

Short Communication

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Mixed Ligand Complexes of Co(II), Ni(II) and Hg(II) Diphenates with Amine Bases

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Agafonova and Ryazanov [1,2] carried out the precipitation and separation studies of Fe^{+2} , Mn^{+2} , Co^{+2} , Ni^{+2} and Zn^{+2} . Diphenic acid has also been used [3] as a selective reagent for the amperometric determination of thorium (IV). Sharma *et al.* [4,5] determined the stability constants of the mixed ligand complexes of Th (VI), Ce (IV) and U(VI). The chelates of Fe(III) and Co(III) diphenates with *o*-phenanthroline and 2,2'-dipyridyl [6] and of bivalent metal diphenates with polyamines have also been reported [7] in the literature.

The present paper deals with the preparation of mixed ligand complexes of Co(II), Ni(II) and Hg(II) with diphenic acid as primary and aniline, *n*-butylamine, ethanol amine and *t*-butylamine as secondary ligands. The characterisation has been done on the basis of elemental analyses, conductivity measurements, magnetic, infrared and UV-visible spectral studies.

A freshly prepared cobalt (II) hydroxide (0.01 mol) and diphenic acid (0.01 mol) were mixed in 100 ml water and

refluxed for 0.5hrs. and then the calculated quantity of an alcoholic solution of secondary ligand was added. The mixture was again refluxed on a water bath for 1 hr. and then cooled. The precipitates formed were filtered, washed several times with water and finally with alcohol and then dried in a desiccator over silica gel.

The elemental analyses results of the complexes along with melting points and solar conductances in dimethyl sulfoxide are given in Table 1.

The strong bands at 1680 and 1450 cm^{-1} due to $\nu(\text{COO})$ in diphenic acid were shifted to 1540-1560 cm^{-1} and 1370-1400 cm^{-1} , respectively, in the spectra of the complexes (Table 2) indicating the coordination of diphenic acid through carboxyl groups. The N-H stretching frequency of free amines observed at around 3360 cm^{-1} were shifted to 3245-3320 cm^{-1} confirming their coordination through nitrogen. Further, the presence of M-O bonds in the complexes are evident from the appearance of $\nu(\text{M-O})$ modes at 425-450 cm^{-1} and that of M-N bonds are evident from the appearance of $\nu(\text{M-N})$ modes at 305-340 cm^{-1} in the far-IR spectra of the complexes.

The complexes of cobalt(II) with aniline, *n*-butylamine and *t*-butylamine gave the values of magnetic moment 4.5 BM indicating their tetrahedral structure. The electronic spectra of Co(II) complex with aniline, *n*-butylamine and *t*-butylamine (Table 3) gave two intense bands at $\sim 24,000 \text{cm}^{-1}$ and $\sim 30,000 \text{cm}^{-1}$ corresponding to the transition $4T_2g(F) \rightarrow 4T_1g(P)(\nu_3)$ and the charge transfer band respectively. The

TABLE I. ANALYTICAL, PERCENTAGE CALCULATED (FOUND) AND PHYSICAL PROPERTIES OF THE COMPLEXES.

Sl. No.	Complexes	Metal	Carbon	Hydrogen	Colour	Molar conductances ($\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	Magnetic moment (B.M.)	Melting point $^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$
1.	[Co(DA)(<i>n</i> -butylamine) ₂]	13.23(13.00)	59.27(60.01)	6.73(6.89)	Pale pink	14.31	4.41	200 - 205 (d)
2.	[Co(DA)(aniline) ₂]	12.14(11.95)	64.24(64.87)	4.53(5.00)	Pink	20.45	4.50	181 - 195 (d)
3.	[Co(DA)(<i>t</i> -butylamine) ₂]	13.24(12.89)	59.26(60.13)	6.74(6.59)	Pale pink	16.29	4.69	175 - 180 (d)
4.	[Co(DA)(ethanolamine) ₂]	13.98(13.25)	51.27(50.78)	5.22(4.13)	Pale pink	—	4.61	162 - 170 (d)
5.	[Co(DA)(ethanolamine) ₄]	10.84(11.70)	48.57(47.77)	6.62(6.03)	Pale pink	—	5.11	185 - 190 (d)
6.	[Ni(DA)(aniline) ₄]	8.75 (9.29)	67.91(68.23)	5.36(4.65)	Light green	15.51	3.31	210 - 215 (d)
7.	[Ni(DA)(ethanolamine) ₄]	10.81(10.24)	48.59(49.17)	6.63(5.75)	Light green	33.46	3.36	195 - 200 (d)
8.	[Ni(DA)(<i>t</i> -butylamine) ₂]	13.19(12.28)	59.29(60.13)	6.73(7.10)	Light green	15.93	3.41	205 - 210 (d)
9.	[Ni(DA)(<i>n</i> -butylamine) ₄]	9.93(10.35)	59.30(58.89)	6.74(6.68)	Light green	24.38	3.96	175 - 178 (d)
10.	[Hg(DA)(<i>t</i> -butylamine) ₂]	34.17(35.09)	44.97(45.02)	5.11(4.79)	Ash	25.83	0.91	158 - 163 (d)
11.	[Hg(DA)(aniline) ₂]	31.98(31.15)	49.75(48.87)	3.51(4.00)	Ash	6.69	Diamagnetic	148 - 150 (d)
12.	[Hg(DA)(<i>n</i> -butylamine) ₂]	34.16(34.05)	44.96(43.99)	5.10(4.66)	Ash	24.49	Diamagnetic	177 - 180 (d)
13.	[Hg(DA)(ethanolamine) ₂]	35.63(36.05)	38.37(38.13)	3.90(3.31)	Ash	27.89	Diamagnetic	144 -

