

## MIXED LIGAND TRANSITION METAL COMPLEXES OF IMIDES AND AMINES

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Mixed ligand complexes of Cu (II), Co (II) and Ni (II) with phthalimide as primary and amines as secondary ligands were prepared and characterised by elemental analysis, conductivity and magnetic measurement and infrared and electronic spectroscopic studies. Cu (II) and Ni (II) complexes were found to have both octahedral and square planar structure with the secondary ligands. Co (II) complexes formed both octahedral and tetrahedral complexes. The composition of the complexes are  $(MP_2L_4)$  and  $(MP_2L_2)$  for six and four coordinate complexes respectively, where, M = Cu (II), Co (II) and Ni (II), P = deprotonated phthalimide and L = aniline, n-butylamine, t-butylamine and ethanolamine.

**Key words:** Mixed ligand, Metal complexes, Amines.

### Introduction

A survey of the available literature revealed that the metal complexes of phthalimide have been studied both from pharmacological [1,2] and industrial [3-7] points of view. The mixed ligand complexes using phthalimide as primary and amines [8-10] polyamins [11,12] and thiocarbamides [13] as secondary ligands have also been prepared and characterised. Recently a number of mixed ligand complexes of imide and heterocyclic amines [14,15] have also been reported. Here we reported the preparation and characterisation of mixed ligand complexes of copper (II), cobalt (II) and nickel (II) with phthalimide and amines i.e. aniline, n-butylamine, t-butylamine and ethanolamine.

### Experimental

**Physical measurements.** Infrared spectra were recorded on a Pye Unicam SP3-300 infrared spectrophotometer using thin film technique. The electronic spectra were run on a Ultrospec K4053 spectrophotometer in solid state. Magnetic measurements were carried out on a Princeton Applied Research model-155 digital vibrating sample magnetometer with an attachment of EG and G, PARC model 152 cryogenic temperature controller, under a magnetic field of 5000 gauss produced by a polytronic electromagnet type H.E.M. 200. Conductivity measurement of soluble complexes were carried out in N, N-dimethylformamide on a WPA CM35 conductivity meter and dipcell with platinized electrodes.

**Reagents and chemicals.** Phthalimide were of Kochlight Laboratories Ltd. (England). All other chemicals were of A. R. grade. The solvents were from B.D.H. and were used as supplied but ethanol which was purified by refluxing the 99% crude with magnesium turnings and iodine and finally distilled.

**Preparation of copper (II) complexes.** Methanolic solution of copper (II) sulphate and potassium salt of phthalimide were mixed in the proper ratio and heated for 10 mins. The

precipitate of potassium sulphate was filtered off from the residual solution. Then amine bases were added and heated again for 10 mins and allowed to stand for 2 hrs. The precipitate formed was collected by filtration washed several times with methanol and dried in a vacuum desiccator over phosphorus pentoxide.

**Preparation of cobalt (II) and nickel (II) complexes.** Ethanolic solution of cobalt (II) chloride or nickel (II) chloride and potassium salt of phthalimide were mixed in the proper ratio and heated for 10 mins. The precipitate of potassium chloride was filtered off from the residual solution. Then amine bases were added and refluxed for half an hour and allowed to stand for 2 hrs. The precipitate formed was collected by filtration washed several times with ethanol and dried in a vacuum desiccator over phosphorus pentoxide.

### Results and Discussion

**Conductivity and elemental analysis.** The low values of molar conductances of the soluble complexes measured in N, N'-dimethylformamide (Table 2) indicated non-electrolytic nature of the complexes. Analytical results for metal, carbon and hydrogen are given in Table 1 and some other physical properties, viz. melting points, magnetic moments and colours are given in Table 2 along with molar conductances.

**I. R. Studies.** Phthalimide is a common constituent of all complexes, which has two important (NH and CO stretching) frequency region and have also two (through O and N<sup>-</sup>) coordination sites. The distinction between O and N<sup>-</sup> coordination of imides is not readily made by IR spectroscopy because shifts in  $\nu$  (CO) may results either from coordination through O or from the formation and coordination of the imide (N<sup>-</sup>) nitrogen. It is expected that coordination through oxygen will be inhibited by steric hindrance. In all the complexes  $\nu$  (CO) is shifted within 1628 - 1665  $\text{cm}^{-1}$  compared to 1720  $\text{cm}^{-1}$  in phthalimide. The  $\nu$

TABLE 1. ANALYTICAL DATA, PERCENTAGE CALCULATED (FOUND).

