

NOTE

Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) with $\text{ON}=\text{NO}$ Donor Chelating Tetradentate Ligands

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Thirteen complexes of $[\text{ML}/\text{L}'(\text{H}_2\text{O})_2]$ composition where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II); $\text{LH}_2 = 1,8\text{-dibenzoyl-2,7-di-}(ortho\text{-hydroxy phenyl})\text{-4-methyl-3, 6-diazaoctane}$ and $\text{L}'\text{H}_2 = 1,9\text{-dibenzoyl-2,8-di-}(ortho\text{-hydroxy phenyl})\text{-3, 7-diazanonane}$ have been synthesised. All the complexes have been characterised to have either octahedral or distorted octahedral geometry basing upon analytical, conductance, magnetic susceptibility, IR, electronic spectra, apart from e.s.r. and X-ray diffraction data.

The study and synthesis of pharmacologically active chalcone and their metal complexes with divalent metal ions is of recent interest. In continuation with our earlier work¹, the present paper describes the preparation of two tetradentate chalcone derivatives with $\text{ON}=\text{NO}$ donor atoms and its thirteen mononuclear metal complexes.

All the chemicals used were of B.D.H. or E. Merck grade.

Preparation of ligands: Salicylidene acetophenone (*o*-hydroxybenzal acetophenone) was prepared following a standard procedure.² 1,8-dibenzoyl-2,7-di-*(o*-hydroxy phenyl)-4-methyl-3,6-diazaoctane and 1,9-dibenzoyl-2,8-di-*(o*-hydroxy phenyl)-3,7-diazanonane were prepared adopting a Michael type of addition reaction of above chalcone with 1,2-diaminopropane and 1,3-diaminopropane respectively.

Found:	C, 71.40%	H, 6.00%	N, 4.90% for L
Calcd:	C, 71.72%	H, 6.20%	N, 5.07%
Found:	C, 71.30%	H, 6.10%	N, 4.90% for L'
Calcd:	C, 71.72%	H, 6.20%	N, 5.07%

Preparation of complexes: The ethanolic solutions of metal chlorides were refluxed with the ligands over a water bath for approx. 2 h. On cooling concentrated ammonia was added dropwise with stirring when metal complexes were separated; some separated on standing under refrigeration. These were then filtered, washed with ethanol-ether and dried *in vacuo*. Metal, C, H, N were estimated by standard methods. Conductances of complexes were measured in 10^{-3} M solution in DMSO. Magnetic susceptibility measurements of solid samples were made by Gouy method. IR spectra (KBr) were recorded on a

Perkin-Elmer 983/781 spectrometer, electronic spectra (in 10^{-2} M solution of complexes) on a Hilger and Watt Uvispeck spectrometer, ESR spectra on an EPR E-112 spectrometer at room temperature and XRD of complex $[\text{Ni}(\text{H}_2\text{O})_2]$ on a PW 1130/100 model X-ray diffractometer, M/s Phillips, Holland.

Based upon analytical and conductance data (Table-1) the complexes are of the type $[\text{ML}/\text{L}'(\text{H}_2\text{O})_2]$ where M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II); $\text{LH}_2 = 1,8\text{-dibenzoyl-2,7-di-}(o\text{-hydroxyphenyl})\text{-4-methyl-3,6-diazaoctane}$ and $\text{L}'\text{H}_2 = 1,9\text{-dibenzoyl-2,8-di-}(o\text{-hydroxyphenyl})\text{-3,7-diazanonane}$. All the complexes are found to be non-electrolytic in nature.

