	0.273	0.387	0.925
340	0.250	0.340	0.822
336	0.232	0.300	0.735
332	0.218	0.265	0.635
328	0.205	0.240	0.535
324	0.193	0.222	0.440
320	0.185	0.208	0.357
316	0.180	0.197	0.290
312	0.181	0.195	0.225
308	0.185	0.199	0.173
304	0.195	0.210	0.137
300	0.205	0.241	0.112
296	0.220	0.275	0.103
292	0.237	0.320	0.103
288	0.252	0.375	0.110
284	0.270	0.438	0.127
280	0.277	0.508	0.152
276	0.285	0.562	0.200
272	0.295	0.600	0.230

Table E-9 (contd.)

(b) Complexes :

Wavelength (mμ)	Optical density	
	BASAO-Ni	AAC-Cu
360	0.125	0.610
356	0.125	0.598
352	0.125	0.570
348	0.124	0.535
344	0.124	0.495
340	0.127	0.445
336	0.131	0.405
332	0.132	0.355
328	0.135	0.315
324	0.140	0.270
320	0.144	0.232
316	0.150	0.205
312	0.159	0.178
308	0.168	0.153
304	0.179	0.142
300	0.194	0.135
296	0.205	0.132
292	0.225	0.135
288	0.245	0.145
284	0.270	0.162
280	0.300	0.175
276	0.347	0.195
272	0.387	0.225

