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Structural Studies on Metal Complexes of 2-Furoin Oxime

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Transition metal complexes of 2-furoin oxime have been synthesized and characterized by elemental analysis, molar conductance, 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 basic of various spectral findings.

INTRODUCTION

Furoin and its oximes were found to be potential chelating agent. Oximes are known for their analytical application[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 charcterization of a few transition metal ocmplexes of ligand 2-furoin oxime. An attempt is made to assign structural geometry to these complexes.

EXPERIMENTAL

All the solvents and reagents were of good laboratory grade. The ligand 2-furoin oxime was prepared from 2-furoin. 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 precipitated complex was filtered, washed and dried at 60°C in the oven. Finally each complex was recrystallized from its ethanolic solution.

The analytical data, conductance measurements, magnetic moment, electronic absorption spectra and IR spectra of ligand and the complexes were recorded. All the experimental findings are summarized in the Tables 1–3.

RESULTS AND DISCUSSION

All the complexes are coloured except zinc (II) complex and are stable to air and moisture. They decomposed 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 conductance of these complexes at 10^{-4} M solution in nitrobenzene lie in the range $1.12–8.76 \times 10^{-2}$

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 suggest that metal complexes have 1 : 2 metal to ligand stoichiometry. Each complex has chemical composition of ML_2 and is in anhydrous state.

TABLE-1

ANALYTICAL PARAMETERS OF 2-FUROIN OXIME AND METAL COMPLEXES

Metal Complex	m.w.	pH	% Analysis, Found (Calcd)				Molar Cond. Siemens
			C	H	N	M	
Ligand L $C_{10}H_9O_4N$	207.18	–	57.56 (57.92)	4.38 (4,34)	6.60 (6.76)	–	1.12×10^{-2}
$Mn(L)_2$	476.29	6.8	50.78 (51.36)	3.16 (3.42)	6.13 (5.99)	12.07 (11.76)	1.82×10^{-2}
$Fe(L)_2$	468.20	6.6	50.66 (51.26)	3.24 (3.42)	6.11 (5.98)	11.72 (11.93)	4.72×10^{-2}
$Co(L)_2$	470.28	7.0	50.58 (50.97)	3.92 (3.40)	6.20 (5.95)	12.76 (12.30)	6.31×10^{-2}
$Ni(L)_2$	471.04	7.1	52.24 (50.95)	3.62 (3.40)	6.21 (5.95)	12.17 (12.46)	1.91×10^{-2}
$Cu(L)_2$	475.90	6.7	50.28 (50.43)	3.30 (3.36)	6.06 (5.88)	13.09 (13.35)	8.76×10^{-2}
$Zn(L)_2$	477.74	6.5	50.25 (50.23)	3.29 (3.25)	5.67 (5.86)	13.24 (13.60)	6.54×10^{-2}

TABLE-2

SALIENT FEATURES OF INFRARED SPECTRA OF METAL COMPLEXS (cm^{-1})

Compound	νOH Oximic	ν(C=N)	ν(N—O)	ν(N—O)	ν(M—N)	ν(M—O)
Ligand (L)	3250	1628	1190	990	–	–
$Mn(L)_2$	3400	1580	1190	1015	500	405
$Fe(L)_2$	3380	1580	1215	1010	540	420
$Co(L)_2$	3400	1565	1215	1000	520	420
$Ni(L)_2$	3420	1595	1195	1005	570	410
$Cu(L)_2$	3430	1585	1200	1010	520	415
$Zn(L)_2$	3470	1580	1210	1015	500	415

The characteristic IR frequencies of the ligand and metal complexes are sumarized in the Table 2. The IR spectrum of the ligand 2-furoin oxime shows a broad band at 3250 cm^{-1}, which is attributed to intramolecularly hydrogen bonded.[6] νOH. A strong absorption pointed in the region 1595–1565 cm^{-1} in the spectra of metal complex is assigned to ν(C=N). This stretching vibration appear at higher frequencies at 1628 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 30–45 cm^{-1} in all the complexes. The appearance of new bands were observed in the range 560–400 cm^{-1} which were assigned to ν(M—O) and ν(M—N) modes[7, 8]. From the IR studies it is inferred that the ligand, 2-furoin oxime is acting as mono basic bidentate with oxygen of the phenolic group and nitrogen of oximic group participating in the coordination.