TABLE
ANALYTICAL AND IR SPECTRAL DATA (cm^{-1}) OF THE COMPLEXES

Compound	Colour	Analysis, Found/(Calcd.)				$\frac{\nu(\text{C}=\text{O})}{\nu(\text{N}=\text{H})}$	$\frac{\nu(\text{M}=\text{O})}{\nu(\text{M}=\text{N})}$
		M	C	H	N		
MnL(H ₂ O) ₂	Brown	8.80 (8.98)	64.4 (64.81)	5.70 (5.93)	4.40 (4.58)	1230/3150	415/525
CoL(H ₂ O) ₂	Green	9.40 (9.57)	64.0 (64.39)	5.70 (5.89)	4.40 (4.55)	1229/3124	417/525
NiL(H ₂ O) ₂	Violet	9.40 (9.54)	64.1 (64.41)	5.60 (5.90)	4.30 (4.55)	1235/3157	410/519
CuL(H ₂ O) ₂	Violet	10.0 (10.25)	63.6 (63.91)	5.60 (5.85)	4.40 (4.52)	1238/3125	418/524
CdL(H ₂ O) ₂	Yellow	16.6 (16.80)	59.0 (59.24)	5.30 (5.42)	4.00 (4.19)	1235/3150	415/515
HgL(H ₂ O) ₂	Yellow	26.2 (26.49)	52.0 (52.34)	4.60 (4.79)	3.60 (3.70)	1230/3155	418/525
MnL'(H ₂ O) ₂	Brown	8.70 (8.98)	64.5 (64.81)	5.80 (5.93)	4.50 (4.58)	1255/3150	415/520
CoL'(H ₂ O) ₂	Brown	9.40 (9.57)	63.9 (64.39)	5.70 (5.89)	4.30 (4.55)	1250/3124	410/517
NiL'(H ₂ O) ₂	Grey	9.30 (9.54)	64.1 (64.41)	5.70 (5.90)	4.40 (4.55)	1255/3125	417/518
CuL'(H ₂ O) ₂	Dark brown	9.90 (10.25)	63.6 (63.91)	5.60 (5.85)	4.30 (4.52)	1230/3130	415/520
ZnL'(H ₂ O) ₂	Yellow	10.3 (10.51)	63.4 (63.72)	5.60 (5.83)	4.40 (4.50)	1270/3120	419/517
CdL'(H ₂ O) ₂	Yellow	16.6 (16.80)	58.9 (59.24)	5.30 (5.42)	4.00 (4.19)	1235/3155	417/520
HgL'(H ₂ O) ₂	Yellow	26.3 (26.49)	52.0 (52.34)	4.60 (4.79)	3.60 (3.70)	1238/3150	415/520

In the IR spectra of the complexes the bands appearing at 1288–1229 cm^{-1} indicates bonding to metal ions through phenolic oxygen atoms.³ The sharp peaks are observed at *ca.* 3250 cm^{-1} and *ca.* 3120 cm^{-1} in the complexes assignable to $\nu(\text{NH})$ vibration supporting the bonding of secondary nitrogen atoms to metal ions. The band position of $\nu(\text{C}=\text{O})$ does not undergo any change indicating the non-coordination of the carbonyl oxygen atoms to metal ions. The band appearing at *ca.* 2960 cm^{-1} in the complexes can be ascribed to the presence of co-ordinated water molecules.⁴

The conclusive evidence of bonding of phenolic oxygen and secondary nitrogen atoms to the metal ions is ascertained by the appearance of $\nu(\text{M—O})$ and $\nu(\text{M—N})$ at $419\text{--}410\text{ cm}^{-1}$ and $527\text{--}517\text{ cm}^{-1}$ respectively.⁵

The Co(II) complexes exhibit four electronic spectral bands at *ca.* 8825 cm^{-1} , *ca.* 17780 cm^{-1} , *ca.* 20495 cm^{-1} and *ca.* 29350 cm^{-1} assignable to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, $\rightarrow {}^4\text{A}_{2g}(\text{F})$, $\rightarrow {}^4\text{T}_{1g}(\text{P})$ and CT transitions respectively, conforming to octahedral configuration.⁶ The proposed configuration is further supported by high μ_{eff} value (5.1 BM) for Co(II) complexes. The Ni(II) complexes show four bands at *ca.* 10130 cm^{-1} , *ca.* 17290 cm^{-1} , *ca.* 23540 cm^{-1} and *ca.* 30210 cm^{-1} attributable to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, $\rightarrow {}^3\text{T}_{1g}(\text{F})$, $\rightarrow {}^3\text{T}_{1g}(\text{P})$ and CT transitions indicating an octahedral structure. The Cu(II) complexes exhibit a broad band at $15460\text{--}13260\text{ cm}^{-1}$ assignable to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition in a distorted octahedral geometry.⁸

In the esr spectrum of $[\text{CuL}(\text{H}_2\text{O})_2]$ complex recorded at x-band at room temperature two 'g' values are obtained ($g_{\perp} = 2.1058$ and $g_{\parallel} = 2.4042$). The trend observed for the complex $g_{\parallel} > g_{\perp} > g_e$ (2.0023) indicates that the unpaired electron is localised in $d_{x^2-y^2}$ orbital and the spectral feature is characteristic to axial symmetry. The axial symmetry parameter "G" calculated for the complex from the relation $G = g_{\parallel} - 2/g_{\perp} - 2$ is found to be 3.82 which indicates the absence of exchange interaction and unit cell contains magnetically equivalent ions. In the esr spectrum of $[\text{CuL}'(\text{H}_2\text{O})_2]$ the g_{av} value calculated⁹ to be 2.1341 may be attributed to random orientation of axes.

The X-ray diffraction study (powder pattern) of $[\text{NiL}(\text{H}_2\text{O})_2]$ complex has been interpreted and the unit cell parameters like *a* (12.076), *b* (94.744), *c* (7.645), α (90.000), β (94.744), γ (90.000) and the volume of unit cell (883.12) have been calculated with the help of a computer. Based on these data, the complex is suggested to be monoclinic in nature.

The Cd(II), Zn(II) and Hg(II) complexes are suggested to be six-coordinated, probably having octahedral stereo-chemistry based upon the analytical, IR and conductance data.

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