



Analytical and Spectroscopic Studies of New Mixed Ligand Complexes of 1,2-diaminobenzene

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ABSTRACT

In the present investigation, we have synthesized Co(II) and Ni(II) mixed ligand complexes with 1,2-diaminobenzene. The complexes so obtained were characterized by conventional physico-chemical techniques, such as elemental analyses, solubility, electrical conductance, metal estimations, molecular weight determinations, infra red, electronic and ESR spectroscopy. These complexes were crystalline, coloured, solid, sparingly soluble in water and alcohol but soluble in DMF and DMSO, quite stable at room temperature. The magnetic and spectral studies confirm that the complexes are octahedral in nature.

Key words: Mixed Ligand Complexes, Spectroscopic studies.

INTRODUCTION

Amongst the nitrogen donor ligands containing -NH_2 groups, hydrazine and its derivatives are of considerable interest as ligands in view of variety of bonding possibilities that they exhibit. A large number of diamines, $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}_2$, have been examined for the complexing behaviour with the several transition and non-transition metal ions. The introduction of alkyl and aryl group may change the complexing behaviour of hydrazine¹⁻³. 1,2-Diaminobenzene is also a good nitrogen donor. It is a valuable starting material for the synthesis of a large number of fused ring system; most notably benzimidazoles, several derivatives of which have been reported to possess a variety of biological activities(4,5). Raman and co-workers(6) studied the electrochemical behaviour and antimicrobial activity of the mixed ligand

complexes of 1,2-diaminobenzene and β -ketoester. A survey of literature shows that studies on mixed ligand complexes of transition metals are limited mainly to kinetics spectrophotometry and potentiometry and only in very few cases their spectral and magnetic properties have been explored(7,8). Therefore, in the present study, we have synthesized and characterized Co(II) and Ni(II) mixed ligand complexes with 1,2-diaminobenzene.

MATERIAL AND METHODS

All chemicals i.e. cobalt chloride, nickel chloride, 1,2-diaminobenzene, ethanol, conc. H_2SO_4 etc. were of AR grade and in the purest form. Picric acid (BDH chemicals) was dried over conc. H_2SO_4 . 1,2-diaminobenzene was obtained from Sd-fine Chemicals and recrystallized before used.

The metal(II) mixed ligand oxalate complexes were prepared by mixing metal salt solution, oxalic acid and the respective ligand in the ethanolic medium with constant stirring in a molar ratio of 1:2:2 and the resulting solution was concentrated by evaporation. On cooling, crystals of complex were appeared which were filtered, washed with methanol followed by ether, dried at room temperature and finally in an electric oven at 60-70°C.

Metal picrates were prepared as reported earlier(9),(10) and its complexes with 1,2-diaminobenzene were synthesized by treating ethanolic solution of metal(II) picrate with an ethanolic solution of 1,2-diaminobenzene in the molar ratio 1:2. After stirring for about 30 minutes and then refluxing at 60-70°C over a hot plate for about 1 hour, a solution was obtained, which was kept undisturbed at room temperature, then a coloured solid precipitated out. It was then filtered, washed with ethanol and ether and dried in vacuo.

The complexes so obtained were characterized by conventional physico-chemical measurements such as elemental analyses, solubility, electrical conductance, metal estimations, molecular weight determinations, infrared, electronic and ESR spectroscopy. Elemental analysis was conducted microanalytically at CDRI, Lucknow. Metal contents of the complexes were estimated by standard methods(11). The magnetic measurements were carried out at room temperature by Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. The diamagnetic corrections of metal-ligand system were calculated using the Pascal's constant.

Electronic and IR spectral studies were carried out at RSIC, CDRI, Lucknow. ESR spectra were carried out at RSIC, IIT, Mumbai.

RESULTS AND DISCUSSION

All the complexes were found to be easily filterable, in crystalline state, coloured, sparingly soluble in water, alcohol, CCl_4 , and ether but soluble in DMF and DMSO and were found to be quite stable at room temperature. The purity of the complexes was checked by TLC method along with ligands.

Table 1: Characterization data of Co(II) and Ni(II) mixed ligand complexes of 1,2-diaminobenzene

S. N.	Complex	Colour	Yield	Molwt. calc.	M%		C%		H%		N%		Molar Conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ_{eff} (BM)
					calc.	(found)	calc.	(found)	calc.	(found)	calc.	(found)		
1-	$[\text{Co}(\text{C}_2\text{O}_4)(\text{C}_6\text{H}_8\text{N}_2)_2]$	Pinkish-brown	85%	363.24	16.22 (16.31)	46.29 (46.38)	4.43 (4.49)	15.42 (16.01)	20.18	4.92				
2-	$[\text{Ni}(\text{C}_2\text{O}_4)(\text{C}_6\text{H}_8\text{N}_2)_2]$	Green	70%	363.01	16.17 (15.06)	46.32 (46.39)	4.44 (4.52)	15.43 (15.69)	30.14	3.22				
3-	$[\text{Co}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2(\text{C}_6\text{H}_8\text{N}_2)_2]$	Dark-pink	75%	731.41	8.05 (7.98)	39.41 (39.48)	2.75 (2.81)	19.15 (19.38)	20.24	4.80				
4-	$[\text{Ni}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2(\text{C}_6\text{H}_8\text{N}_2)_2]$	Dark-blue	80%	731.18	8.02 (7.82)	39.42 (39.51)	2.75 (2.79)	19.15 (19.41)	19.11	3.32				

