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Synthesis and Characterization of Some Transition Metal Complexes of 2-Naphthoin Oxime

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Transition metal complexes of 2-naphthoin oxime have been synthesized and characterized by elemental analysis, molar conductance, and magnetic and spectral data. Various bonding features were established on the basis of IR spectral data. The electronic spectral data are calculated. The structural geometry is assigned on the basis of various spectral findings.

Key words: Transition metal complexes, 2-naphthoin oxime.

INTRODUCTION

Naphthoin and its oximes were found to be potential chelating agents. Oximes are known for their analytical applications[1] Transition metal complexes of different oximes with oxygen and nitrogen donors have been reported.[2, 3] In recent years considerable interest has been shown on the synthesis of metal complexes of catalytic and physiologically important metal chelates with nitrogen as donor atom.[4] In the present paper we report synthesis and characterization of a few transition metal complexes of ligand 2-naphthoin oxime. An attempt is made to assign structural geometry to these complexes.

EXPERIMENTAL

All the solvents and reagents were of laboratory reagent (LR) grade. The ligand 2-naphthoin oxime was prepared from 2-naphthoin. The metal complexes were synthesized by mixing metal ion solution (1 mg/cm^3) with ethanolic solution (1% w/v) of ligand. The pH of the resulting mixture was adjusted to optimum value to obtain precipitate. The metal chelates were filtered, washed and dried at 60°C in the oven. Finally each complex was recrystallized from its ethanolic solution.

RESULTS AND DISCUSSION

All the complexes are colored except zinc(II) complex and are stable to air and moisture. They decompose at high temperature and are insoluble in many common organic solvents. However, they are soluble in solvents like methanol, chloroform, nitrobenzene, DMSO, DMF, etc. The molar conductances of these complexes at 10^{-4} M solution in nitrobenzene lie in the range $1.36–3.49 \times 10^{-2}$ siemens. The low values of the molar conductance indicate non-electrolytic nature of the complexes. Greenwood *et al.*[5] have suggested similar range for the non-electrolytes. The results of elemental analysis (Table-1) suggest that metal complexes have 1 : 2 metal to ligand stoichiometry. Each complex has chemical composition of ML_2 and is anhydrous in nature.

TABLE-1
ANALYTICAL DATA OF NAPHTHOIN OXIME AND ITS METAL COMPLEXES

Metal complex	m.w.	pH	% Analysis, found (calcd.)				Molar cond., siemens
			C	H	N	M	
Ligand L $C_{22}H_{17}O_2N$	327.37	–	80.08 (80.64)	5.62 (5.19)	4.30 (4.28)	–	0.25×10^{-2}
$Mn(L)_2$	707.67	6.6	73.81 (74.61)	4.16 (4.52)	4.13 (3.96)	7.81 (7.76)	1.36×10^{-2}
$Fe(L)_2$	708.59	5.8	73.39 (74.51)	3.96 (4.52)	4.11 (3.95)	7.70 (7.89)	2.98×10^{-2}
$Co(L)_2$	711.67	6.7	73.81 (74.19)	4.06 (4.50)	3.87 (3.93)	7.89 (8.23)	3.18×10^{-2}
$Ni(L)_2$	711.43	6.8	73.39 (74.22)	4.11 (4.50)	3.90 (3.94)	7.94 (8.25)	2.58×10^{-2}
$Cu(L)_2$	716.32	6.0	72.81 (73.71)	3.94 (4.47)	4.23 (3.91)	9.12 (8.88)	1.56×10^{-2}
$Zn(L)_2$	718.12	6.7	73.39 (73.53)	3.99 (4.46)	4.19 (3.90)	8.95 (9.10)	3.49×10^{-2}

The characteristic IR frequencies of the ligand and metal complexes are summarized in Table-2. The IR spectrum of the ligand 2-naphthoin oxime shows a broad band at 3250 cm^{-1}, which is attributed to intramolecularly hydrogen bonded[6] ν(OH). A strong absorption pointed in the region 1665–1615 cm^{-1} in the spectra of metal complexes assigned to ν(C=N). This stretching vibration appears at higher frequencies at 1670 cm^{-1} in the spectrum of ligand. The involvement of oximic nitrogen in coordination is deduced by a negative shift in ν(C=N) to the extent of 10–55 cm^{-1} in all the complexes. The appearances of new bands were observed in the range 535–520 and 450–410 cm^{-1}, which were assigned to ν(M—O) and ν(M—N) modes[7,8] respectively. From the IR studies it is inferred that the ligand 2-naphthoin oxime is acting as mono-basic bidentate ligand with oxygen of the phenolic group and nitrogen of the oximic group participating in coordination.

