

Magnetic and Spectral Studies of Divalent Metal Complexes of Isonitroso-5-Methyl-2-Hexanone and Its Derivative

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The metal complexes of isonitroso-5-methyl-2-hexanone (HIMH) and 5-methyl-2,3-hexanedione dioxime (H₂MHDDO) with Fe(II), Cu(II) and Hg(II) have been synthesized. Their structures have been investigated by using elemental analyses, electrical conductance, magnetic susceptibility measurements, ESR, UV-Visible, reflectance, IR and NMR spectral measurements. Thermal studies have also been carried out. Results are reported here.

Keywords metal complexes, spectral measurements, thermal analysis

INTRODUCTION

The literature survey shows that a number of transition metal complexes with various isonitroso ligands have been synthesized and their structures have been investigated by magnetic and spectral methods (Patel and Haldar, 1967; Pathak and Haldar, 1972; Talwar and Haldar, 1970; Thakkar and Haldar, 1980; Deshmukh and Thakkar, 1985; Dhadke and Haldar, 1978; Khatavkar and Haldar, 1974; Donde et al., 2002, 2003; Bose et al., 1973). Isonitroso compounds are potentially ambidentate ligands capable of forming metal complexes through oxygen or nitrogen donor atoms. Metal complexes of oxime-containing compounds have been widely used in coordination chemistry due to their versatility and antimicrobial activity (Patel and Haldar, 1967; Pathak and Haldar, 1972; Talwar and Haldar, 1970; Thakkar and Haldar, 1980; Deshmukh and Thakkar, 1985; Dhadke and Haldar, 1978; Khatavkar and Haldar, 1974; Donde et al., 2002; Bose et al., 1973). The therapeutic action of such compounds consists in binding of the metal contained in the organisms. Numerous investigations in the domain of coordination chem-

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istry have been conducted towards understanding the chemical composition, structure and properties of such compounds that serve as potential antimicrobial drugs (Mehta and Ghogale, 2000). Oxime-containing compounds form coloured and stable complexes with many metal ions, hence their analytical applications in the spectrophotometric determination of critical metals is of interest (Tandel et al., 2001; Jadhav et al., 2001).

We report here the synthesis and characterization of the ligands isonitroso-5-methyl-2-hexanone (HIMH), 5-methyl-2,3-hexanedione dioxime (H₂MHDDO) (Figure 1) and their corresponding divalent metal complexes involving the metal salts of Cu(II), Hg(II) and Fe(II). Elemental analyses, electrical conductance, magnetic susceptibility, ESR, NMR, IR, UV-visible, reflectance spectra, TGA-DTA analysis have been employed to assign the structures of these complexes.

EXPERIMENTAL

All reactions were carried out with A. R. (Analytical Reagent) grade chemicals. The C. P. (Chemically Pure) grade chemicals used were purified by standard methods. Melting points determined were uncorrected. Electrical conductance was recorded on an Equip-Electronic Conductivity Meter model No. EQ-660. Magnetic susceptibility was determined using Gouy's method at room temperature with Co[Hg(CN)₄] as a calibrant. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer using KBr pellets. The proton magnetic resonance spectra were recorded on a Bruker AMX-500 spectrometer in CDCl₃, and chemical shifts were reported in δ ppm values relative to the internal standard tetramethyl silane (TMS). UV-Visible and reflectance spectra were recorded on a Shimadzu UV 2100 spectrophotometer. The elemental microanalyses of C, H, and N were carried out with a Thomas and Coleman Analyser-Carlo Erba 1106. Thermal analyses were carried out on a SETARAM simultaneous TG-DTA recording unit (Model No-92-16). Thin layer chromatographic (TLC) analyses were performed to confirm the purity of the compounds on plates coated with silica gel G (Merck).

HIMH and H_2 MHDDO were synthesized by following the procedure reported in the literature (Patil et al., 2002, 2003).

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FIG. 1. Structures of ligands HIMH (I) and H₂MHDDO (II).

