

## Structural Studies on Metal Complexes of Benzthienoin Oxime

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Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Mo(VI) complexes have been prepared by reacting metal salts with the ligand benzthienoin oxime in alcoholic medium. All the complexes are coloured crystalline solids and are non-electrolytes in nitrobenzene. Elemental analysis confirm the 1 : 1 stoichiometry for Mn(II), Cu(II) and Zn(II) complexes while other metals form 1 : 2 complexes. Magnetic, electronic and IR spectral information suggest that Mn(II), Cu(II), Pd(II), Ni(II) and Co(II) exhibit planar geometry while Fe(II) and Mo(VI) crystallise with octahedral geometry. The tetrahedral environment is suggested for the Zn(II) complex.

### INTRODUCTION

Oxime derivatives of *o*-hydroxy ketones are well known complexing agents<sup>1</sup>. Many acyloin oximes of aliphatic ketones and benzoin oximes of aromatic ketones are studied in detail<sup>2</sup>. These reagents have —CH(OH)·C(NO<sub>2</sub>)— as the common group in their structures which is chiefly responsible for their complexing properties. The proton of alcoholic group is weakly acidic whereas the N atom acts as a base by donating the lone pair of electrons to the metal ion. Literature survey reveals<sup>3, 4</sup> that oximes of symmetrical benzoin molecule have better coordination properties and can exhibit different structural geometry after chelating with the metal ions. In the present work, we have studied complexing properties of the unsymmetrical ligand benzthienoin oxime with a few selected transition metal ions.

### EXPERIMENTAL

An unsymmetrical benzoin is the one in which the aromatic groups attached to the —CH(OH)·C(NO<sub>2</sub>)— are different. This can be obtained by benzoin condensation reaction of two different aromatic aldehydes<sup>5</sup>. The reactivity of aldehydes determines the products as well as the rate of the reaction. The ketone benzthienoin, C<sub>6</sub>H<sub>5</sub>CH(OH)C(NO<sub>2</sub>)—C<sub>4</sub>H<sub>3</sub>S (m.p. 127°C), was prepared by benzoin condensation of freshly distilled benzaldehyde and thiophene-2-aldehyde in presence of KCN. The oxime of the purified ketone was prepared by the usual method<sup>5</sup> for oximation using hydroxylamine hydrochloride and sodium acetate (m.p. 155°C).

The metal complexes were prepared by treating aqueous solution of metal ion with an ethanolic solution of the oxime in appropriate proportions and after adjusting the pH to the optimum value. The precipitated complexes were filtered, washed and dried in an oven at 60°C. The product was recrystallised from ethanolic solution. All the recrystallised complexes were characterised for their physico-chemical properties and elemental analysis. The metal complexes were also charac-

terised by recording their electronic absorption, infrared and diffused reflectance spectra. The magnetic measurements at room temperature were made on Gouy's balance. All the experimental findings are presented in Tables 1–3.

TABLE-1  
ANALYTICAL PARAMETERS OF METAL COMPLEXES

Compounds	m.w	Colour	% Analysis, found (calcd.)				
			C	H	N	S	M
Ligand	233	Brown	61.19 (61.80)	4.29 (4.72)	5.87 (6.01)	13.12 (13.73)	—
Mn(L)	286	Dark brown	50.13 (50.36)	3.00 (3.15)	4.09 (4.90)	10.56 (11.19)	18.35 (19.18)
Cu(L)	294.5	Green	48.24 (48.89)	2.67 (3.05)	4.56 (4.75)	10.12 (10.86)	21.07 (21.57)
Zn(L)	296	White	48.32 (48.59)	2.87 (3.04)	4.35 (4.72)	10.11 (10.80)	21.46 (22.06)
Fe(HL) <sub>2</sub>	520	Red brown	54.97 (55.40)	3.13 (3.85)	5.01 (5.39)	11.38 (12.31)	10.53 (10.74)
Co(HL) <sub>2</sub>	523	Dirty brown	54.84 (55.07)	3.29 (3.82)	5.01 (5.35)	11.85 (12.24)	10.95 (11.27)
Ni(HL) <sub>2</sub>	523	Buff	54.04 (55.10)	3.26 (3.83)	5.12 (5.36)	11.80 (12.24)	10.98 (11.23)
Pd(HL) <sub>2</sub>	570	Yellow	49.48 (50.49)	2.99 (3.51)	4.39 (4.91)	10.56 (11.22)	17.54 (18.66)
MoO <sub>2</sub> (HL) <sub>2</sub>	592	White	48.01 (48.65)	2.75 (3.38)	4.39 (4.73)	10.12 (10.81)	15.23 (16.21)