The magnetic and electronic spectral data of complexes are reported in Table 3. The room temperature magnetic moment of Mn(II) complex shows a magnetic moment 5.16 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 4.78 B.M. which is indicative of high spin octahedral geometry. The Co(II), Ni(II) and Cu(II) complexes show magnetic moment of 4.12, 3.17 and 1.64 B.M. respectively, which is in agreement with the spin only value[10]. However, Cu(II) complex exhibits little subnormal value probably due to super exchange phenomena. Zn(II) complex is diamagnetic in nature.

TABLE-3
ELECTRONIC ABSORPTION SPECTRAL AND MAGNETIC MOMENT

Metal Complexes	Magnetic Moment (B.M.)	Band Maxima (cm^{-1})	Transition	Dq	B	β	ν_2/ν_1
$Mn(L)_2$	5.16	8400		–	–	–	–
		23700	$^5E_g \longrightarrow {}^2T_{2g}(F)$				
$Fe(L)_2$	4.78	9900		–	–	–	–
		15400	$^5T_{2g} \longrightarrow {}^5E_g$				
		27705					
$Co(L)_2$	4.12	8400	$^4T_{1g} \longrightarrow {}^4T_{2g}(F)$	772	830	0.855	1.919
		16120	$^4T_{1g} \longrightarrow {}^4A_{2g}(F)$				
		19200	$^4T_{1g} \longrightarrow {}^4T_{2g}(P)$				
$Ni(L)_2$	3.17	8560	$^3A_{2g} \longrightarrow {}^3T_{2g}(F)$	856	918	0.900	1.647
		14095	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$				
		25360	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$				
$Cu(L)_2$	1.64	13800	$^5E_g \longrightarrow {}^2T_{2g}$	1380	–	–	–
		26000					
$Zn(L)_2$	Diamag.	–	–	–	–	–	–

The electronic absorption spectra of metal complexes display various d-d transitions and charge transfer transitions. Mn(II) complex exhibits very weak absorption bands at 8400 and 23700 cm^{-1}. Owing to very weak absorption, the band could not be assigned with centainty. The Fe(II) complex exhibits two main absorption bands at 9900 and 27705 cm^{-1} which are assigned to $^5T_{2g} \longrightarrow {}^5E_g$ transition and charge transfer respectively[11, 12]. The Co(II) complex show three bands in the region 8400, 16120 and 19200 cm^{-1} while Ni(II) complex is characterized by three absorption bands at 8560, 14095 and 25360 cm^{-1}. Various ligand field parameters Dq, B, and β alongwith different d-d transitions for these complexes are calculated and depicted in the Table 3. The ligand field parameters are inconsistent with the 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 13800 and 26000 cm^{-1}. The change transfer transition is assigned to band appearing at 26000 cm^{-1} while d-d transition is assigned to band appeared at 13600 cm^{-1}.

On the basis, of elemental analysis, conductivity, magnetic measurements, IR and electronic spectral data, 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-Furoin oxime and its metal complexes were screened for their microbial studies on the three common fungi, *Aspergillus niger, Aspergillus nidulense* and *Gandida 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 have no specific active center. Hence it can exert a powerful inhibitory effect on intracellular biological process by concentrating at the susceptible site from which it slowly dissolves.

REFERENCES

1. Y. Shechter and S.J.D. Karlish, *Nature*, **284,** 556 (1980).
2. D.B. Ingle and D. Khanolkar, *J. Indian, Chem. Soc.*, **50,** 103 (1973).
3. G.R. Reddy, *Curr. Sci. (India)* **38,** 137 (1969).
4. R.S. Sharma, R.B. Pathak and S.C. Bahl, *J. Indian Chem. Soc.*, **62,** 625 (1985).
5. N.N. Greenwood, B.P. Straughan and A.E. Wilson, *J. Chem. Soc.*, 2209 (1968).
6. A.K. Rana and J.R.Shah, *J. Indian Chem Soc.*, **58,** 1100 (1981).
7. K. Nakamoto, Infrared Spectroscopy of Inorganic and Coordination Compounds, J. Willey & Sons., New Youk (1970).
8. V. Atre, G. Reddy, L.N. Sharda and M.C. Ganorkar, *Indian J. Chem.*, **21A,** 924 (1982).
9. R.H. Holm, G.W. Everett and A. Chakravorthy, *Proc. Inorg. Chem.*, **7,** 83, 120 (1966).
10. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **20A,** 810 (1964).
11. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern Limited, New Delhi, 3rd Edn., p. 538 (1972).
12. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, New York, p. 344 (1968).
13. G.C. Donald and A.R. Williams, Assay Methods of Antibiotics: A Laboratory Manual, Medical Encyclopaedia Inc.

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