Synthesis of the Fe(II) Complexes

An ethanolic solution of ligand $(1.028 \text{ g HIMH}/1.1003 \text{ g H}_2\text{MHDDO}, 2 \text{ mmol}, 25 \text{ ml})$ was mixed with the aqueous solution of metal salt of FeSO₄·7H₂O (1 gm, 1 mmol, 25 ml) at room temperature. The pH of the solution was adjusted by 0.1 N NaOH up to 9.5 and 10 for the complexes of HIMH and H₂MHDDO, respectively. The preparation of the Fe(II) complex was carried out in the presence of an excess of sodium thiosulphate. The complexes were digested at 60°C on a water bath, filtered and washed with water followed by drying under vacuum.

Synthesis of the Cu(II) and Hg(II) Complexes

An aqueous solution of metal salt $CuSO_4 \cdot 5H_2O$ or $HgCl_2$ (1 g, 1 mmol, 25 ml) was mixed with warm ethanolic solution of the ligand (1.225–1.145 g of HIMH/1.127–1.053 g of H₂MHDDO, 2 mmol, 25 ml) at room temperature and the mixture was stirred vigorously. The pH of the solution was adjusted by using 0.1 N NaOH up to 6.0, 6.5 and 8.5 for the complexes of Cu(II) and Hg(II) with HIMH and H₂MHDDO respectively. The complexes obtained were filtered, washed with warm water followed by 50% ethanol and dried at 105°C.

RESULTS AND DISCUSSION

The analytical data (Table 1) indicate that the complexes of HIMH with Fe(II), Cu(II) and Hg(II) may be represented by the general formula $ML_2 \cdot nH_2O$

$$M + 2L + nH_2O \rightarrow ML_2 \cdot nH_2O$$

where M = Fe(II), Cu(II) for n = 1 and M = Hg(II) for n = 2; L = HIMH.

The metal complexes of H_2MHDDO were represented by the general formula ML_2 ;

$$M + 2L \rightarrow ML_2$$

where M = Fe(II), Cu(II) and Hg(II) and L = H₂MHDDO.

The metal complexes of HIMH are insoluble in water and dilute alkali solutions suggesting the absence of a free oxime group due to removal of oximino proton during complexation. The metal complexes of H_2MHDDO were insoluble in water but soluble in dilute alkali due to the presence of one free oxime group in the complexes after bonding. This was further supported by the infrared as well as ¹H NMR spectral data for these complexes, discussed later, the poor solubility

in common oxygenated organic solvents like alcohol, methanol and acetone. However, the metal complexes of HIMH and H₂MHDDO were somewhat more soluble in more polar solvents like dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The molar conductance had been measured using 10^{-2} M solution in DMF. The values indicate that they are non-ionic in nature (Geary, 1971; Naik et al., 1999).

Magnetic Behavior

The room temperature magnetic moments for $Fe(IMH)_2 \cdot H_2O$ and $Fe(HMHDDO)_2$ are 1.87 and 2.10 B.M., respectively. The magnetic susceptibility measurements of both the Fe(II) complexes were performed over the temperature range 10–300 K. A plot of $1/\chi_{M \text{ (corr.)}}$ against T gives a straight line (Figure 2) for [Fe(IMH)_2] \cdot H_2O indicating that it obeys the Curie-Weiss law (Figure 2) with the Weiss constant $\theta = -170$ K. While [Fe(HMHDDO)_2] does not give a straight line and does not obey the Curie-Weiss law.

Fe(II) has little tendency to form four-coordinate tetrahedral complexes (Cotton and Willkinson, 1980). The observed magnetic moments of both Fe(II) complexes are intermediate between the moments expected for octahedral spin-paired and spin-free configuration and is close to the spin-only value for one unpaired electron (Malve et al., 1990). Though possible oxidation of Fe(II) during the preparation of the complex can account for such intermediate moment values, considering this fact, the preparation of the complex has been carried out in the presence of sodium thiosulphate, and that the colour of the complex does not change for a long time. Alternatively, some kind of spin-pairing can occur as a result of exchange between the states S = 0 and S = 2, giving rise to such an intermediate magnetic moment. It is observed that Fe(II) complexes of isonitrosoketones shows such intermediate magnetic moments (Haldar, 1974; Singh and Singh, 1979)