No.	Complexes	Metal	Carbon	Hydrogen	Nitrogen
1.	[Cu P <sub>2</sub> (Ani) <sub>2</sub> ]	11.72 <sub>(11.60)</sub>	61.98 <sub>(61.36)</sub>	4.06 <sub>(4.01)</sub>	10.34 <sub>(10.24)</sub>
2.	[CuP <sub>2</sub> (Ani) <sub>4</sub> ]	8.72 <sub>(8.63)</sub>	65.40 <sub>(64.74)</sub>	4.94 <sub>(4.89)</sub>	11.54 <sub>(10.23)</sub>
3.	[CuP <sub>2</sub> (n-but) <sub>2</sub> ]	12.60 <sub>(12.47)</sub>	57.13 <sub>(56.55)</sub>	4.36 <sub>(4.32)</sub>	11.11 <sub>(10.99)</sub>
4.	[CuP <sub>2</sub> (n-but) <sub>4</sub> ]	9.73 <sub>(9.63)</sub>	58.86 <sub>(57.27)</sub>	7.97 <sub>(7.90)</sub>	12.88 <sub>(12.75)</sub>
5.	[CuP <sub>2</sub> (t-but) <sub>2</sub> ]	12.60 <sub>(12.45)</sub>	57.13 <sub>(56.54)</sub>	4.37 <sub>(4.35)</sub>	11.11 <sub>(11.00)</sub>
6.	[CuP <sub>2</sub> (ETA) <sub>2</sub> ]	13.29 <sub>(13.15)</sub>	50.21 <sub>(49.70)</sub>	4.60 <sub>(4.55)</sub>	11.72 <sub>(11.60)</sub>
7.	[CuP <sub>2</sub> (ETA) <sub>4</sub> ]	10.59 <sub>(10.48)</sub>	47.99 <sub>(47.51)</sub>	7.53 <sub>(7.29)</sub>	14.00 <sub>(13.87)</sub>
8.	[CoP <sub>2</sub> (Ani) <sub>2</sub> ]	10.98 <sub>(10.87)</sub>	62.52 <sub>(61.89)</sub>	4.09 <sub>(4.04)</sub>	10.42 <sub>(10.31)</sub>
9.	[CoP <sub>2</sub> (Ani) <sub>4</sub> ]	8.14 <sub>(8.05)</sub>	66.32 <sub>(65.85)</sub>	4.97 <sub>(4.92)</sub>	11.61 <sub>(11.50)</sub>
10.	[CoP <sub>2</sub> (n-but) <sub>2</sub> ]	11.798 <sub>(11.68)</sub>	57.66 <sub>(57.07)</sub>	6.01 <sub>(5.93)</sub>	11.22 <sub>(11.11)</sub>
11.	[CoP <sub>2</sub> (n-but) <sub>4</sub> ]	9.10 <sub>(9.01)</sub>	59.28 <sub>(58.67)</sub>	8.08 <sub>(7.99)</sub>	12.97 <sub>(12.84)</sub>
12.	[CoP <sub>2</sub> (t-but) <sub>2</sub> ]	11.798 <sub>(11.69)</sub>	57.66 <sub>(57.05)</sub>	6.006 <sub>(5.95)</sub>	11.22 <sub>(11.09)</sub>
13.	[Co(P) <sub>2</sub> (y-but) <sub>4</sub> ]	9.10 <sub>(9.02)</sub>	59.28 <sub>(58.79)</sub>	8.08 <sub>(7.00)</sub>	12.97 <sub>(12.84)</sub>
14.	[CoP <sub>2</sub> (ETA) <sub>2</sub> ]	12.45 <sub>(12.32)</sub>	50.70 <sub>(50.19)</sub>	4.65 <sub>(4.59)</sub>	11.84 <sub>(11.71)</sub>
15.	[CoP <sub>2</sub> (ETA) <sub>4</sub> ]	9.90 <sub>(9.79)</sub>	48.36 <sub>(47.90)</sub>	6.04 <sub>(5.96)</sub>	14.11 <sub>(13.96)</sub>
16.	[Ni P <sub>2</sub> (Ani) <sub>2</sub> ]	10.93 <sub>(10.81)</sub>	62.64 <sub>(61.92)</sub>	4.09 <sub>(4.06)</sub>	10.43 <sub>(10.32)</sub>
17.	[Ni P <sub>2</sub> (Ani) <sub>4</sub> ]	8.11 <sub>(8.03)</sub>	66.34 <sub>(65.88)</sub>	4.98 <sub>(4.96)</sub>	11.62 <sub>(11.50)</sub>
18.	[Ni P <sub>2</sub> (n-but) <sub>2</sub> ]	11.76 <sub>(11.63)</sub>	57.68 <sub>(57.10)</sub>	6.01 <sub>(5.95)</sub>	11.22 <sub>(11.12)</sub>
19.	[Ni P <sub>2</sub> (n-but) <sub>4</sub> ]	9.07 <sub>(8.97)</sub>	59.03 <sub>(58.65)</sub>	8.03 <sub>(7.96)</sub>	12.98 <sub>(12.86)</sub>
20.	[Ni P <sub>2</sub> (t-but) <sub>2</sub> ]	11.76 <sub>(11.65)</sub>	57.68 <sub>(57.08)</sub>	6.01 <sub>(5.96)</sub>	11.22 <sub>(11.10)</sub>
21.	[Ni P <sub>2</sub> (t-but) <sub>4</sub> ]	9.07 <sub>(8.96)</sub>	59.03 <sub>(58.70)</sub>	8.03 <sub>(7.01)</sub>	12.98 <sub>(12.86)</sub>
22.	[Ni P <sub>2</sub> (ETA) <sub>2</sub> ]	9.86 <sub>(9.76)</sub>	48.37 <sub>(47.87)</sub>	6.05 <sub>(5.98)</sub>	14.12 <sub>(13.97)</sub>