TABLE-2
SALIENT FEATURES OF INFRARED SPECTRA (cm^{-1}) OF METAL COMPLEXES

Metal complex	ν(OH) Oximic	ν(C=N)	ν(N—O) Asym.	ν(N—O) Sym.	ν(M—N)	ν(M—O)
Ligand L $C_{22}H_{17}O_2N$	3250	1670	1200	970	–	–
$Mn(L)_2$	3300	1640	1180	945	520	410
$Fe(L)_2$	3400	1625	1215	950	535	450
$Co(L)_2$	3370	1665	1225	985	530	420
$Ni(L)_2$	3400	1660	1205	965	530	435
$Cu(L)_2$	3360	1615	1205	975	520	420
$Zn(L)_2$	3450	1620	1210	1020	525	440

The magnetic and electronic spectral data of complexes are reported in Table-3. The room temperature magnetic moment for Mn(II) complex shows a magnetic moment 5.12 B.M. The observed moment is low when compared to spin only value (5.92 B.M.) for high spin Mn(II) complexes. This may be due to the presence of Mn(II) species or spin exchange in solid state[9]. The observed room temperature magnetic moment of Fe(II) complex is 4.67 B.M. which is indicative of high spin octahedral geometry. The Co(II), Ni(II) and Cu(II) complexes show magnetic moment of 3.96, 2.85 and 0.95 B.M. respectively, which is in agreement with the spin only value[10]. However, Cu(II) complex exhibits subnormal value probably due to super exchange phenomena. Zn(II) complex is diamagnetic in nature.

TABLE-3
ELECTRONIC ABSORPTION SPECTRAL DATA AND MAGNETIC MOMENT OF METAL COMPLEXES

Metal complexes	Magnetic moment (B.M.)	Band maxima (cm^{-1})	Transition	Dq	B	β	ν_2/ν_1
$Mn(L)_2$	5.12	8200	–	–	–	–	–
		22300	$^2E_g \rightarrow {}^2T_{2g}(F)$	–	–	–	–
		9700					
$Fe(L)_2$	4.67	15550	$^5T_{2g} \rightarrow {}^5E_g$	–	–	–	–
		26710					
		8100	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$				
$Co(L)_2$	3.96	15250	$^4T_{1g} \rightarrow {}^4A_{2g}(F)$	810	871	0.897	1.883
		19000	$^4T_{1g} \rightarrow {}^4T_{2g}(P)$				
		8500	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$				
$Ni(L)_2$	2.85	14200	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	850	867	0.530	1.671
		24300	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$				
$Cu(L)_2$	0.95	11900	$^2E_g \rightarrow {}^2T_{2g}$	1190			
		25800			–	–	–

The electronic absorption spectra of metal complexes displays various d-d transitions and charge transfer transitions. Mn(II) complex exhibit very weak absorption bands at 8200 and 22300 cm^{-1}. Owing to very weak absorption, the band could not be assigned with certainty. The Fe(II) complex exhibits two main absorption bands at 9700 and 26710 cm^{-1} which are assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition and charge transfer respectively[11, 12]. The Co(II) complex shows three bands in the regions 8100, 15250 and 19000 cm^{-1} while Ni(II) complex is characterized by three absorption bands at 8500, 14200 and 24300 cm^{-1}. Various ligand field parameters Dq, B, and β, along with different d-d transitions for these complexes, are calculated and presented in Table-3. The ligand field parameters are consistent with octahedral geometry. The Racah inter-electronic repulsion parameter B is less than free ion value suggesting a considerable covalent character of the bond. The calculated value of ν_2/ν_1 ratio is within the range expected for an octahedral geometry. Similarly, Cu(II) complex shows bands at

11900 and 25800 cm^{-1}. The charge transfer transition is assigned to band appearing at 25800 cm^{-1} while d-d transition is assigned to band appearing at 11900 cm^{-1}.

On the basis of elemental analyses, molar conductivity, magnetic measurements, IR and electronic spectral data an octahedral geometry have been proposed for Mn(II), Fe(II), Co(II), and Ni(II) complexes, while Cu(II) and Zn(II) complexes are assigned distorted octahedral and tetrahedral geometry respectively.

2-Naphthoin oxime and its metal complexes were screened for their antimicrobial studies on the three common fungi, *Aspergillus niger, Aspergillus nidulense* and *Candida albicans* at room temperature and on both gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria by several dilution method[13]. The minimum inhibitory concentration value indicates that the metal chelates exhibit higher antimicrobial activity than that of the involved free ligand molecule. It is evident that the metal complexes are stable and chemically inert having no specific active centre. Hence it can exert a powerful inhibitory effect on intracellular biological process by concentrating at the susceptible site from which it slowly dissolves.

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