DA = Diphenic acid ($\text{C}_{14}\text{H}_8\text{O}_4$); Complex no. 4 and 5 are insoluble.

intensity (ϵ values) of ν_3 (≈ 420) also confirmed their tetrahedral structure.

For octahedral the magnetic moment was found to be 5.11 B.M and the electronic spectra in dimethylsulfoxide gave two bands at $14,500 \text{ cm}^{-1}$ (ν_2) and $17,000 \text{ cm}^{-1}$ (ν_3) corresponding to the transitions $4T_{1g}(F) \rightarrow 4A_{2g}$ and $4(T_{1g})(F) \rightarrow 4T_{1g}(P)$ respectively.

The transition $4T_{1g}(F) \rightarrow 4T_{2g}(F)$ (ν_1) could not be observed which was calculated assuming [8] the transition ratio $\nu_2/\nu_1 = 2.1$. The ϵ value in this case was found to be 5 only. The magnetic measurements at different temperature were also carried out (Fig.1). The magnetic moment shows a considerable decrease with decreasing temperature, also suggesting the octahedral geometry while the values for the other complexes of Co(II) were almost independent of temperature indicating their tetrahedral geometry [9].

The complexes of Ni (II) except with *t*-butylamine gave three bands at $\sim 8,000$, $\sim 14,500$ and $\sim 26,000 \text{ cm}^{-1}$ corresponding to the transitions $3A_{2g}(F) \rightarrow 3T_{2g}(F)$ (ν_1), $3A_{2g}(F) \rightarrow 3T_{1g}(F)$ (ν_2) and $3A_{2g}(F) \rightarrow 3T_{1g}(P)$ (ν_3), respectively, (Table 3). The values of B, the Racah parameter were calculated using

the diagonal sum rule [10]. The energies of bands ν_2 and ν_3 were calculated using the expression.

$$\nu_{2,3} = 15/2 B + 3/2 (10 Dq) \pm 1/2 [(9B - 10 Dq)^2 + 144 B^2]^{1/2}$$

The values of magnetic moment were found in the range 3.31 - 3.96 BM. The calculated values of ν_2 and ν_3 were also not in good agreement with the experimental values, hence suggested a tetragonal distortion of octahedral symmetry. Secondly the ratio of ν_2/ν_1 were also greater than the usual range for octahedral complexes.

The complexes of Ni(II) with *t*-butylamine was found to be tetrahedral. The electronic spectra gave the bands at $14,500 \text{ cm}^{-1}$ corresponding to the transition $3T_{1g}(F) \rightarrow 3T_1(P)$ which is in good agreement with the published value [12]. The complexes of Hg(II) were diamagnetic and gave charge transfer bands from $25,000$ to $42,000 \text{ cm}^{-1}$.

The Co(II) complexes are tetrahedral, whereas ethanolamine can form complexes of tetrahedral and octahedral structures. It gives octahedral complexes when the mixing ratio is maintained 1:1:4, but in other complexes result tetrahedral structure. *t*-Butylamine gives tetrahedral complexes with Ni(II) diphenate due to its larger size and basicity whereas other ligands produce octahedral complexes. The complexes of Hg(II) were found to be tetrahedral.