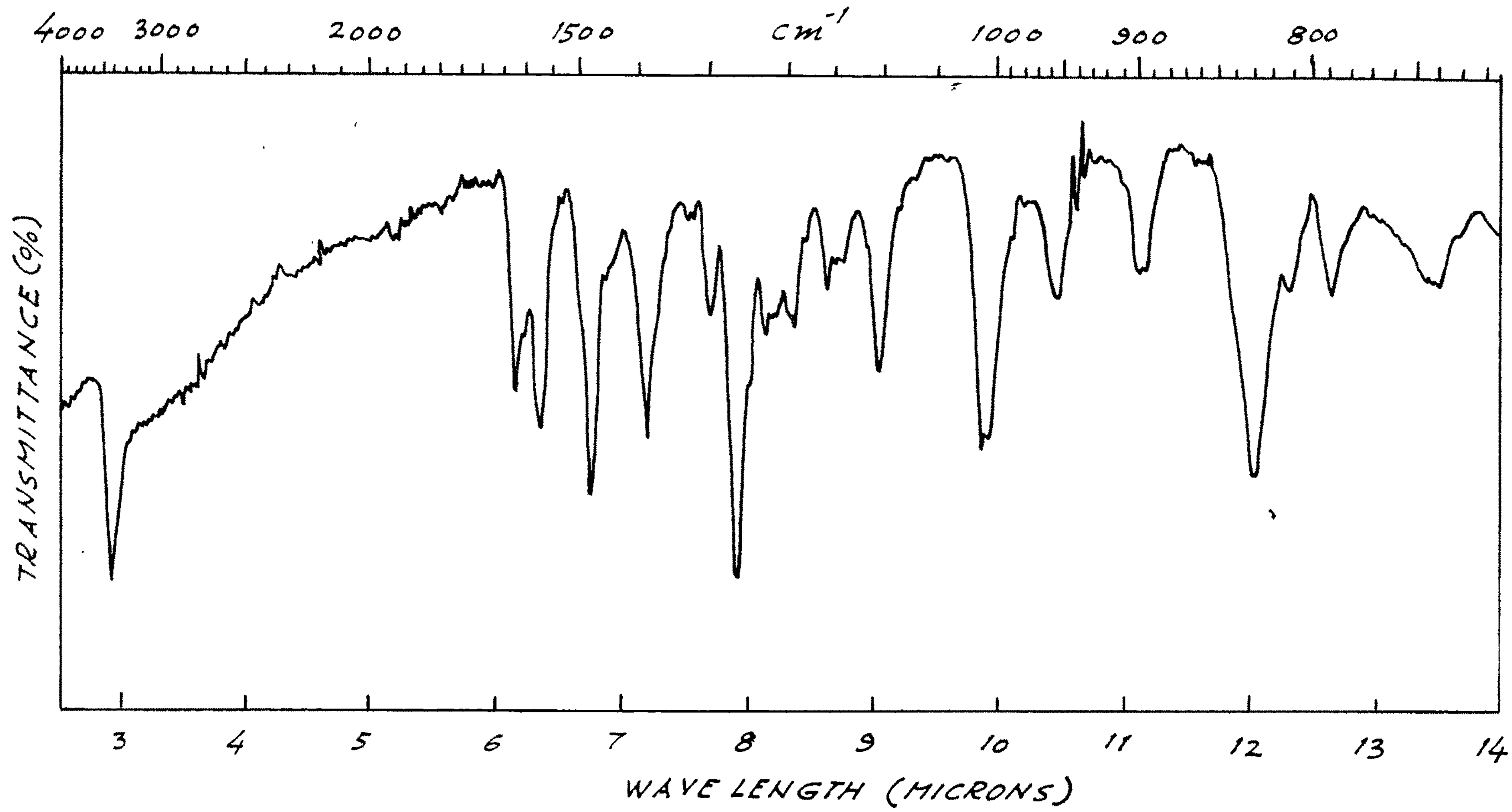

FIG. E-2(a) : IR SPECTRUM OF BASAO

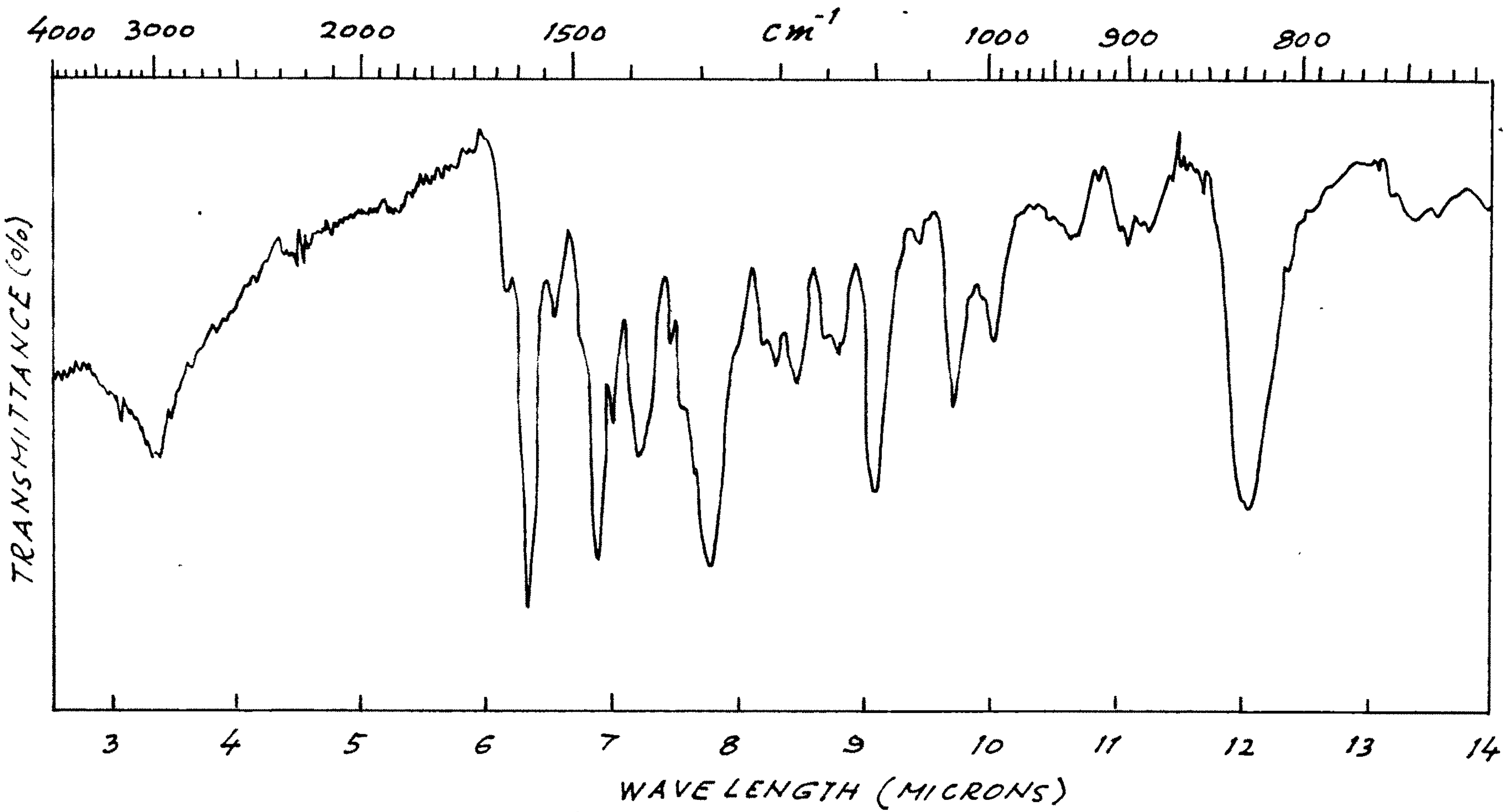

FIG. E-2(b) : IR SPECTRUM OF BASAO-Ni

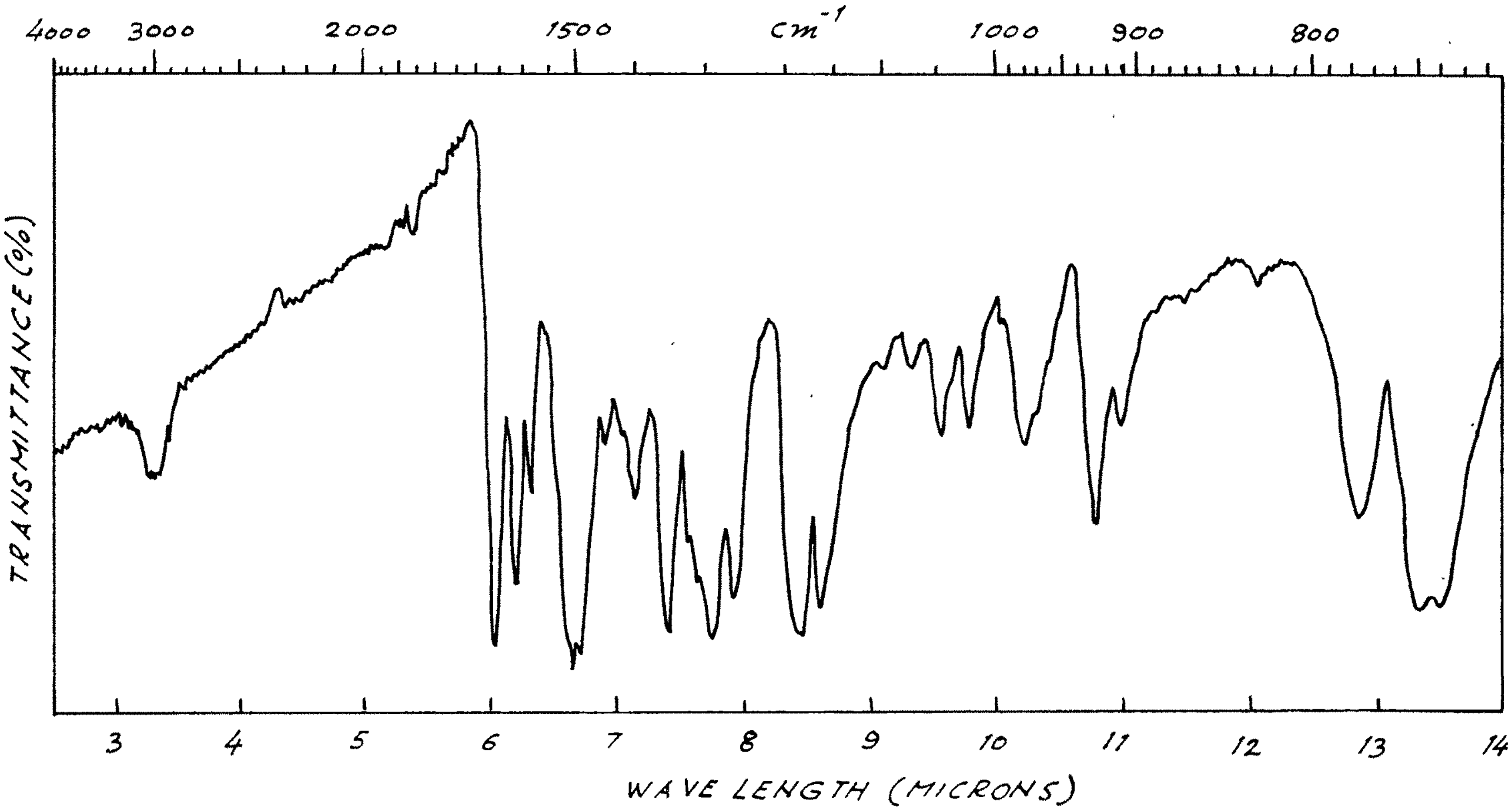

FIG. E-2(c) : IR SPECTRUM OF AAC

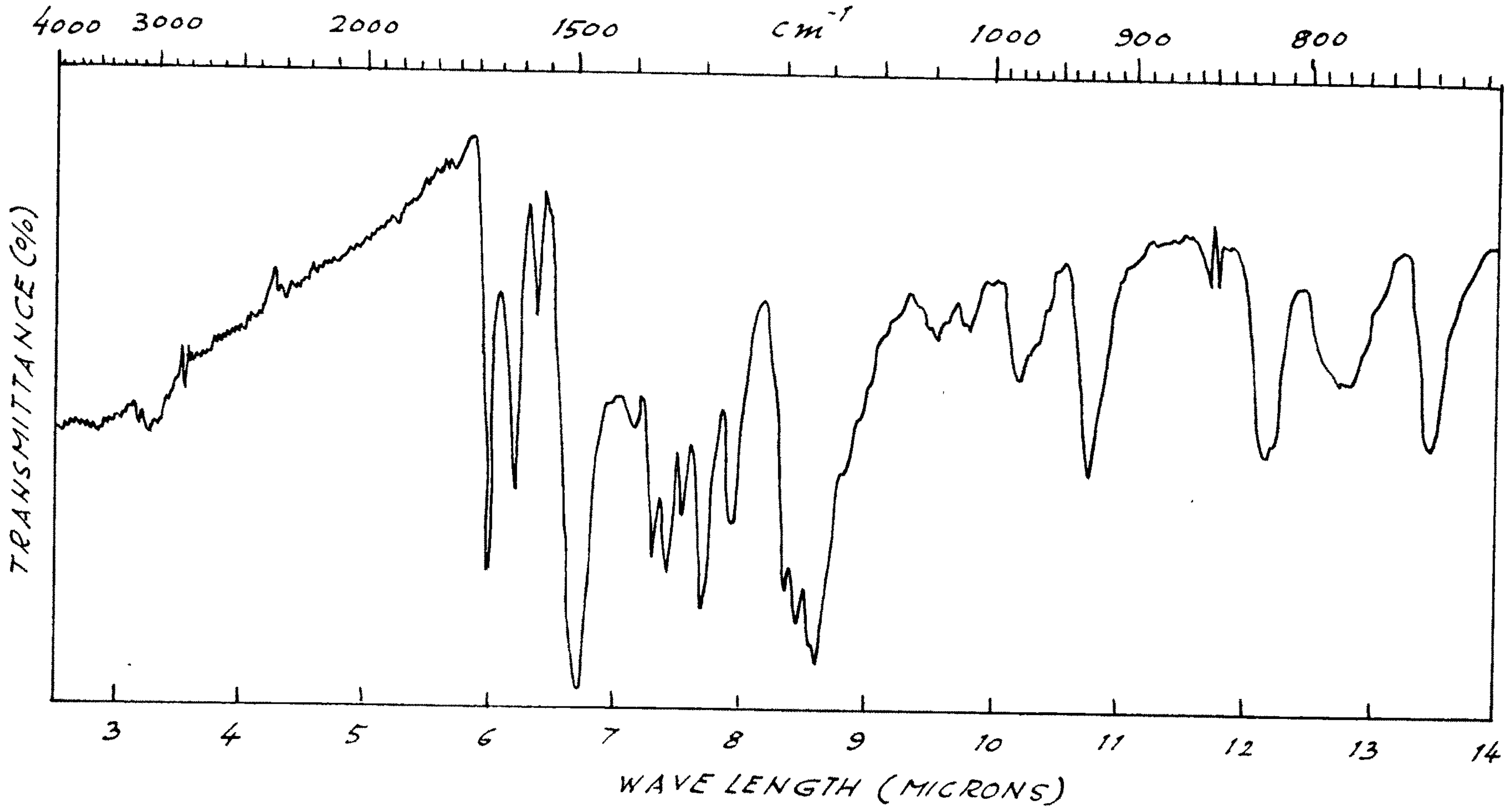

FIG. E-2(d) : IR SPECTRUM OF BAAC

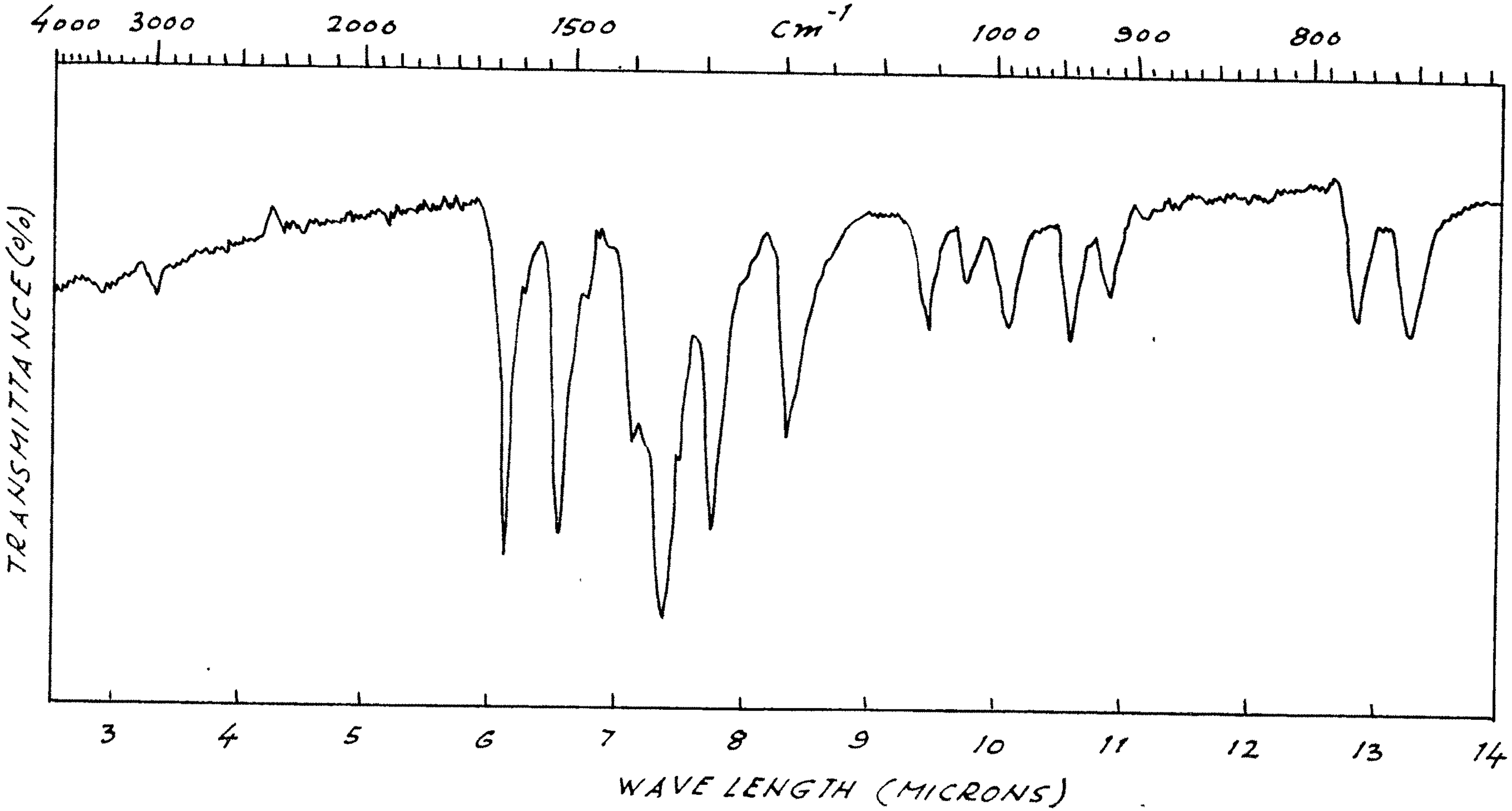

FIG. E-2(e) : IR SPECTRUM OF AAC-Cu

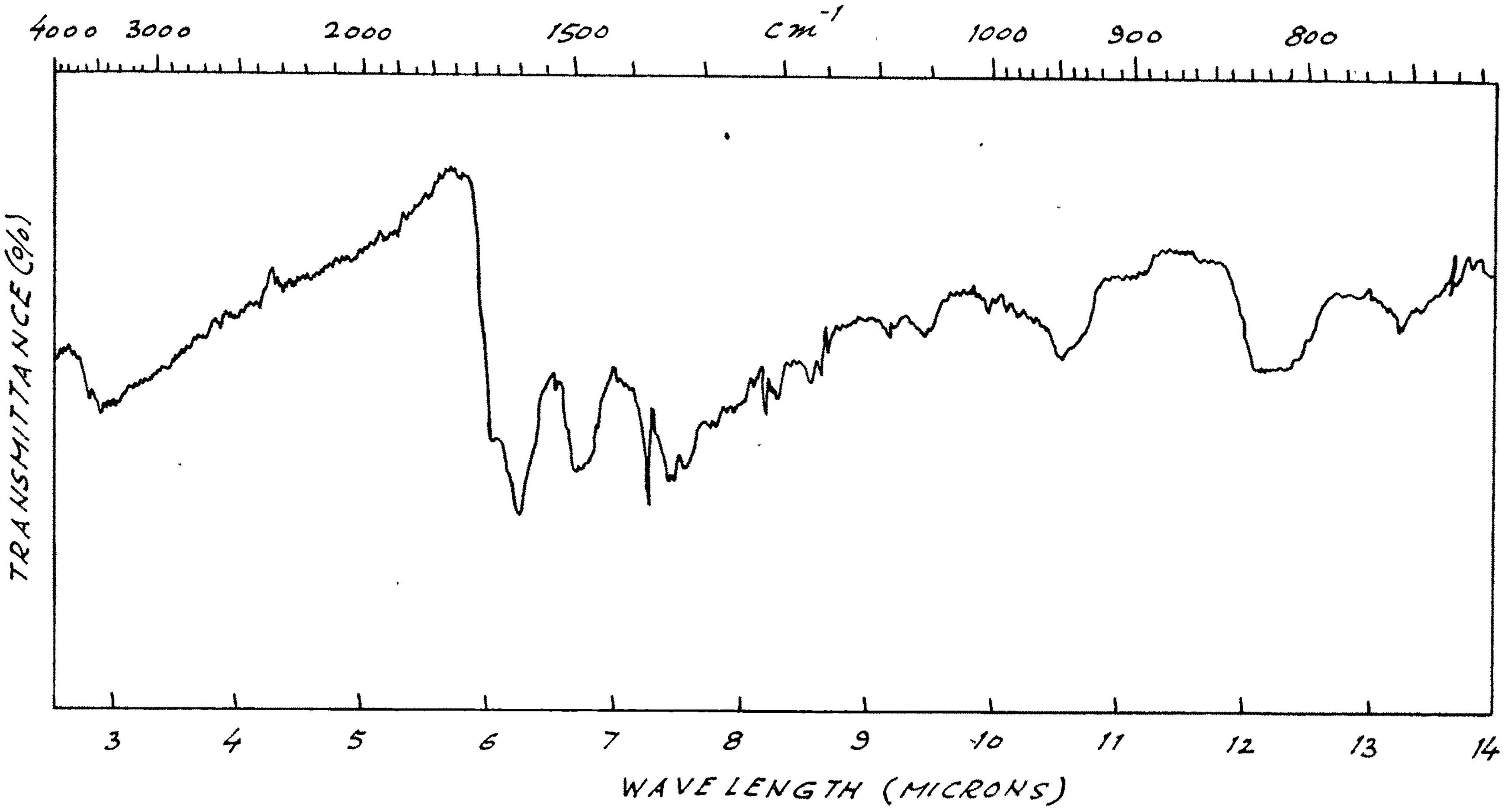

FIG. E-2(f) : IR SPECTRUM OF BAAC-Cu

Table E-10

Thermal analyses of the complexes

Temp	BASAO-Ni		BAAC-Cu	AAC-Cu
(°C)	ΔW(mg)	ΔT(°C)	ΔW(mg)	ΔW(mg)
100	0.5	+ 9.0	1.0	6.0
150	2.5	+14.5	3.5	11.5
210	3.5	+20.0	5.5	31.5
255	3.5	+25.5	6.0	32.0
305	3.5	+34.9	7.0	32.0
355	6.0	+33.0	7.5	32.0
400	9.0	+31.0	9.0	32.0
450	12.5	+32.0	9.5	32.0
500	15.0	+38.0	13.0	32.0
550	17.5	+36.0	16.5	32.0
600	19.0	+32.5	19.5	32.0
650	21.0	+32.5	21.0	32.0
700	23.0	+32.5	21.0	32.0
750	25.0	+32.5	21.0	32.0
800	25.0	+32.5	21.0	32.0

II.6. Schiff bases of salicylaldehyde and their transition metal complexes.

(i) Schiff bases :

(a) N,N' (disalicylidene) benzidine (SAB)

Benzidine (1.9 g.) dissolved in alcohol was mixed with salicylaldehyde (2.5 g.). Yellow precipitates were obtained; these were left overnight. The product was filtered, washed with water, alcohol and ether and dried. It was recrystallised from acetic acid. It melts at 257 °C. It is insoluble in water and all common organic solvents.

Attempts to prepare Cu(II), Co(II), and Ni(II) complexes of the above ligand under various conditions were unsuccessful.

(b) N,N' (disalicylidene) p-phenylenediamine.(SAP)

p-phenylenediamine (1.1 g.) dissolved in alcohol was mixed with salicylaldehyde (2.5 g.). Violet precipitates were obtained; these were left overnight. The product was filtered, washed with water, alcohol and ether and dried. It melts at 311 °C.

Attempts to prepare Cu(II), Co(II) and Ni(II) complexes of the above ligand under various conditions were unsuccessful.

(ii) Cu(II), Ni(II) and Co(II) complexes of salicylaldehyde.

Metal acetate dissolved in 50 % alcohol was mixed with salicylaldehyde in the same solvent (salt : ligand :: 1:2) the mixture was stirred at room temperature for three to four hours. The precipitates were filtered, washed with water, alcohol and ether and dried.

All complexes are sparingly soluble in alcohol, acetone, benzene, carbontetrachloride, ether, petroleum ether etc.

(iii) Reaction of metal complexes with benzidine or p-phenylenediamine.