The green Cu(II) complexes are paramagnetic at room temperature. There magnetic moments at 299 K are 0.92 and 1.69 B.M. for $[Cu(IMH)_2] \cdot H_2O$ and $[Cu(HMHDDO)_2]$, respectively. The magnetic moment found for $[Cu(IMH)_2] \cdot H_2O$ has much lower than the spin-only value for one unpaired electron. Such subnormal values of magnetic moment have been reported for Cu(II) acetate (Figgis and Martin, 1956; Srivastava, 1981) and Cu(II) complexes of some isonitrosoketones (Haldar, 1974; Singh and Singh, 1979). Hence indicative of anti-ferromagnetic

				Elemental analysis found (Calc.) %						70	Mol. cond. ^{<i>a</i>}	h
Compound	Colour	Empirical formula	Mol. wt.	рН	Decomp. temp. (°C)	С	Н	Ν	0	М	$(Ohm^{-1} cm^{-2})$ mole ⁻¹)	$\mu_{\rm eff}$ (B. M.)
HIMH	Yellow	C ₇ H ₁₃ NO ₂	143		>25 ^c	58.60	9.07	9.70	22.63			
						(58.20)	(9.01)	(9.20)	(22.59)			
$[Fe(IMH)_2] \cdot H_2O$	Blue	$Fe(C_7H_{12}NO_2)_2 \cdot H_2O$	197.84	9.5	250	48.92	6.44	7.52	22.06	15.00	0.052	1.87
						(48.94)	(6.45)	(7.53)	(22.07)	(15.01)		
$[Cu(IMH)_2] \cdot H_2O$	Green	$Cu(C_7H_{12}NO_2)_2 \cdot H_2O$	206.55	6.0	182	48.37	6.87	8.03	18.41	18.23	0.053	0.92
						(48.33)	(6.90)	(8.05)	(18.44)	(18.28)		
$[Hg(IMH)_2] \cdot 2H_2O$	Off-white	$Hg(C_7H_{12}NO_2)_2 \cdot 2H_2O$	343.59	8.5	300	34.62	4.98	5.75	13.22	41.35	0.050	0.0
						(34.66)	(4.95)	(5.78)	(13.20)	(41.39)		
H ₂ MHDDO	Colourless	$C_7H_{14}N_2O_2$	153	_	76^c	53.16	8.86	17.72	20.26	_		_
						(53.12)	(8.81)	(17.78)	(20.21)			
[Fe(HMHDDO) ₂]	Brown	$Fe(C_7H_{13}N_2O_2)_2$	202.79	10.0	250	38.75	5.95	12.90	29.51	12.85	0.060	2.10
						(38.76)	(5.99)	(12.92)	(29.48)	(12.88)		
[Cu(HMHDDO) ₂]	Green	$Cu(C_7H_{13}N_2O_2)_2$	216.55	6.5	182	44.50	6.86	14.80	16.99	16.85	0.001	1.69
						(44.49)	(6.88)	(14.83)	(16.97)	(16.83)		
[Hg(HMHDDO) ₂	Off-white	$Hg(C_7H_{13}N_2O_2)_2$	353.59	8.5	300	32.60	5.02	10.84	12.50	38.91	0.003	0.0
		-				(32.64)	(5.05)	(10.88)	(12.45)	(38.98)		

TABLE 1 Physicochemical and analytical data of HIMH, H₂MHDDO and their metal complexes

^{*a*}10⁻² M conc. in DMF. ^{*b*}300 K. ^{*c*}Melting point.

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FIG. 2. Magnetic susceptibility measurements of $[Fe(IMH)_2] \cdot H_2O$ at low temperature.

interactions or spin-spin interaction. The observed magnetic moment is intermediate between the moments expected for octahedral spin-paired and spin-free configuration, and is close to the spin-only value for one unpaired electron (Khatavkar, 1974) A special case of such antiferromagnetic interaction is observed in the binuclear structures maintained by copper(II) salts and typified by the copper(II) acetate structures. The magnetic interaction in this case may be viewed as occurring through overlap of copper-copper orbitals, or through ligand participation. The lack of structural data for many of these low-moment copper(II) complexes precludes a ready distinction between exchange that arises from a direct copper-copper bond or ligand participation. The Hg(II) complexes are diamagnetic as expected.

