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Synthesis and Characterization of Cobalt(II) and Nickel(II) Complexes of Substituted Isoxazoles

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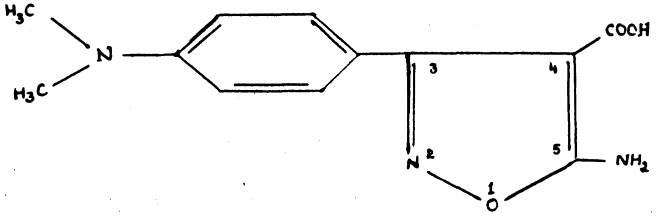
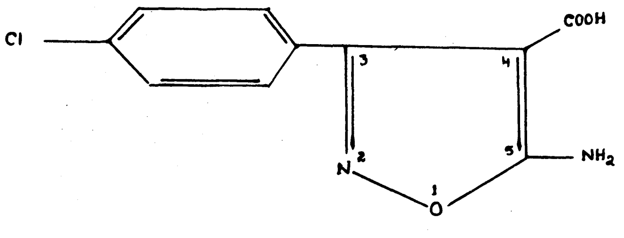
Complexes of Co(II) and Ni(II) have been synthesised using substituted isoxazoles. The complexes were characterized on the basis of elemental analysis, molar conductance, IR, UV and magnetic data. Co(II) and Ni(II) complexes showed μ_{eff} indicative of their distorted octahedral structure.

INTRODUCTION

Isoxazole and its derivatives are found to possess antiinflammatory, analgesic antipyretic and antitussive activity.[1] The introduction of carboxylic acid and amino group at 4th and 5th positions respectively results in a moiety comparable to anthranilic acid which is a good bidentate ligand. With these ideas in mind we have prepared 5-amino-3-(4-dimethylaminophenyl) isoxazole 4-carboxylic acid (L_1) and 5-amino-3-(4-chlorophenyl) isoxazole-4-carboxylic acid (L_2). The structures of the ligands are shown below.





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EXPERIMENTAL

Analytical grade reagents were used to prepare ligands. The metal(II) chlorides were of AnalaR quality. Solvents were purified by standard methods. The ligands L_1 and L_2 were prepared by the available procedures.[2]

Synthesis of complexes: The ligand (0.002 mol) was dissolved in 10 mL of ethanol. To this, metal chloride (0.001 mol) dissolved in 5 mL ethanol was added. The resulting mixture was refluxed for 2 h. The solid complexes obtained were filtered, washed with ethanol and dried *in vacuo* over anhydrous calcium chloride.

Elemental analyses were done by conventional methods.[3, 4] Conductance measurements were made at 25°C on 10^{-3} M solutions of the complexes in DMF. UV-VIS spectra were recorded in DMF. IR spectra were recorded using KBr (4000–200 cm^{-1}) and magnetic susceptibilities were measured at 300 K using Gouy balance.

RESULTS AND DISCUSSION

The elemental analyses of the complexes, magnetic moments and molar conductance data are given in Table-1. The metal to ligand ratio in the complexes has been found to be 1 : 2.

TABLE-1
ANALYTICAL, CONDUCTANCE AND MAGENTIC MOMENTS OF COMPLEXES

S. No.	Complex	Co(II) L_1	Co(II) L_2	Ni(II) L_1	Ni(II) L_2
1.	Mol. formula	$(C_{12}H_{12}N_3O_3)_2$ Co·2H_2O	$(C_{10}H_6N_2O_3)_2$ Co·2H_2O	$(C_{12}H_{12}N_3O_3)_2$ Ni·2H_2O	$(C_{10}H_6N_2O_3)_2$ Ni·2H_2O
2.	Colour	Reddish Brown	Brown	Light blue	Brown
3.	MP/Dec. point(°C)	160–162	106–108	224–226	134–136
4.	Molar Conductance $\Lambda_m \Omega^{-1}$ cm^2 mol^{-1}	16.16	3.23	3.03	8.58
5.	Magnetic moments μ_{eff} (B.M.)	5.12	5.08	2.97	2.90
6.	Elemental analysis % Found (Calcd) :				
	C				
	H	50.74 (49.06)	42.25 (42.11)	50.00 (49.08)	40.10 (42.12)
	N	5.00 (4.77)	3.00 (2.80)	5.01 (4.77)	2.95 (2.80)
	Metal	14.00 (14.31)	9.78 (9.82)	14.05 (14.31)	9.90 (9.82)
		9.86 (10.04)	10.10 (10.33)	10.10 (10.00)	10.25 (10.30)

The low molar conductance values 3.03–16.16 indicate that all the four complexes are non-electrolytes and practically no interchange reactions occur between the solvent and the dissolved complexes.