The complex of Cu(II), Ni(II) or Co(II) with salicylaldehyde dissolved in alcohol was mixed with alcoholic solution of benzidine or p-phenylenediamine (metal complex : diamine :: 1:1) and refluxed on water bath for three to four hours. The products were filtered, washed with water, alcohol and ether and dried. They are insoluble in water and common organic solvents except dimethylformamide and dioxane in which they are sparingly soluble. The colour, m.p., analysis etc. of these complexes are presented in Table E-11; the magnetic susceptibilities and dimagnetic corrections of these complexes are presented in Table E-12.

Optical density of the compound in dimethylformamide in the visible region of the spectrum are presented in Table E-13. Infra-red spectra of some of the compounds are presented in fig. E-3.

Wt. loss (ΔW) in mg. per 50 mg. sample and temperature difference (ΔT) at a few selected temperatures observed in thermal analyses (D.T.A. and T.G.A.) of the complexes are presented in Table E-14.

Table E-11

Transition metal complexes

No.	Complex	Colour	m.p. °C.	Formula	Analysis			
					%M Found	%N Found	%M reqd.	%N reqd.
1	SAB-Cu	Chocolate	300	$C_{26}H_{18}N_2O_2Cu$	13.53	6.90	14.01	6.17
2	SAB-Co	Red	300	$C_{32}H_{24}N_3O_2Co$	11.36	7.97	10.89	7.76
3	SAB-Ni	Greenish yellow	300	$C_{40}H_{41}N_5O_6$	15.16	9.24	14.60	8.70
4	SAP-Cu	Dirtygreen	300	$C_{23}H_{18}N_3O_2Cu$	14.54	9.07	14.72	9.72
5	SAP-Co	Dirtyred	300	$C_{29}H_{30}N_5O_4Co$	9.85	12.27	10.31	12.26
6	SAP-Ni	Bluishash	300	$C_{30}H_{25}N_5O_4$	18.51	10.60	18.46	11.00

Table E-12

Magnetic susceptibility of the complexes

No.	Complex	Mass Magnetic Susceptibiluty X_g x 10^6	Temp.in (°C.)	Diamagnetic corrections (per metal atom) X x 10^6
1	SAB-Cu	3.18	31.5	247
2	SAB-CO	15.53	31.5	302
3	SAB-Ni	10.06	32.0	223
4	SAP-Cu	3.56	32.00	226
5	SAP-Co	18.28	32.5	305
6	SAP-Ni	21.36	32.0	165

Table E-13

Optical density of the compounds in dimethylformamide in the visible region (400-800 mμ)

Wavelength (mμ)	Optical density SAB-Cu	SAB-Ni	SAB-Co
800	0.017	0.059	0.008
780	0.011	0.049	0.005
760	0.013	0.046	0.009
740	0.013	0.032	0.009
720	0.013	0.022	0.004
700	0.022	0.018	0.004
680	0.022	0.027	0.009
660	0.027	0.041	0.009
640	0.032	0.056	0.018
620	0.032	0.066	0.022
600	0.041	0.076	0.032
580	0.046	0.086	0.056
560	0.056	0.076	0.097
540	0.081	0.097	0.187
520	0.119	0.114	0.301
500	0.260	0.119	0.398
480	0.523	0.137	0.585
460	0.745	0.155	1.155
440	1.301	0.201	1.699
420	1.959	0.253	1.968
400	1.880	0.294	1.531

Table E-13 (contd.)