TABLE-2  
ELECTRONIC ABSORPTION SPECTRAL DATA AND MAGNETIC MOMENTS

Compounds	$\mu_{\text{eff}}$ (B.M.)	Molar conductance mhos. cm <sup>-1</sup>	Absorption bands (in solution) cm <sup>-1</sup>	Absorption bands (in solid) cm <sup>-1</sup>
Ligand	—	—	36760	—
Mn(L)	4.95	$5.34 \times 10^{-2}$	39220	15600, 24500*
Cu(L)	Diamagnetic	$1.76 \times 10^{-2}$	—	22000*, 25700*
Zn(L)	Diamagnetic	$1.47 \times 10^{-2}$	36360	—
Fe(HL) <sub>2</sub>	4.40	$4.56 \times 10^{-2}$	38910, 24700*	14700
Co(HL) <sub>2</sub>	2.82	$9.89 \times 10^{-2}$	33900, 20000	17250, 23800*
Ni(HL) <sub>2</sub>	2.10	$2.70 \times 10^{-2}$	39220, 29400*	13500, 23500*
Pd(HL) <sub>2</sub>	Diamagnetic	$1.35 \times 10^{-2}$	37500, 32260*	—
MoO <sub>2</sub> (HL) <sub>2</sub>	Diamagnetic	$0.67 \times 10^{-2}$	37000, 35000	—

\*Charge Transfer transitions

TABLE-3  
KEY INFRARED SPECTRAL BANDS ( $\text{cm}^{-1}$ ) OF METAL COMPLEXES

Compounds	$\nu(\text{OH})$ Oximic	$\nu(\text{C}=\text{N})$	$\delta(\text{OH})$ Def.	$\nu_{\text{asym}}(\text{N}-\text{O})$	$\nu(\text{C}-\text{O})$ Sec. alc	$\nu_{\text{sym}}(\text{N}-\text{O})$	$\nu(\text{M}-\text{L})$
Ligand	3200	1625	1315	1290	1115	940	—
Mn(L)	—	1552	—	1285	1102	990	500
Cu(L)	—	1560	—	1285	1100	985	460
Zn(L)	—	1565	—	1290	1100	995	505
Fe(HL) <sub>2</sub>	3400	1565	1320	1285	1110	962	550
Co(HL) <sub>2</sub>	3430	1555	1315	1285	1115	980	535
Ni(HL) <sub>2</sub>	3410	1560	1305	1278	1115	975	540
Pd(HL) <sub>2</sub>	3425	1555	1310	1288	1116	980	495
MoO <sub>2</sub> (HL) <sub>2</sub>	3200	1618	—	1280	1105	978	—

## RESULTS AND DISCUSSION

The Cu(II), Pd(II) and Mo(VI) complexes are formed in weakly acidic pH while other complexes are obtained from neutral solution except the Zn(II) complex which is formed at pH 8.5–9.0. All the complexes are coloured and crystalline in nature. The results of Table-1 indicate that complexes of Mn(II), Cu(II) and Zn(II) show metal : ligand stoichiometry as 1 : 1 whereas Fe(II), Co(II), Ni(II) and Pd(II) exhibit 1 : 2 stoichiometry. The Mo(VI) complex involves Mo in its oxocationic form and has composition MoO<sub>2</sub> (oxime)<sub>2</sub>.

The electronic spectrum of ligand benzthienoin oxime in dioxane reveals an intense absorption band at  $36760 \text{ cm}^{-1}$ . This intraligand band is observed at  $39220 \text{ cm}^{-1}$  and  $36360 \text{ cm}^{-1}$  in the corresponding spectra of Mn(II) and Zn(II) complexes respectively. The insolubility of the Cu(II) complex in common solvents prohibits the detailed spectral study in solution but diffused reflectance spectrum exhibits absorption band at  $16600 \text{ cm}^{-1}$ . This band can be assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$  d-d transition suggesting highly distorted, virtually planar configuration to Cu(II) complex. The absorption bands in the diffused reflectance spectra of Cu(II) complex appearing at  $22000 \text{ cm}^{-1}$  and  $25700 \text{ cm}^{-1}$  can be assigned to charge transfer transitions. A strong interaction between Cu atoms, either directly or through bridging oxygen atoms in a dimeric structure for such complex, containing Cu—O—Cu ring, probably accounts for its dimeric nature. The Mn(II) complex shows a subnormal magnetic moment together with its electronic absorption spectrum, indicating the existence of a planar geometry for Mn(II) complex. The subnormal value is probably due to spin exchange through bridged atoms<sup>6-8</sup>. The colourless and diamagnetic Zn(II) complex is tetrahedral and shows the modified ligand band at  $36360 \text{ cm}^{-1}$ .