P = Phthalimide -C<sub>8</sub>H<sub>5</sub>O<sub>2</sub>N, Ani = Aniline -C<sub>6</sub>H<sub>7</sub>N, n-but = n-butyl amine -C<sub>6</sub>H<sub>11</sub>N, t-but = t-butyl amine -C<sub>6</sub>H<sub>11</sub>N, ETA - Ethanolamine -C<sub>2</sub>H<sub>7</sub>N.

TABLE 2. PHYSICAL PROPERTIES OF COMPLEXES.

No*.	Colour	Moler conduc- tances (Ohm <sup>-1</sup> (mole) <sup>-1</sup> cm <sup>2</sup> )	Melting point (±5°C)	Magnetic moment (B. M.)
1.	Deep green	8.414	160 - 164 d	1.53
2.	Light green	13.206	161 - 166 d	1.68
3.	Pink	—	161 - 162 d	1.70
4.	Pink	8.946	164	1.83
5.	Blackish ash	—	205 - 210 d	1.65
6.	Black	—	194	1.60
7.	Black	5.325	203 - 205 d	1.59
8.	Violet	—	104 - 110 d	4.5
9.	Light violet	—	105 - 111 d	5.2
10.	Ash	—	250 - 255 d	4.5
11.	Ash	—	245 - 250 d	5.0
12.	Ash	—	> 300	4.5
13.	Ash	—	> 300	5.3
14.	Pink	—	104 - 112 d	5.1
15.	Light pink	—	> 300	5.1
16.	Green	—	190 - 195 d	0.00
17.	Green	—	190 - 196 d	2.80
18.	Green	—	240 - 245 d	0.65
19.	Green	—	242 - 248 d	2.76
20.	Yellow	—	270 275 d	0.34
21.	Yellow	—	270 - 280 d	2.72
22.	Light blue	—	290 - 295 d	0.00

\*Please see Table 1; d = decompose.

(CN) stretching frequency at 1310 cm<sup>-1</sup> for the imide is shifted within 1368 - 1395 cm<sup>-1</sup> in the complexes indicating thereby N<sup>-</sup> formation and coordination [17]. The band obtained at about 3350 and 3500 cm<sup>-1</sup> for phthalimide due to ν (NH) disappeared in the spectrum of complexes. But the band observed in the region 3160-3450 cm<sup>-1</sup> in the complexes is due to the ν (NH<sub>2</sub>) for the secondary ligand (amines).

In the spectra of free secondary ligands (amines) ν (NH<sub>2</sub>) band is most diagnostic in the coordination with the metal ion. These bands shifted towards lower frequency side in the complexes (from 3500 and 3350 cm<sup>-1</sup> to 3450 and 3160 cm<sup>-1</sup> respectively). This negative shift indicated the coordination of amine bases. For the ethanolamine complexes one broad band observed at about 3450 cm<sup>-1</sup> which is due to the presence of OH group in ethanol amine.

*Electronic spectra and magnetic studies.* Observed magnetic moment of all the Cu (II) complexes (Table 2) indicated the complexes are paramagnetic with one unpaired electron. In the electronic spectra of six coordination complexes one broad band at 14125 cm<sup>-1</sup> for [Cup<sub>2</sub>(Ani)<sub>4</sub>], 14063