Wavelength	Optical density		
($m\mu$)	SAP-Cu	SAP-Ni	SAP-Co
800	0.087	0.008	0.222
780	0.099	0.005	0.218
760	0.114	0.004	0.222
740	0.125	0.004	0.229
720	0.143	0.004	0.260
700	0.169	0.004	0.301
680	0.222	0.004	0.377
660	0.301	0.007	0.495
640	0.387	0.009	0.620
620	0.456	0.013	0.770
600	0.538	0.013	0.921
580	0.620	0.018	1.097
560	0.699	0.018	1.222
540	0.864	0.022	1.523
520	1.046	0.027	1.699
500	1.222	0.032	2.000
480	1.699	0.041	2.000
460	2.000	0.046	1.699
440	2.000	0.051	1.699
420	1.977	0.074	0.603
400	1.832	0.098	0.525

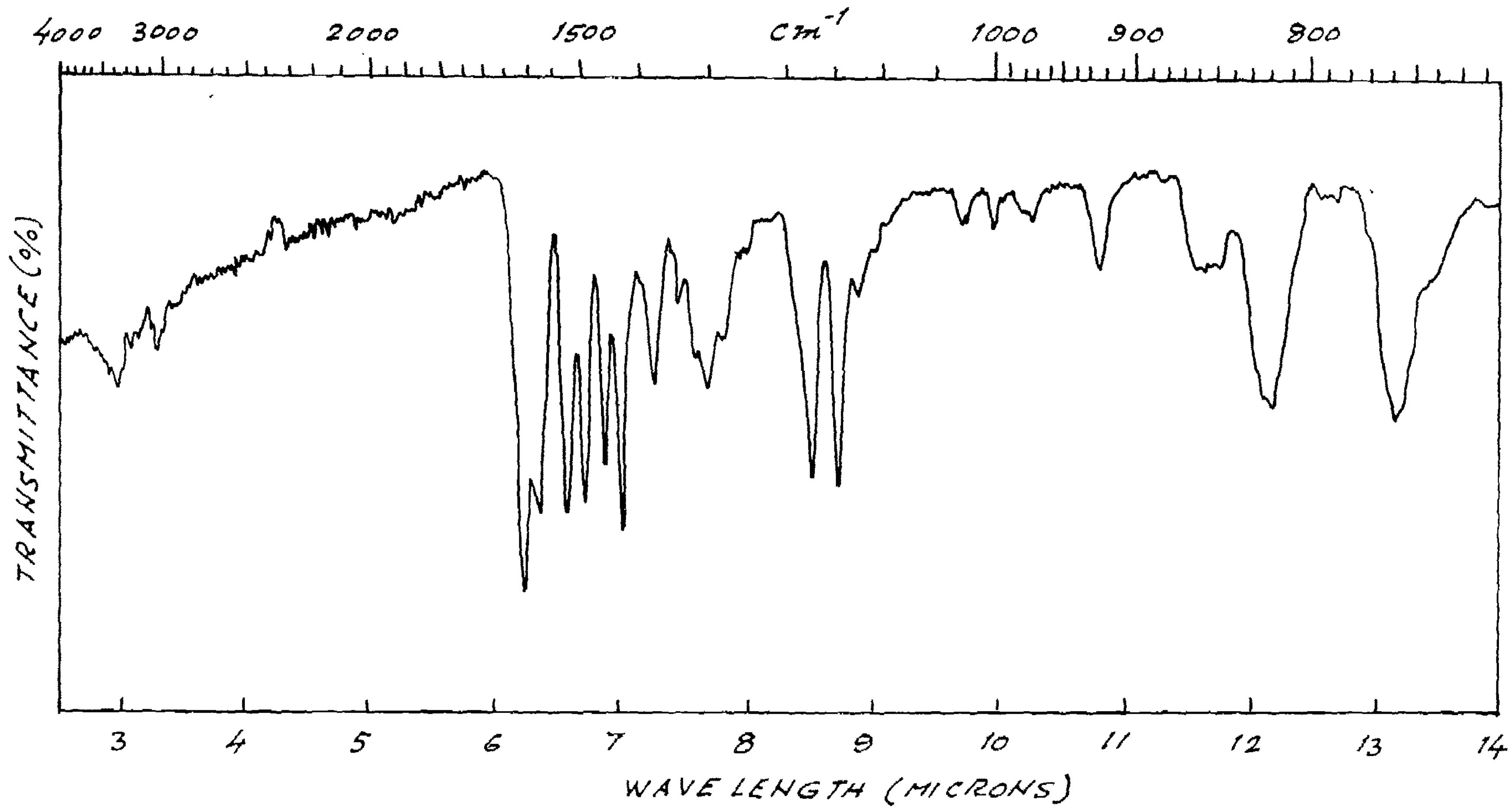

FIG. E-3(a) : IR SPECTRUM OF SAB-Co

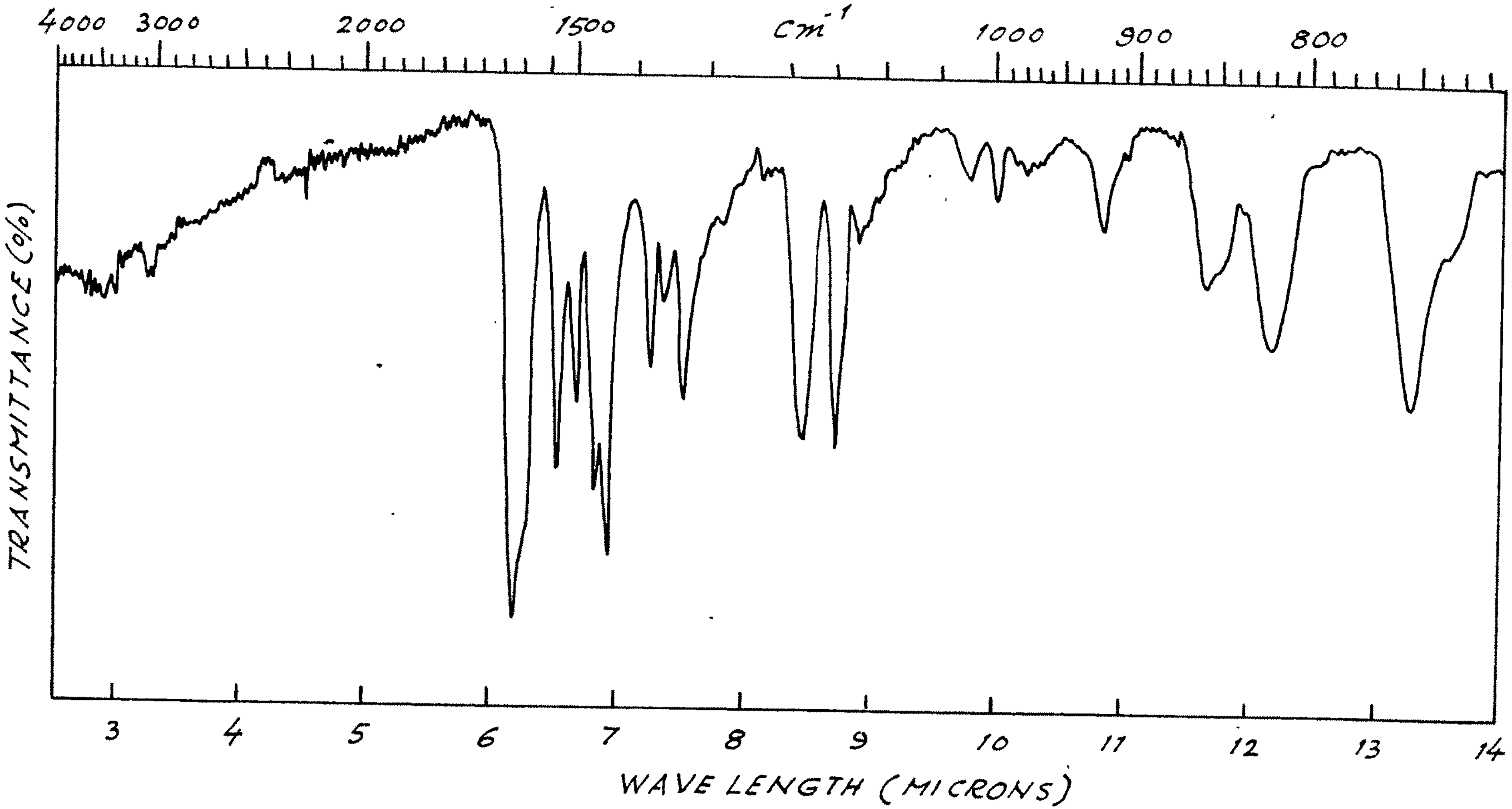

FIG. E-3(b) : IR SPECTRUM OF SAB-Cu

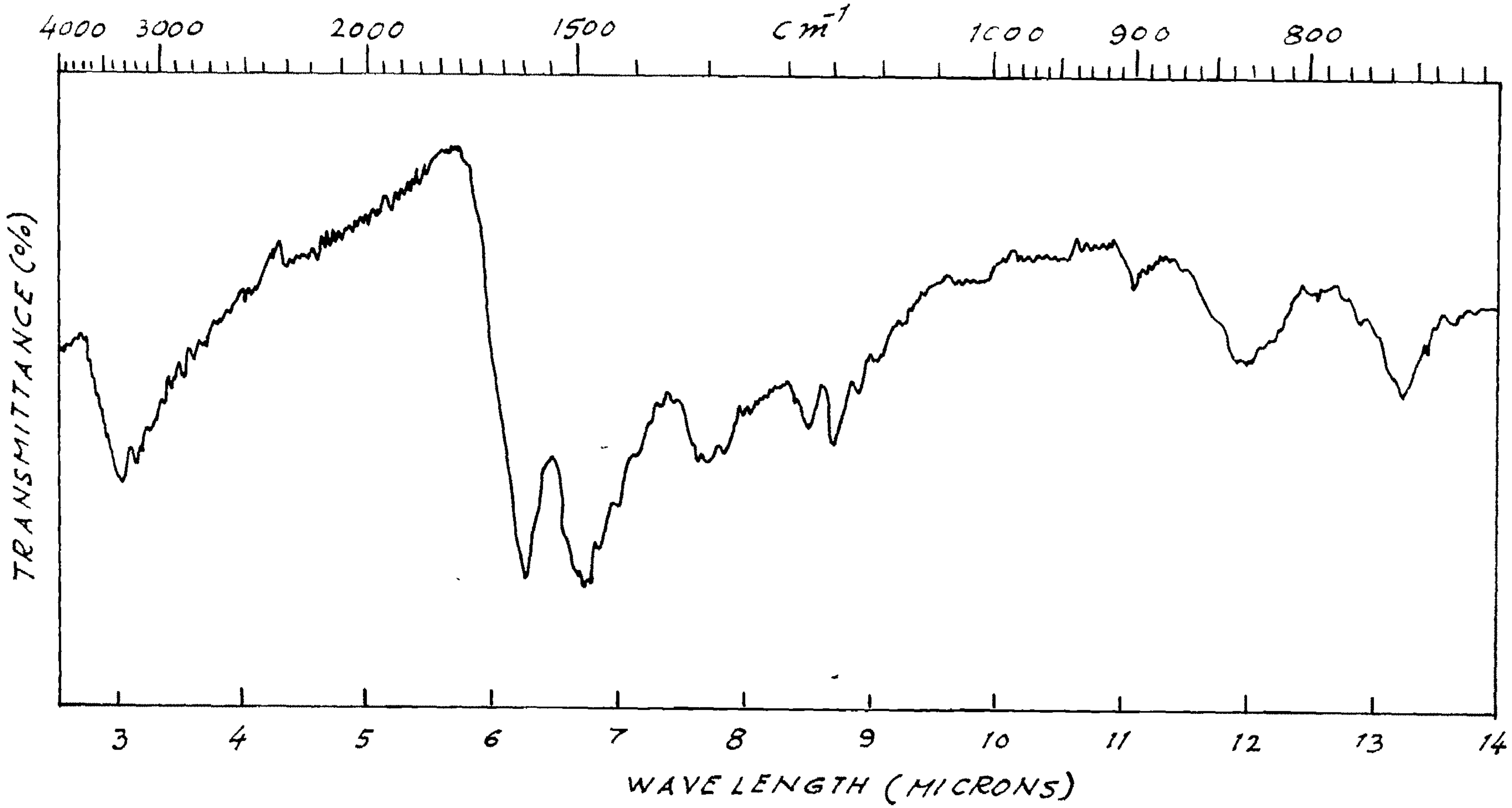

FIG. E-3(c) : IR SPECTRUM OF SAP-Co

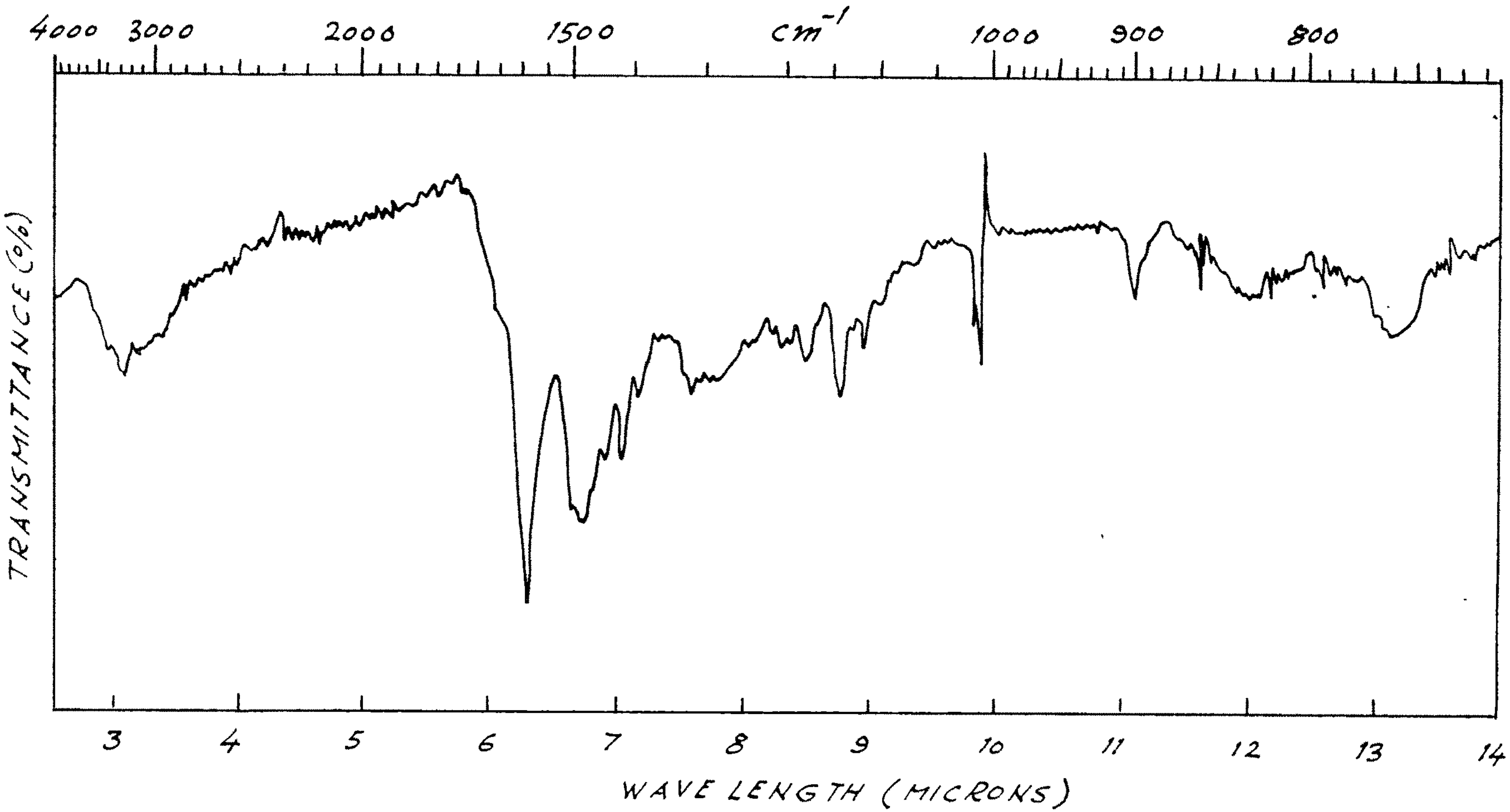

FIG. E-3(d): IR SPECTRUM OF SAP-Cu

Table E-14

Thermal analyses of the complexes

Temp.	SAB-Cu	SAB-Co		SAB-Ni	
(°C)	ΔW(mg)	ΔW(mg)	ΔT(°C)	ΔW(mg)	ΔT(°C)
100	4.0	0.5	+ 0.5	6.0	- 1.0
150	4.0	0.5	+ 0.5	7.0	- 3.5
200	4.0	0.5	+ 0.5	7.0	- 6.0
255	4.0	0.5	- 0.5	7.0	- 7.0
305	4.0	3.0	+ 1.0	7.0	- 8.5
355	5.0	9.5	+ 2.0	7.0	- 9.0
400	6.0	10.5	+ 2.0	12.0	- 9.0
450	6.0	13.0	+ 2.0	18.0	-11.0
500	7.0	18.0	+ 7.0	24.0	- 6.0
550	8.0	22.0	+ 4.0	27.0	-13.0
600	8.0	27.0	+ 2.5	27.0	-12.0
650	8.0	34.0	+ 1.0	27.0	-11.0
700	8.0	38.0	+ 0.5	27.0	-11.0
750	8.0	38.0	-	27.0	-11.0
800	8.0	38.0	-	27.0	-11.0

Table E-14 (contd.)

Temp.	SAP-Cu	SAP-Co		SAP-Ni	
(°C)	ΔW(mg)	ΔW(mg)	ΔT(°C)	ΔW(mg)	ΔT(°C)
100	3.0	4.5	+ 1.0	3.0	+ 8.0
150	5.0	5.5	+ 1.0	5.0	+ 6.0
200	9.0	8.0	+ 1.0	11.0	+ 4.0
255	14.0	9.0	+ 1.0	16.5	+ 4.0
305	18.0	11.0	+ 1.0	20.0	+ 4.0