Table 2: Ligand field parameters and IR spectral bands

S. No.	Complex	10Dq (cm ⁻¹)	B (cm ⁻¹)	β	β°	ν_2/ν_1
1.	[Co(C ₂ O ₄)(C ₆ H ₈ N ₂) ₂]	9450	763.33	0.786	21.4	2.03
2.	[Ni(C ₂ O ₄)(C ₆ H ₈ N ₂) ₂]	9810	758.00	0.735	26.5	1.62
3.	[Co(C ₆ H ₂ O ₇ N ₃) ₂ (C ₆ H ₈ N ₂) ₂]	9290	784.66	0.808	19.2	2.03
4.	[Ni(C ₆ H ₂ O ₇ N ₃) ₂ (C ₆ H ₈ N ₂) ₂]	9915	795.00	0.771	22.9	1.63

Table 3: Important IR spectral bands (cm⁻¹) of metal(II) mixed ligand oxalato complexes with 1-2, diaminobenzene

S. No.	Complex	$\nu(\text{NH}_2)/\text{NH}$ Stretching	$\nu_{\text{as}}(\text{C}=\text{O})$	$\nu_{\text{s}}(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})+$ $\nu(\text{C}-\text{O})$	$\nu(\text{NO}_2)$	$\nu(\text{C}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
1	[Co(C ₂ O ₄)(C ₆ H ₈ N ₂) ₂]	3395 s, br	1680 s 1620 s	1438 m	-	-	1185 m	490 w 475 w	547 w 521 w
2	[Ni(C ₂ O ₄)(C ₆ H ₈ N ₂) ₂]	3350 m, br	1695 s	1380 m	-	-	1180 m	498 w	548 w
3	[Co(C ₆ H ₂ O ₇ N ₃) ₂ (C ₆ H ₈ N ₂) ₂]	3240 m, br	-	-	1180 s	1500 w	-	540 m	519 w
4	[Ni(C ₆ H ₂ O ₇ N ₃) ₂ (C ₆ H ₈ N ₂) ₂]	3280 m, br	-	-	1185 s	1480 s	-	520 m	410 w
						1480 m	-	525 m	440 m

The conductivity of the complexes in DMF (10^{-3} M) lie in the range 19.11-30.14 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, which is for non-electrolytes. The characterization data of the complexes are given in Table -1.

Co(II) complexes showed magnetic moment 4.80 and 4.92 indicating that the complexes are paramagnetic and have three unpaired electrons confirming a high spin octahedral configuration(1). The magnetic moment values for Ni(II) complexes was found to be 3.22 and 3.32 corresponding to two unpaired electrons.

In the present study of Co(II) complexes, the bands were observed around 9010 and 9100 (ν_1), 18300 and 18500(ν_2), 20200 and 20500(ν_3) cm^{-1} due to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) charge transfer transitions, respectively, in an octahedral symmetry. The ν_2/ν_1 values for Co(II) complexes was found to be 2.03 as reported for the majority of octahedral Co(II) complexes¹²⁻¹⁷. The reduction of the Racah parameter from the free ion value and the β° value indicate the presence of covalence in the compounds. The electronic spectral parameters are given in the Table-2.

Ni(II) complexes exhibited three bands in the region 9915 and 9810 (ν_1), 16255 and 15900 (ν_2), 25415 and 24900 (ν_3) cm^{-1} , due to the spin allowed transitions and may be assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), respectively, in an octahedral symmetry. The ν_2/ν_1 values for Ni(II) complexes were found to be 1.62 and 1.63, which are in the usual range reported for the majority of octahedral Ni(II) complexes¹²⁻¹⁷.

In the ESR spectra of Co(II) complexes, characteristic isotropic lines have been observed. The observed g_{\perp} (2.005) and g_{\parallel} (2.083) values are comparable to the results reported in the literature(18) and suggest the covalent nature of the metal-ligand bond in the complexes. The deviation of 'g' values from the free electron value (2.0023) may be due to angular momentum contributions in the complexes. In the case of Ni(II)

complexes ESR spectra did not give much information about the environment around metal ion.

IR spectra of oxalato complexes show bands at 1620-1695 and 1380-1438 cm^{-1} , identified as $\nu_{as}(\text{C}=\text{O})$ and $\nu_s(\text{C}=\text{O})$. NH stretching vibrations were observed in the region 3350 and 3395 cm^{-1} and $\nu(\text{M}^n\text{N})$ stretching vibrations occurring at 519-548 cm^{-1} (Table-3).

In the case of picrato complexes the absence of $\nu(\text{OH})$ mode(19,20) at 3385 cm^{-1} and appearance of a medium band at about 1260 cm^{-1} in all the complexes, suggests the coordination of picrate ion in a monodentate fashion. The mode of coordination through the deprotonated phenolic oxygen, is further manifested by the appearance of new band in the region 520-540 cm^{-1} due to $\nu(\text{M}-\text{O})$ vibrations²¹.

In the case of 1,2-diaminobenzene complexes with metal picrate, the C-N stretching vibrations observed in the ligand shifted by 15-25 cm^{-1} due to the coordination of the nitrogen atom to the metal ions^{22,23}. The complexes also show bands corresponding to phenyl ring vibrations²². The IR spectra of the complexes of 1,2-diaminobenzene gave bands in the region 1428-1528, 1080-1120 and 740-785 cm^{-1} , which may be assigned to bands characteristic of phenyl group²⁴ and the bands observed in the region 2965-2990 cm^{-1} may be due to aromatic C-H group.

In all the picrato complexes¹⁰, new bands observed in the far infrared region of the complexes at 520-540, 410-440 and 370-375 cm^{-1} , are probably due to the formation of M-O²¹, M-N^{25,26} and M-O-C bonds, respectively^{27,28} Table 3.

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