$\text{cm}^{-1}$  for  $[\text{CuP}_2(\text{n-but})_4]$  and  $13998 \text{ cm}^{-1}$  for  $[\text{CuP}_2(\text{ETA})_4]$  are obtained. Corresponding to the transition  ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ , which indicates their octahedral stereochemistry. For the four coordinated complexes three bands at 15300, 19600 and  $22200 \text{ cm}^{-1}$  were obtained corresponding to the transitions  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ ,  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$  and charge transfer respectively which indicate their square-planar stereochemistry [18]. The magnetic moment of assumed six coordinated Co(II) complexes (5.0 - 5.3 B. M.) indicating their high spin octahedral structure. Their electronic spectra gave two bands at  $\sim 16000 \text{ cm}^{-1}$  ( $\nu_2$ ) and  $\sim 18500 \text{ cm}^{-1}$  ( $\nu_3$ ) corresponding to the transitions  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  respectively. Here the transition  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  ( $\nu_1$ ) were calculated assuming the transition ratio [19]  $\nu_2/\nu_1 = 2.1$ . The electronic transitions of the complexes indicating their octahedral stereo-chemistry. The values of electronic parameters  $10\text{Dq}$ ,  $B$  and  $\beta$  were calculated using the following equations and are presented in Table 3.

$$10\text{Dq} = 1/2 [(2\nu_1 - \nu_3) + (\nu_3^2 + \nu_1 \nu_3 - \nu_1^2) / 1/2]$$

$$15B = \nu_3 - 2\nu_1 + 10\text{Dq}$$

In the case of assumed four coordinated complexes magnetic moment were found to be 4.4 - 4.7 B. M., and the electronic spectra gave two intense bands at  $\sim 24100$  and  $\sim 30200 \text{ cm}^{-1}$  corresponding to the transition  ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  and charge transfer respectively. Electronic spectral values and their magnetic moment indicated their tetra-hedral stereochemistry. The magnetic measurement of all the Co (II)

TABLE 3. ELECTRONIC SPECTRAL DATA OF OCTAHEDRAL CO (II) COMPLEXES

No*.	$\zeta_2$ ( $\text{cm}^{-1}$ )	$\zeta_3$ ( $\text{cm}^{-1}$ )	$\zeta_1 = \frac{\zeta_2}{2.1}$ ( $\text{cm}^{-1}$ )	B ( $\text{cm}^{-1}$ )	$\beta$	10Dq ( $\text{cm}^{-1}$ )	LFSE (KJ/ mole)
9.	15953	18395	7596	790	0.71	8650	62.05
11.	15998	17990	7618	761	0.68	8656	62.09
13.	15900	18522	7571	800	0.71	8629	61.90
15.	16050	18112	7642	768	0.69	8694	62.36

\* See Table 1.

TABLE 4.  $\mu_{\text{eff}}$  (IN B. M.) DIFFERENT TEMPERATURE OF CO (II) COMPLEXES

No*.	298 °k	268 °k	238 °k	208 °k	178 °k	148 °k	135 °k	118 °k	103 °k	88 °k
9.	5.20	5.03	4.92	4.83	4.68	4.51	4.32	4.20	4.11	4.04
11.	5.01	4.04	4.73	4.64	4.49	4.32	4.13	4.01	3.92	3.85
13.	5.35	5.19	5.08	4.98	4.84	4.66	4.49	4.36	4.27	4.20
15.	5.16	4.99	4.89	4.78	4.64	4.48	4.28	4.16	4.07	4.00
8	4.51	4.50	4.50	4.48	4.46	4.45	4.43	4.42	4.42	4.41
10.	4.62	4.60	4.58	4.58	4.56	4.55	4.53	4.52	4.50	4.50
12.	4.57	4.56	4.54	4.52	4.52	4.51	4.49	4.49	4.48	4.47
14.	4.71	4.70	4.68	4.65	4.63	4.61	4.60	4.58	4.55	4.53

\* See Table 1.

complexes were carried out in different temperature (Table 4). Considerable decrease in magnetic moment with decreasing temperature for six coordinated complexes confirmed their octahedral geometry, which in the case of four coordinated complexes magnetic moment values were almost independent of the temperature indicating their tetrahedral geometry [20].

Observed electronic spectra of coordinated Ni (II) complexes at  $\sim 9000$ ,  $\sim 15500$  and  $\sim 28500 \text{ cm}^{-1}$  which correspond to the transitions  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  ( $\nu_2$ ) and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) respectively, indicating the octahedral stereochemistry which has now been well established [21]. The calculated [22] values of  $\nu_2$  and  $\nu_3$  were not in good agreement with the experimental value and the ratio of  $\nu_2/\nu_1$  were also greater than the useful range for octahedral complexes again the value of  $B$  was sufficiently higher than the free ion values, moreover the magnetic moment value were found in the range 2.7 - 2.8 B.M. which are indicating the distortion of Oh symmetry for a high spin  $d^8$  system

The four coordinated Ni (II) complexes were diamagnetic and their electronic spectra gave three charge transfer band at  $\sim 41000$ ,  $\sim 33500$  and  $\sim 32200 \text{ cm}^{-1}$  corresponding to the transitions  ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_u$ ,  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2u}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2u}$  respectively indicating a squareplanar geometry.

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