355	23.0	16.0	+ 1.0	22.5	+ 4.0
400	26.0	19.5	+ 1.0	25.0	+ 4.0
450	30.0	23.0	+ 1.0	35.0	- 1.0
500	34.0	26.0	+ 3.0	42.5	+ 8.0
550	36.0	29.5	+ 3.0	43.0	+ 2.0
600	36.0	34.0	+ 1.0	43.0	-
650	36.0	38.5	+ 1.0	43.0	+ 2.0
700	36.0	42.0	+ 1.0	43.0	+ 3.0
750	36.0	42.0	+ 1.0	43.0	+ 3.0
800	36.0	42.0	+ 1.0	43.0	+ 3.0

II.7 Schiff bases of Vic-oxime ketones with diamines and their transition metal complexes.

(i) Schiff bases :

Attempts to prepare Schiff bases of 2,3-dioxobutyranilide 2-oxime with diamine such as benzidene, p-phenylenediamine etc. resulted in the formation of product which could not be identified as Schiff bases.

(ii) (a) Chloride method (for Cu and Ni).

The solutions of metal chloride 2,3-dioxobutyranilide and benzidene or p-phenylenediamine in ethanol were mixed in the molar proportion of 1:2:1 respectively. The mixture became turbid, gradually forming precipitates. These were refluxed on water bath for about two hours and left overnight. They were then filtered, washed with water and dilute alcohol and dried. They are insoluble in water and all common organic solvents except pyridine and dimethylformamide.

(b) Acetate method (for Cu and Co).

The solutions of metal acetate, 2,3-dioxobutyranilide and benzidene or p-phenylenediamine in ethanol were mixed in the molar proportion of 1:2:1 respectively. The mixture became turbid, gradually forming precipitates. These were refluxed on water bath for about two hours and left overnight. They were then filtered, washed with water and dilute alcohol and dried. They are insoluble in water and all common organic solvents except pyridine and dimethylformamide.