TABLE 2. IR SPECTRAL DATA FOR THE COMPLEX BAND MAXIMA (cm^{-1})^a.

Compound	ν (N-H)	ν (COO)	ν (M-O)	ν (M-N)
1	3260s	1540m	1380s	445w
2	3245s	1550m	1400s	450m
3	3250sh	1540m	1395sh	440sh
4	3315s	1550br	1390m	450m
5	3320s	1550sh	1400s	445m
6	3280m	1540m	1385s	450s
7	3315s	1545br	1380m	450sh
8	3270s	1540m	1400s	435w
9	3295sh	1545m	1400s	450m
10	3270sh	1560s	1375m	450w
11	3280s	1545m	1380m	435w
12	3260s	1555m	1370m	440m
13	3320s	1550m	1375s	425w

^aThe relative band intensities are denoted by s, m, w, sh and br corresponding to strong, medium, weak, shoulder and broad, respectively.

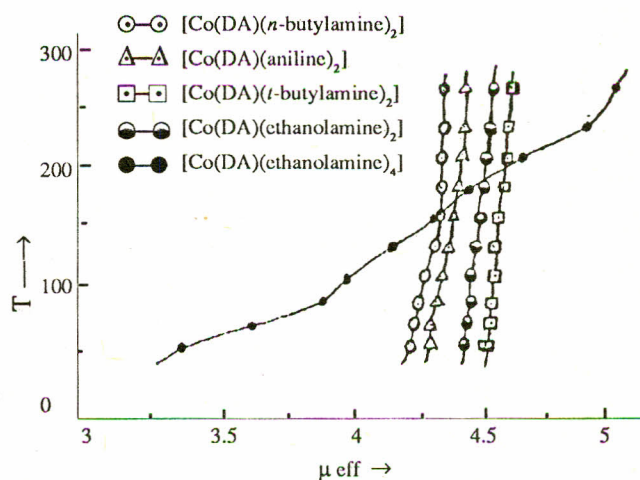


Fig. 1

TABLE 3. ELECTRONIC SPECTRAL DATA OF OCTAHEDRAL NICKEL (II) COMPLEX.

S. No.	Complexes	Observed bands (cm^{-1})			Calculated band positions (cm^{-1})	$(\nu_3 - \nu_2)$ cal. (cm^{-1})	$(\nu_3 - \nu_2)$ obs. (cm^{-1})	ν_2/ν_1	B	LFSE kJ/mol
		ν_1	ν_2	ν_3						
6.	Ni (DA) (aniline) ₄]]	8400	14500	26000	14118	26382	764	1.72	1020	120.51
7.	Ni (DA) (ethanolamine) ₄]]	8500	14600	16200	14271	26529	658	1.71	1020	121.95
8.	[Ni (DA) (<i>n</i> -butylamine) ₄]]	8600	14600	26100	14388	26308	420	1.69	993	123.38

References

1. V.I. Agafonova, and I.P. Ryazanov, *IZV. Vyssh. Vcheo. Zaved., Khim. Khim. Tikhno.*, **10** (II), 1200 (1967).
2. V.I. Agafonova and I.P. Ryazanov, *IZV. Vyssh. Vcheo. Zaved., Khim. Khim. Tikhno.*, **12** (10), 1326 (1969).
3. C.L. Sharma and P.K. Jain, *Talanta*, **24**, 754 (1977).
4. C.L. Sharma and P.K. Jain, *J. Indian Chem.*, **15A**, 1110 (1977).
5. C.L. Sharma and P.K. Jain, *J. Indian Chem. Soc.*, **55**, 892 (1978).
6. C.L. Sharma and P.K. Jain, *Indian J. Chem. Soc.*, **20A**, 1030 (1981).
7. C.L. Sharma, and P.K. Jain, *J. Indian Chem. Soc.*, **56**, 128 (1979).
8. A.B.P. Lever, *J. Chem. Soc., A.*, 2041 (1967).
9. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6**, 186 (1971).
10. O. Bostrup and C.K. Jorgensen, *Acta. Chem. Scand.*, **II**, 1223 (1957).
11. C.L. Sharma and M.S. Islam, *Synth. React. Inorg., Met. - Org. Chem.*, **16** (4), 553 (1986).
12. B.N. Figgis, *Introduction to Ligand Fields* (Inter Science, New York, 1967), pp.240.