The magnetic moments of the cobalt(II) complexes have been found to be 5.12 B.M. and 5.08 B.M. which are in the range 4.7–5.2 B.M. expected for octahedral cobalt complexes. The nickel complexes showed magnetic moments 2.97 B.M. and 2.90 B.M. indicating octahedral stereochemistry.

The electronic spectral data of the complexes are given in Tables 2 and 3. The electronic spectra of cobalt compexes exhibit two bands in the region 6744–6756 and 18532–16750 cm^{-1}owing to the transitions $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ (ν_1) and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ (ν_3) respectively, which are in consistent with the octahedral geometry for the complexes. The ν_2 band which involves two electron transitions was not observed. Its position was calculated using Konig equantion.[5] The various ligand field parameters have been calculated. The ν_2/ν_1 for cobalt(II) complexes has been found to be 2.1 which is in good agreement with that expected for octahedral cobalt(II) complexes.

Three bands observed for nickel(II) complexes in the 10030–9699, 16287–15625, 26810–22522 cm^{-1} regions may be assigned to the transitions $^3T_{2g} \leftarrow {}^3A_{2g}$ (F)(ν_1), $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ (F) (ν_2) and $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ (ν_3) commensurate with octahedral stereochemistry.[6] The various spectral parameters have been calculated and the ν_2/ν_1 ratio is close to that required for octahedral geometry.

A comparison of the IR spectra of the ligands and their complexes indicates coordination of the ligand to the metal through the nitrogen atom of the amino group and oxygen atom of the carboxyl group.[7] The ligand L_1 shows sharp bands at 3320 $cm^{-1}$and 1620 cm^{-1} which are assigned to $\nu(NH_2)$ and ν(—C═O) respectively. The ligand L_2 also shows similar bands. In the complexes a spectral shift of 15–20 cm^{-1} towards lower energy was observed for $\nu(NH_2)$ and 20–30 cm^{-1}·for ν(—C═O). This indicates that the coordination of the amino group with metals (the formation of a nitrogen to metal dative bond) results in an appreciable decrease in the frequency of the N—H stretching vibrations. The carbonyl of carboxyl group was found at 1620 cm^{-1} in the ligands but in the complexes it was observed at 1600 cm^{-1}suggesting that the oxygen of the carboxylate ion takes part in the formation of a bond. Coordination through N and O is further supported by the presence of non-ligand bands at 440 cm^{-1}[ν(M—N)] and 410 cm^{-1} [ν(M—O)] region. The presence of coordinated water molecules in the complexes is indicated by a medium broad band in the 3600–3400 cm^{-1}, and a sharp band at 830–810 cm^{-1} region.[8] This is further supported by TGA studies.

The TGA studies indicate that the complexes are generally stable upto 100°C. Afterwards, oxidation of organic moiety begins. It has been found that concurrent with the decomposition and oxidation of organic substances, some volatilisation also takes place. The final product obtained in each case has been chemically pure cobalt/nickel oxide.

The above studies suggest that the complex may tentatively be assigned the distorted octahedral structure.

TABLE-2
ELECTRONIC SPECTRAL DATA OF OCTAHEDRAL Co(II) COMPLEXES

No.	Complex	ν_1		ν_2 calc		ν_3		ν_2/ν_1	B′ cm^{-1}	β	Dq·	LFSE Kcal mol^{-1}
		nm	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}					
1.	$Co(L_1)_2 2H_2O$	1480	6756	688	14514	539	18552	2.1	853.2	0.878	775.8	13.30
2.	$Co(L_2)_2 2H_2O$	1440	6944	673	14849	597	16750	2.1	717.8	0.739	790.5	13.55

TABLE-3
ELECTRONIC SPECTRAL DATA OF OCTAHEDRAL Ni(II) COMPLEXES

No.	Complex	ν_1		ν_2 calc		ν_3		ν_2/ν_1	B' cm^{-1}	β	Dq	LFSE Kcal mol^{-1}
		nm	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}					
1.	$Ni(L_1)_2 2H_2O$	1031	9699	614	16287	373	26810	1.67	933.3	0.896	969.9	33.25
2.	$Ni(L_2)_2 2H_2O$	997	10030	640	15625	444	22522	1.55	537.1	0.515	1003.0	34.38

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