(c) Sulphate method(for Fe)

The solutions of ferrous sulphate (in water), 2,3-dioxybutyranilide (in alcohol) and benzidine or p-phenylenediamine (in alcohol) were mixed in the molar proportions of 1:2:1 respectively. Precipitates were gradually obtained, which were left overnight. These were filtered, washed with dilute alcohol and dried. They are soluble in all common solvents. The colour, m.p., analysis etc. of these complexes are presented in Table E-15; the magnetic susceptibilities and diamagnetic corrections of these complexes are presented in Table E-16.

Optical density of the compounds in dimethylformamide in the visible region of the spectrum are presented in Table E-17.

Wt. loss (ΔW) in mg. per 50 mg. sample and temperature difference (ΔT) at a few selected temperatures observed in thermal analysis (D.T.A. and T.G.A.) of the complexes are presented in Table E-18.

Table E-15

Transition metal complexes

No.	Complex	Colour	m.p.	Formula	Analysis			
					%M Found	%N Found	%M reqd.	%N reqd.
(a) Chloride method								
1	OB-NiCl	Greenish yellow	300	$C_{26}H_{24}N_5O_5Cl_2Ni$	10.69	11.40	9.56	11.37
2	OB-CuCl	Brown	300	$C_{16}H_{14}N_3O_2Cl_2Cu$	15.32	10.27	15.32	10.42
3	OP-NiCl	Dull ash	300	$C_{16}H_{16}N_4O_2Cl_2Ni$	14.08	12.41	13.79	13.15
4	OP-CuCl	Brown	300	$C_{26}H_{24}N_6O_4Cl_2Cu$	9.97	13.93	10.28	13.58

Table E-15 (contd.)

No.	Complex	Colour	m.p. (°C)	Formula	Analysis %M Found	%N Found	%M reqd.	%N reqd.
(b) Acetate method								
5	OB-Cu	Greenish brown	300	$C_{26}H_{22}N_5O_5Cu$	12.54	12.35	11.60	12.77
6	OB-Co	Dull red	300	$C_{32}H_{30}N_6O_6Co$	9.01	13.43	8.99	12.86
7	OP-Cu	Greenish brown	300	$C_{23}H_{22}N_5O_5Cu$	13.19	12.69	12.42	13.68
8	OP-Co	Violet shining crystalline	300	$C_{58}H_{72}N_{14}O_{18}Co_2$	8.71	14.09	8.6	14.32
(c) Sulphate method								
9	OB-Fe	Blue	300	$C_{32}H_{32}N_6O_{10}SFe$	7.60	11.83	7.46	11.23
10	OP-Fe	Blue	300	$C_{26}H_{24}N_6O_{16}S_3Fe_3$	17.98	9.29	17.87	8.93

Table E-16

Magnetic susceptibility of the complexes

No.	Complex	Mass Magnetic susceptibility $X_g \times 10^6$	Temp. in (°C.)	Diamagnetic corrections (per metal atom) $X \times 10^6$
1	OB-Cu	1.56	30	- 279
2	OB-Co	3.89	30.5	- 334
3	OB-NiCl	7.20	30	- 309
4	OB-CuCl	4.68	30	- 198
5	OP-Cu	1.72	31.5	- 260
6	OP-Co	4.42	30.5	- 368
7	OP-NiCl	9.95	31.5	- 222
8	OP-CuCl	7.92	31.5	- 327
9	OB-Fe	5.72	29	- 384
10	OP-Fe	35.86	30.5	- 102

Table E-17

Optical density of the compounds in dimethylformamide in the visible region (400-800 mμ)

Wavelength	Optical density			
(mμ)	OB-Cu	OB-Co	OB-NiCl	OB-CuCl
800	0.043	0.006	0.005	0.244
780	0.047	0.005	0.005	0.244
760	0.051	0.004	0.004	0.244
740	0.051	0.004	0.004	0.222
720	0.051	0.004	0.004	0.222
700	0.056	0.009	0.004	0.229
680	0.066	0.013	0.009	0.260
660	0.081	0.022	0.009	0.292
640	0.092	0.027	0.009	0.319
620	0.094	0.032	0.018	0.337
600	0.097	0.036	0.022	0.357
580	0.114	0.046	0.028	0.377
560	0.118	0.051	0.032	0.387
540	0.131	0.066	0.036	0.552
520	0.181	0.086	0.097	1.046
500	0.244	0.114	0.131	1.699
480	0.357	0.168	0.125	2.000
460	0.538	0.252	0.108	2.000
440	0.824	0.377	0.102	2.000
420	1.155	0.562	0.125	1.939
400	1.518	0.812	0.204	1.792

Table E-17 (contd.)

Wavelength	Optical density			
(mμ)	OP-Cu	OP-Co	OP-NiCl	OP-CuCl
800	0.103	0.016	0.018	0.015
780	0.119	0.016	0.011	0.010
760	0.131	0.018	0.004	0.009
740	0.137	0.018	0.004	0.009
720	0.143	0.022	0.004	0.009
700	0.161	0.027	0.018	0.009
680	0.187	0.046	0.018	0.013
660	0.237	0.066	0.018	0.013
640	0.276	0.076	0.022	0.022
620	0.301	0.092	0.027	0.022
600	0.347	0.108	0.036	0.027
580	0.377	0.119	0.041	0.036
560	0.377	0.125	0.041	0.036
540	0.469	0.155	0.046	0.046
520	0.602	0.187	0.056	0.051
500	0.824	0.222	0.061	0.056
480	1.155	0.276	0.108	0.061
460	1.699	0.347	0.201	0.066
440	2.000	0.444	0.252	0.086
420	1.648	0.544	0.265	0.106
400	1.806	0.699	0.349	0.137

Table E-18

Thermal analyses of the complexes

Temp.	OB-Cu	OB-CuCl	OB-NiCl		OB-Co	
(°C)	ΔW(mg)	ΔW(mg)	ΔW(mg)	ΔT(°C)	ΔW(mg)	ΔT(°C)
100	0.00	0.5	2.00	- 2.00	0.5	- 1.0
150	1.00	1.0	2.50	- 6.0	2.0	- 7.0
210	7.00	4.0	4.00	- 6.5	3.5	-11.5
255	17.0	4.0	6.50	- 5.5	15.0	- 6.0
305	22.0	6.5	11.0	- 7.0	17.0	-17.0
355	26.0	10.0	14.5	-11.5	21.5	-20.5
400	29.0	13.0	18.0	-12.5	24.0	-21.0
450	32.5	18.5	20.0	-11.0	26.5	-22.0
500	35.0	24.0	25.0	- 8.0	30.0	-18.0
550	35.0	31.0	29.5	-13.5	32.5	-29.0
600	35.0	34.0	31.0	-12.5	32.5	-33.0
650	35.0	34.0	31.0	-12.0	32.5	-28.0
700	35.0	34.0	31.0	-12.0	32.5	-20.0
750	35.0	34.0	31.0	-12.0	32.5	-20.0
800	35.0	34.0	31.0	-12.0	32.5	-20.0

Table E-18 (contd.)

Temp.	OP-Cu	OP-CuCl	OP-NiCl		OP-Co	
(°C)	ΔW(mg)	ΔW(mg)	ΔW(mg)	ΔT(°C)	ΔW(mg)	ΔT(°C)
100	1.0	0.00	0.00	- 3.5	0.5	- 4.0
150	2.5	0.00	1.00	-10.5	1.0	- 13.0
210	10.5	2.5	3.5	-16.0	1.5	- 18.0
255	16.5	6.0	5.0	-17.0	10.0	- 12.0
305	20.0	8.0	14.0	-18.5	13.0	- 21.0
355	24.0	10.5	18.0	-24.5	18.0	- 30.0
400	26.5	14.0	22.0	-26.5	20.5	- 31.0
450	28.0	18.0	27.0	-25.5	23.5	- 31.5
500	30.0	22.5	29.0	-20.0	26.0	- 27.0
550	30.5	28.0	31.5	-30.0	26.5	- 40.0
600	30.5	30.5	31.5	-25.0	26.5	- 34.0
650	30.0	30.5	31.5	-24.0	26.5	- 35.0
700	30.5	30.5	31.5	-24.0	26.5	- 28.5
750	30.5	30.5	31.5	-24.0	26.5	- 28.5
800	30.5	30.5	31.5	-24.0	26.5	- 28.5

II.8 N-ligand from vic-oxime ketones and their transition metal complexes.

(i) Schiff base from 2,3-dioxobutyranilide-2-oxime and p-Toluidine (TO).

It was prepared by the method of Talati and Patel.[143]

2,3-dioxobutyranilide-2-oxime (2.1 g.) dissolved in alcohol was mixed with p-toluidine (1.1 g.). The mixture was warmed gently and then kept at room temperature for a long period. Crystals appear after keeping the mixture for about four days. The product was filtered, washed with aqueous alcohol and dried. It was recrystallised from alcohol. It melts at 163°C.

(ii) 2,3-dioxobutyranilide-2-oxime-3-thiosemicarbazone.(TSO)

It was prepared by the method of Patel and Mankad.[144]

2,3-dioxobutyranilide-2-oxime (2.1 g.) dissolved in aqueous alcohol was mixed with aqueous solution of thiosemicarbazide (1.0 g.). On standing crystals were obtained. These were left overnight; they were filtered, washed with water and dilute alcohol and dried. It melts at 176-78°C. The product was repeatedly recrystallised from aqueous alcohol in white shining leaflets. Melting point was raised to 186-87°C.

(iii) 2,3-dioxobutyranilide-2-oxime-3-semicarbazone (SCO)

It was prepared by the method of Patel and Mankad.[144]

2,3-dioxobutyranilide-2-oxime (2.1 g.) dissolved in aqueous alcohol was mixed with aqueous solution of semicarbazide (0.8 g.). On standing yellow crystals were obtained. Tsese were left overnight; they were filtered, washed with little water and dilute alcohol and dried. The product was crecrystallised from aqueous alcohol in pale yellow shining needles. It melts at 147-48°C.

(iv) Reaction of Ni(II) with 2,3-dioxobutyranilide-2-oxime and p-Toluidine.