The Fe(II) complex exhibits the intraligand band at  $38910 \text{ cm}^{-1}$  and charge transfer bands at  $23810 \text{ cm}^{-1}$  and  $24700 \text{ cm}^{-1}$ . Also the band at  $14700 \text{ cm}^{-1}$  is assigned to d-d transition  ${}^5T_{2g} \rightarrow {}^5E_g$  resulting from a high spin octahedral

configuration in a weak ligand field<sup>9</sup>. In the spectrum of Co(II) complex, the intraligand band was observed at  $33900\text{ cm}^{-1}$ , while d-d transition was assigned to band at  $20000\text{ cm}^{-1}$  which appears at  $17250\text{ cm}^{-1}$  in the diffused reflectance spectrum. A band at  $23800\text{ cm}^{-1}$  was assigned to charge transfer band. This observation on spectra reveals that Co(II) complex precipitates with planar geometry. Syamal<sup>10</sup> found that planar Co(II) complex exhibit the band in the similar range.

The solution spectrum of Ni(II) complex shows bands at  $7140\text{ cm}^{-1}$ ,  $13180\text{ cm}^{-1}$  and  $16130\text{ cm}^{-1}$  while these bands appear at  $8700\text{ cm}^{-1}$ ,  $13500\text{ cm}^{-1}$  and  $16000\text{ cm}^{-1}$  in the diffused reflectance spectrum assignable to various d-d transitions. The values of room temperature magnetic moment and band positions in the electronic absorption spectrum suggest that Ni(II) complex has octahedral geometry. Similarly, the diamagnetic Pd(II) complex can be assigned planar structure which exhibits the charge transfer transition at  $37500\text{ cm}^{-1}$ . The solution spectrum of Mo(VI) complex showing intraligand band at  $37000\text{ cm}^{-1}$  can be assigned octahedral structure to  $\text{MoO}_2(\text{II})$  group.

The infrared spectrum of benzthienoin oxime shows strongly bonded  $\nu(\text{OH})$  at  $3200\text{ cm}^{-1}$  as a broad band. In the spectra of Fe(II), Co(II), Ni(II) and Pd(II) this band is observed at  $3400\text{ cm}^{-1}$  as a weak broad band while in case of Mo(VI) complex the same is observed at  $3200\text{ cm}^{-1}$ . The absence of this band in the IR spectra of Mn(II), Cu(II) and Zn(II) indicates that the oxime binds to the metal ions through the alcoholic as well as oximic oxygen atom.

The  $\nu(\text{C}=\text{N})$  stretching vibrations were found in the spectrum of ligand at  $1625\text{ cm}^{-1}$ . This band appears in the range  $1565\text{--}1552\text{ cm}^{-1}$  in the corresponding spectra of metal complexes, except for Mo(VI) complex in which it appears at  $1618\text{ cm}^{-1}$ . Similar lowering in this frequency is reported in literature<sup>11,12</sup>. The  $\delta(\text{OH})$  deformation vibrations can be assigned to the band pointing at  $1315\text{ cm}^{-1}$  in the spectrum of ligand. This band is absent in the corresponding spectra of 1 : 1 metal complexes and it is meagrely lowered in the 1 : 2 complexes. The asymmetric  $\nu(\text{N}=\text{O})$  stretching of oximic group is located at  $1290\text{ cm}^{-1}$  in the spectrum of ligand while, in the spectra of complexes it is found at slightly lower frequencies. The medium intensity band at  $940\text{ cm}^{-1}$  in the ligand spectrum is assigned to symmetric  $\nu(\text{N}=\text{O})$  vibration, which appeared at higher frequencies in the corresponding spectra of the complexes.

The spectrum of  $\text{MoO}_2(\text{II})$  complex shows two additional bands at  $931\text{ cm}^{-1}$  and  $910\text{ cm}^{-1}$  which are assignable to symmetric and asymmetric stretching vibrations of *cis*- $\text{MoO}_2$  group in the complex respectively. The new additional bands of weak intensities at  $615\text{--}600\text{ cm}^{-1}$  and  $550\text{--}460\text{ cm}^{-1}$  in the far-infrared region are assigned to  $\nu(\text{M}=\text{N})$  and  $\nu(\text{M}=\text{O})$  stretching vibrations. Similar assignments on the metal complexes of bidentate ligands containing nitrogen and oxygen donor atoms is reported in literature<sup>13-15</sup>.

Conclusively, all the metal ions coordinate with the bidentate ligand benzthienoin oxime through both the probable donor atoms. The Mn(II), Cu(II), Co(II), Ni(II) and Pd(II) complexes can be assigned planar geometry, while Fe(II) and Mo(VI) can be assigned octahedral geometry.

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