Electronic Spectra

Various electronic absorption bands exhibited by HIMH, H_2MHDDO and their metal complexes in solution and/or reflectance spectra and their tentative assignments are summarized in Table 2. The shifting of the ligand bands in the spectra of the metal complexes indicates that the energy states of the electron system of the anions IMH⁻ and HMHDDO⁻ undergo considerable alterations on complex formation. The spectral features indicate distorted octahedral geometry for the Fe(II), Cu(II) and Hg(II) complexes. The electronic spectra of the Fe(II) complexes shows a weak band at 10,869–11,363 cm⁻¹ due to the ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$ transition and is characteristic of octahedral symmetry (Haldar, 1974; Lever, 1968). A second transition has been seen at 12,048 and 13,333 cm⁻¹. A broad band in the region 11,363–

	Solution	0.111		
Compound	ν (λ) cm ⁻¹ (nm)	\in L/cm/mol	cm^{-1} (nm)	Туре
$[Fe(IMH)_2] \cdot H_2O$	10,869 (920)	555	10,920 (915)	d-d
	12,048 (830)	805	12,830 (779)	d-d
	24,691 (405)	985		C.T.
$[Cu(IMH)_2] \cdot H_2O$	11,363-14,820	531	14,925 (670)	d-d
	(880-675)			
	2,727 (440)	777	_	C.T.
	25,316 (395)	878	—	C.T.
$[Hg(IMH)_2]\cdot 2H_2O$	26,315 (380)	886	28,169 (355)	C.T.
[Fe(HMHDDO) ₂]	11,363 (880)	444	11,422 (876)	d-d
	13,333 (750)	536	12,292 (814)	d-d
	22,727 (440)	472	_	C.T.
	27,397 (365)	749	—	C.T.
[Cu(HMHDDO) ₂]	11,627-14,492	547	14,184 (75)	d-d
	(860-690)			
	16,949 (590)	283	16,129 (620)	d-d
	25,974 (385)	896	—	C.T.
[Hg(HMHDDO) ₂]	27,777 (360)	836	26,109 (383)	C.T.

 TABLE 2

 Visible spectral data of HIMH, H₂MHDDO and their metal complexes

Solvent used: DMF; C.T.: Charge transfer.

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 $14,492 \text{ cm}^{-1}$ and another bands in the region 22,727- $25,974 \text{ cm}^{-1}$ are observed in the spectrum of the Cu(II) complexes. The former band may be assigned to the ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transitions, suggesting a distorted octahedral geometry for this complex (Haldar, 1974; Proctor et al., 1968; Sharma et al., 1992; Khan et al., 1997). The latter two bands can be attributed to a L-M charge transfer band. The band at 16.949 cm^{-1} observed in the [Cu(HMHDDO)₂] complex is due to the green coloration of the complex. Only one absorption band is expected for octahedral Cu(II) complexes (Tandel et al., 2001; Jadhav et al., 2001). Since the ${}^{2}E_{g}$ state is highly susceptible to Jahn-Teller distortion, the Cu(II) complexes posses a distorted octahedral geometry. In the case of Hg(II) complexes it is difficult to arrive at any definite conclusion regarding the geometry. The analytical and spectral data indicate that it is presumably of octahedral geometry (Bootwala and Thakkar, 1995).

IR Spectra

The infrared spectra of HIMH and its complexes are quite complex; however, important bands have been assigned on the basis of their correlation with other isonitrosoketone complexes (Deshmukh and Thakkar, 1985; Haldar, 1974; Limin, 1997). An important feature of the IR spectrum of HIMH complexes is the absence of an O-H stretching vibration band of the = NOH group of HIMH. This observation leads to the conclusion that the complex formation takes place by deprotonation of the oxime. The broad band observed in the range $3420-3390 \text{ cm}^{-1}$ is due to the -OH vibration of water molecule (Limin, 1997) (Table 3). The IR spectrum of H_2MHDDO shows a broad band centered at 3322 cm^{-1} , due to the -OH stretching vibration of the oxime group (Geary, 1971; Naik et al., 1999). This -OH band is observed in the range $3240-3360 \text{ cm}^{-1}$ in the H₂MHDDO complexes, which indicates that, one oxime group is not involved in the bonding. A band found in free ligands, HIMH and H₂MHDDO at 962 and 910 cm^{-1} , respectively, has been