(a) Solutions of nickel acetate (1.2 g.), 2,3-dioxobutyranilide-2-oxime (2.0 g.) and p-toluidine (1.[illegible] g.)) in 50 % alcohol were mixed. The mixture became turbid and slowly browinish green precipitates were obtained. The mixture was kept for three days. The precipitates were then filtered, washed several times with water, dilute alcohol and ether and dried. The product is insoluble in all common organic solvents except pyridine and dimethylformamide.

(b) Solutions of 2,3-dioxobutyranilide-2-oxime (2.0 g.), nickel acetate (1.2 g.) and p-toluidine (1.1 g.) in 50 % alcohol were mixed. The mixture became turbid and slowly brownish green precipitates were obtained. It was refluxed on water bath for about three hours and left overnight. The precipitates were filtered, washed several times with water, dilute alcohol and ether and dried. It is insoluble in all common organic solvents except pyridine and dimethylformamide.

(v) Reaction of Co(II) with 2,3-dioxobutyranilide-2-oxime and p-Toluidine.

(a) Solutions of 2,3-dioxobutyranilide-2-oxime (2.0 g.), cobalt acetate (1.2 g.) and p-toluidine (1.1 g.) in 50 % alcohol were mixed. The mixture was kept for four days at room temperature. Orange red precipitates were obtained. These were filtered, washed with water, dilute alcohol and ether and dried. The product was recrystallised from benzene + petroleum ether. It is soluble in all common organic solvents except petroleum ether.

(b) Solutions of 2,3-dioxobutyranilide-2-oxime (2.0 g.), cobalt acetate(1.2 g.) and p-toluidine (1.1 g.) in 50 % alcohol were mixed. The mixture became turbid and orange red precipitates were obtained. These were refluxed on water bath for about three to four hours and left overnight; they were filtered, washed several times with water, dilute alcohol and ether and dried.

(Vi) Reaction of Ni(II) with 2,3-dioxobutyranilide-2-oxime and thiosemicarbazide.

Solutions of 2,3-dioxobutyranilide-2-oxime (2.0 g.), nickel acetate (1.2 g.) and thiosemicarbazide (2.0 g.) in 50 % alcohol were mixed. The mixture was kept for four days at room temperature. Dirty red precipitates were slowly obtained. These were filtered, washed with water, dilute alcohol and ether and dried. The product is insoluble in all common organic solvents except pyridine and dimethylformamide in which it is sparingly soluble.

(vii) Ni(II) complex of 2,3-dioxobutyranilide-2-oxime-3-thiosemicarbazone.

Solutions of nickel acetate (1.2 g.) and 2,3-dioxobutyranilide-2-oxime-3-thiosemicarbazone (2.5 g.) were mixed. The mixture became turbid, it was refluxed on water bath for two to three hours and left overnight. The precipitates were filtered, washed with water, alcohol and ether and dried. It is insoluble in all common organic solvents except pyridine and dimethylformamide.

(viii) Co(II) complex of 2,3-dioxobutyranilide-2-oxime-3-thiosemicarbazide.

Solutions of cobalt acetate (1.2 g.) and 2,3-dioxobutyranilide-2-oxime-3-thiosemicarbazide (2.5 g.) were mixed. The mixture became turbid. It was refluxed on water bath for three to four hours and left overhight. The precipitates were filtered, washed with water, alcohol and ether and dried. It is insoluble in all common organic solvents except pyridine and dimethylformamide.

(ix) Co(II) complex of 2,3-dioxobutyranilide-2-oxime- and semicarbazide.

Solutions of 2,3-dioxobutyranilide-2-oxime (2.1 g.), semicarbazide (1.1 g.) and cobalt acetate (1.2 g.) in 50 % alcohol were mixed and a few drops of ammonium hydroxide solution were added. The mixture became turbid. It was refluxed on water bath for three to four hours and left overnight. The precipitates were filtered, washed with water, alcohol and ether and dried. The colour, m.p. analysis, etc. of these complexes are presented in Table E-19; the mass magnetic susceptibilities and diamagnetic corrections of these complexes are presented in Table E-20.

Optical density of the ligands and their above

Table E-19

Transition metal complexes

No.	Complex	Colour	m.p. °C.	Formula	Analysis %M Found	 %N Found	 %M reqd.	 %N reqd.
1 (a)	OT-Ni(C)	Brownish green	300	$C_{34}H_{32}N_6O_4Ni$	9.92	12.22	9.06	12.93
2 (b)	OT-Ni(R)	Dirty-brown	300	$C_{27}H_{29}N_5O_7Ni$	9.52	12.93	9.91	11.80
3 (a)	OT-Co(C)	Orange-red	300	$C_{27}H_{27}N_5O_6Co$	10.17	12.13	10.23	12.15
4 (b)	OT-Co(R)	Orange-red	300	$C_{27}H_{27}N_5O_6Co$	10.12	12.66	10.23	12.15
5	OTS-Ni	Dirty-red	300	$C_{11}H_{11}N_5O_2SNi$	17.87	24.32	17.49	20.85
6	TSO-Ni	Dirty-red	300	$C_{11}H_{11}N_5O_2SNi$	17.30	21.80	17.49	20.85
7	TSO-Co	Black-shining	300	$C_{22}H_{28}N_{10}O_6S_2Co$	9.84	20.46	9.04	21.50

Table E-20

Magnetic susceptibility of the complexes

No.		Complex	Magnetic susceptibility $X_g \times 10^6$	Temp. in (°C.)	Diamagnetic corrections (per metal atom) $X \times 10^6$
1	(a)	OT-Ni(C)	5.03	31.5	- 348
2	(b)	OT-Ni(R)	4.739	31.5	- 297
3	(a)	OT-Co(C)	5.061	31.0	- 297
4	(b)	OT-Co(R)	5.549	30.0	- 297
5		OTS-Ni	3.143	31.0	- 150
6		TSO-Ni	0.390	31.0	- 150
7		TSO-Co	0.158	33.0	- 333
8		SCO-Co			

Optical density of the compounds in dimethylformamide in the visible region of the spectrum is presented in Table E-21.

Wt. loss (Δ W) in mg. per 50 mg. sample and temperature difference (Δ T) at a few selected temperatures observed in thermal analysis (D.T.A. and T.G.A.) of the complexes are presented in Table E-22.

II 9. Oxime-azine (oxime-hydrazone) hydroxy-azine and their transition metal complexes :

(i) Reaction of Cu(II), Ni(II) and Co(II) with 2,3-dioxobutyranilide-2-oxime in presence of hydrazine.

When aqueous solution of hydrazine sulphate and sodium acetate was mixed with solutions of 2,3-dioxobutyranilide-2-oxime and metal acetate in 50 % alcohol (metal acetate: oxime : hydrazine 1:2:1), precipitates were obtained. These were refluxed on waterbath for about three hours and left overnight. These were then filtered, washed with water, dilute alcohol and ether and dried. They are insoluble in all common organic solvents except pyridine and dimethylformamide.

(ii) Reaction of Fe(II) with 2,3-dioxobutyranilide-2-oxime in presence of hydrazine :

When solution of 2,3-dioxobutyranilide-2-oxime (2.1 g.) in 50 % alcohol was mixed with aqueous solution of hydrazine sulphate (0.7 g.) sodium acetate (1.4 g.) and iron(II) sulphate (1.4 g.), blue precipitates were obtained. These were kept for three days. They were then filtered, washed with water, dilute alcohol and little ether and dried. It is

Table E-21

Optical density of the compounds in dimethylformamide in the visible region (400-800 mμ)

Wave length	Optical density			
(mμ)	OT-Ni (C)	OT-Ni (R)	OT-Co (C)	OT-CO (R)
800	0.017	0.008	0.008	0.009
780	0.011	0.005	0.010	0.006
760	0.013	0.004	0.010	0.004
740	0.013	0.004	0.013	0.004
720	0.013	0.004	0.018	0.004
700	0.018	0.009	0.027	0.009
680	0.018	0.009	0.046	0.013
660	0.022	0.009	0.076	0.018
640	0.022	0.009	0.108	0.022
620	0.027	0.009	0.137	0.032
600	0.032	0.013	0.169	0.037
580	0.036	0.013	0.201	0.046
560	0.041	0.018	0.222	0.051
540	0.051	0.022	0.284	0.071
520	0.066	0.032	0.377	0.097
500	0.086	0.041	0.495	0.131
480	0.114	0.046	0.699	0.187
460	0.169	0.056	1.000	0.292
440	0.229	0.076	1.301	0.469
420	0.338	0.123	1.676	0.737
400	0.664	0.262	1.832	1.064

Table E-21 (Contd.)

Wavelength (mμ)	Optical density		
	OTS-Ni	TSO-Ni	TSO-Co
800	0.00	0.018	0.008
780	0.00	0.005	0.011
760	0.00	0.004	0.011
740	0.004	0.009	0.013
720	0.004	0.009	0.013
700	0.004	0.018	0.013
680	0.004	0.027	0.013
660	0.004	0.046	0.027
640	0.009	0.071	0.036
620	0.009	0.097	0.056
600	0.009	0.119	0.081
580	0.009	0.131	0.108
560	0.013	0.131	0.143
540	0.013	0.149	0.215
520	0.013	0.201	0.292
500	0.022	0.260	0.347
480	0.027	0.337	0.387
460	0.032	0.509	0.398
440	0.056	0.921	0.469
420	0.100	1.352	0.729
400	0.173	1.505	1.120

Table E-22

Thermal analyses of the complexes

Temp.	OT-Co(C)		OT-Co(R)	
°C	ΔW(mg)	ΔT(°C)	W(mg)	TΔ(°C)
100	1.0	+ 8.0	0.0	+ 9.0
150	2.0	+14.0	0.5	+11.0
210	5.0	+19.5	2.5	+12.0
255	18.0	+16.0	22.0	+11.0
305	22.5	+15.0	26.0	+ 7.0
355	29.5	+16.0	31.0	+ 6.0
400	31.5	+17.0	34.0	+ 6.5
450	32.0	+17.5	35.0	+ 6.0
500	32.0	+20.0	35.0	+10.0
550	32.0	+23.0	35.0	+ 7.5
600	32.0	+15.0	35.0	- 3.0
650	32.0	+14.0	35.0	+ 3.5
700	32.0	+12.0	35.0	+ 3.0
750	32.0	+10.0	35.0	+ 2.0
800	32.0	+10.0	35.0	+ 1.0

Table E-22 (Contd.)

Temp.	TSO-Ni		TSO-Co	
(°C)	ΔW(mg)	ΔT(°c)	ΔW(mg)	ΔT(°c)
100	0.5	+ 11.0	0.0	- 5.0
150	6.0	+ 12.0	1.0	- 19.0
210	14.0	+ 10.0	1.0	- 27.0
255	22.0	+ 12.0	11.0	- 55.0
305	25.0	+ 17.0	14.0	- 37.0
355	27.0	+ 15.0	17.0	- 37.0
400	28.0	+ 15.0	20.0	- 39.5
450	29.0	+ 15.0	22.5	- 39.0
500	37.0	+ 19.0	28.0	- 33.0
550	38.0	+ 19.0	33.0	- 60.0
600	38.0	+ 10.0	35.0	0.0
650	38.0	+ 7.5	34.5	+ 2.5
700	38.0	+ 4.5	34.5	+ 4.0
750	38.0	+ 3.5	34.5	+ 6.5
800	38.0	+ 3.0	34.5	+ 7.0

soluble in all common organic solvents.

(iii) B-Resorcyaldazine.

It was prepared by the method of Kazuo Miyatake.[145]

Aqueous solutions of hydrazine sulphate (1.3 g.) and potassium acetate (2.0 g.) were added to the alcoholic solution of β-resorcylaldehyde (2.0 g.) and the mixture was heated on waterbath for one hour. The product was filtered, washed with water and dilute alcohol and dried. It was recrystallised from glacial acetic acid in yellow shining needles. It does not melt upto 300°C.

(iv) Complexes of Cu(II) and Co(II) with β-resorcyaldazine.

β-Resorcylaldazine dissolved in dimethylformamide was mixed with calculated amount of metal acetate in water (salt : ligand ::1:1), and stirred for two hours at room temperature, the precipitates were filtered, washed with little dimethylformamide, water and ether and dried. They are insoluble in all common organic solvents except pyridine and dimethylformamide. The colour, m.p., analysis etc. of these complexes are presented in Table E-23; the mass magnetic susceptibilities and diamagnetic correstions of these complexes are presented in Table E-24.

Optical density of these compounds in dimethylformamide in the visible region of the spectrum is presented in Table E-25.

II.10. Oxalyldihydrazide, its condensation with Vic-oxime ketone and their transition metal complexes.

(i) Oxalyldihydrazide.

It was prepared by the method of Curtius and Schoffer.[146]

Diethyl oxalate (1.2 g.) and hydrazine hydrate (1.0 g.)

Table E-23

Transition metal complexes

No.	Complex	Colour	m.p. (°C.)	Formula	Analysis %M Found	%N Found	%M reqd.	%N reqd.
1	OZ-Cu	Green	300	$C_{10}H_{10}N_3O_3Cu$	24.20	15.35	22.40	14.81
2	OZ-Co	Orangered	300	$C_{20}H_{22}N_7O_5Co$	12.48	19.36	11.81	19.60
3	OZ-Ni	Greenish brown	300	$C_{30}H_{36}N_{12}O_8Ni_2$	14.97	20.23	14.51	20.76
4	OZ-Fe	Blue	300	$C_{10}H_{16}N_4O_8SFe$	13.83	13.83	13.68	13.73
5	RZ-Cu	Brown	300	$C_{14}H_{10}N_2O_4Cu$	18.93	8.35	19.04	8.40
6	RZ-Co	Snuff	300	$C_{14}H_{14}N_2O_6Co$	16.08	7.42	16.14	7.67

Table E-24

Magnetic susceptibility of the complexes

No.	Complex	Mass Magnetic susceptibility $X_g \times 10^6$	Temp. (°C)	Diamagnetic corrections (per metal atom) $X \times 10^6$
1	OZ-Cu	5.14	31.0	- 135
2	OZ-Co	15.93	31.0	- 250
3	OZ-Ni	9.83	31.5	- 192
4	OZ-Fe	25.7	30.0	- 187
5	RZ-Cu	145.5	30.0	- 147
6	RZ-Co	11.42	31.0	- 168

Table E-25

Optical density of the compounds in dimethylformamide in the visible region (400-800 mμ).

Wavelength (mμ)	Optical density			
	OZ-Cu	OZ-Co	OZ-Ni	OZ-Fe
800	0.477	0.016	0.030	0.043
780	0.477	0.016	0.026	0.045
760	0.472	0.018	0.031	0.056
740	0.469	0.018	0.032	0.056
720	0.469	0.022	0.046	0.076
700	0.469	0.022	0.046	0.097
680	0.469	0.032	0.056	0.143
660	0.469	0.051	0.071	0.237
640	0.456	0.076	0.073	0.387
620	0.420	0.102	0.075	0.538
600	0.387	0.131	0.081	0.620
580	0.367	0.161	0.086	0.658
560	0.319	0.174	0.097	0.620
540	0.377	0.237	0.114	0.602
520	0.538	0.337	0.142	0.538
500	0.921	0.469	0.215	0.495
480	1.699	0.745	0.357	0.523
460	2.000	1.155	0.638	0.638
440	2.000	1.523	1.074	0.854
420	1.968	1.602	1.356	1.109
400	1.819	1.447	1.221	1.329

(80 % solution) were mixed in a cooled flask and allowed to stand when precipitates were obtained. These were filtered, washed with little alcohol and dried. It was recrystallied from water. It melts at 241°C. It is soluble in water and dimethylformamide and insoluble in alcohol, ether, chloroform, benzene etc.

(ii) Cu(II), Co(II) and Ni(II) complexes of oxalyldihydrazide.

Oxalyldihydrazide dissolved in dimethylformamide was mixed with calculated amount of metal acetate in dimethylformamide (salt : ligand :: 1:1). A few drops of liquor ammonia were added and the mixture was refluxed on sandbath for three to four hours and left overnight. They were then filtered, washed with little dimethylformamide, water and alcohol and dried. The products are insoluble in all common organic solvents.

The colour, m.p., analysis etc. of these complexes are presented in Table E-26. The mass magnetic susceptibilities and diamagnetic corrections of these complexes are given in Table E-27.

II 11. Polymerization of malonates :

(i) Potassium cobalt(II) malonate (Mal CoK)

It was prepared by the method of percival and Wardlaw.[147] To a solution of malonic acid (10.0 g.) in water (20 ml.), potassium carbonate (6.0 g.) was added slowly; cobalt carbonate (5.3 g.) was then added with heating and stirring. The mixture was boiled and filtered hot; fine red crystals separated on cooling. They were filtered, washed with little water and dried. Further crops were

Table E-26

Transition metal complexes

No.	Complex	Colour	m.p. (°C.)	Formula	Analysis			
					%M Found	%N Found	%M reqd.	%N reqd.
1	DZ-Cu	Olivgreen	300	$C_3H_5N_2O_3Cu$	36.37	17.05	35.18	15.51
2	DZ-Co	Brown	300	$C_3H_{10}N_3O_4Co$	28.36	18.30	28.05	20.00
3	DZ-Ni	Blue	300	$C_3H_{12}O_5N_3Ni$	24.46	19.96	25.66	18.36

Table E-27

Magnetic susceptibility of the complexes

No.	Complex	Magnetic susceptibility $X_g \times 10^6$	temp. (°C)	Diamagnetic corrections (per metal atom) $X \times 10^6$
1	DZ-Cu	7.1	30.0	- 60
2	DZ-Co	56.0	31.0	- 80
3	DZ-Ni	22.0	31.0	- 103

recovered from the motherliquor. It is soluble in water but insoluble in all organic solvents.

(ii) Potassium copper(II) malonate (Mal CuK) and potassium nickel(II) malonate (Mal NiK):

These complexes (Mal CuK) and (Mal NiK) were prepared by the above method using copper carbonate (7.0 g.) and nickel carbonate (5.3 g.) instead of cobalt carbonate (5.3 g.). They are soluble in water but insoluble in all organic solvents.

(iii) Reaction of potassium metal(II) malonate with formaldehyde

Potassium metal(II) malonate (4.5 g.) dissolved in water was mixed with formaldehyde (35 % solution) (2.0 g.). It was refluxed on sandbath for about three hours and filtered hot, gummy mass was obtained on allowing the solution to evaporate slowly at room temperature. It was washed with little water and ether and recrystallised from water + ethanol. It is soluble in water but insoluble in all common organic solvents.

The colour, m.p., analysis etc. of these complexes are presented in Table E-28; the mass magnetic susceptibility and diamagnetic corrections of these complexes are presented in Table E-29.

Table E-28

Transition metal complexes

No.	Complex	Colour	m.p. (°C.)	Formula	Analysis			
					%M Found	%C Found	%M reqd.	%C reqd.
1	Mal Co K	Red	280 (decomp)	$C_6H_{20}O_{16}CoK_2$	12.5	14.70	12.2	14.91
2	Mal Cu K	Blue	240 (decomp)	$C_6H_{14}O_{13}CuK_2$	12.5	16.72	14.58	16.54
3	Mal Ni K	Bluish green	300	$C_6H_{10}O_{11}NiK_2$	16.0	16.78	15.31	18.71
4	Mal F Co K	Red	300	$C_7H_8O_{10}COK_2$	15.2	22.29	15.14	21.60
5	Mal F Cu K	Greenish blue	300	$C_9H_{14}O_{14}CuK_2$	12.8	22.80	13.03	22.16
6	Mal F Ni K	Bluish green	300	$C_9H_{10}O_{12}NiK_2$	13.4	23.78	13.18	24.16

Table E-29

Magnetic susceptibility of the complex

No.	Complex	Mass magnetic susceptibility $X_g \times 10^6$	temp. (°C.)	Diamagnetic corrections (per metal atom) $X \times 10^6$
1	Mal Co K	22.6	33.5	- 180
2	Mal Ni K	16.4	32.5	- 175
3	Mal F Co K	18.2	32.5	- 124
4	Mal F Ni K	14.6	29.5	- 150