assigned to $\nu(N-O)$ of the oxime group. This band is not observed in the complexes of HIMH due to bonding, but in case of the H₂MHDDO metal complexes this band is observed between 918–960 cm⁻¹. This observation leads to the conclusion that the complex formation takes place by deprotonation of one of the oxime groups of H₂MHDDO indicating coordination occurring through the nitrogen donor atom of the oxime group. This conclusion is further supported by the observation that a new band, attributed $\nu(N \rightarrow O)$, is observed in the range $1160-1190 \,\mathrm{cm}^{-1}$ in the spectrum of the complexes of H₂MHDDO. This is further supported by the observation that the stretching frequency $\nu(C=N)$ is observed at 1461 and $1450 \,\mathrm{cm}^{-1}$ in the spectrum of HIMH and H₂MHDDO that is found to be shifted to the range 1330- 1440 cm^{-1} in the spectra of the complexes, indicating coordination through the nitrogen donor atom of the oxime group. The shift of C=O towards lower wave number from its position at $1688 \,\mathrm{cm}^{-1}$ in HIMH to the range 1585- 1640 cm^{-1} in the complexes suggest the involvement of the carbonyl group of the ligand in bonding to the metal ion. In FTIR spectra of the metal complexes of HIMH, the medium to weak intensity bands observed around 720-864 and 520- $659 \,\mathrm{cm}^{-1}$ are assigned to M–N and M–O stretching modes, respectively. These assignments are based on the fact that oxygen is more electronegative than nitrogen, the M-O bond tends to be more ionic than the M-N bond and, therefore, M–O vibrations were expected to appear at lower frequencies than the M-N vibration (Malve 1990). The infrared spectra of the metal complexes indicate coordination through the carbonyl oxygen and oximino nitrogen atoms in HIMH as shown in Figure 3. Where O^{*} represents the oxygen atom of neighbouring ligand molecule due to quenching or having a polymeric structure (Thakkar and Thakkar, 2000). From the thermal analysis data it had been observed that the loss of water molecules appears at the temperature range 60-110°C due to dehydration, therefore, the presence of water molecules in the present complexes is due to water of crystallisation, therefore, the structure of the complexes is as shown in the

Compound	$\nu(-OH)^a$	$\nu (=NOH)$	ν(C==0)	ν(C==N)	v(N-O)	$\nu(N \to O)$	$\nu(M-N)$	ν(M–O)
HIMH		3312 b	1688 s	1461s	962 s			_
$[Fe(IMH)_2] \cdot H_2O$	3420 b	_	1640 s	1358 s	_	1120 s	864 sh	520 w
$[Cu(IMH)_2] \cdot H_2O$	3440 b	_	1625 s	1330 s	_	1120 s	720 w	620 w
$[Hg(IMH)_2] \cdot 2H_2O$	3390 b	_	1585 s	1390 s	_	1130 s	765 w	659 w
H ₂ MHDDO		3322 b	_	1450 s	910 s	_		
[Fe(HMHDDO) ₂]		3270 b	_	1440 s	960 s	1190 s	760 w	
[Cu(HMHDDO) ₂]		3340 b	_	1430 s	955 s	1175 s	480 w	
[Hg(HMHDDO) ₂]		3340 b		1430 s	918 s	1160 s	520 w	

TABLE 3 Some important FTIR bands for HIMH and H_2MHDDO and their metal complexes in cm⁻¹

s-sharp; sh-short; w-weak; m-medium; a-water molecule.



FIG. 3. O^* = the oxygen atom of neighbouring molecule; n = 1 when M = Cu(II) and Fe(II) and n = 2 when M = Hg(II).

Figure 3. While in the case of the metal complexes of H_2MHDDO only M–N vibrations observed in the range $520-760 \text{ cm}^{-1}$. This indicates that the bonding takes place through the oximino nitrogen donor atoms. On the basis of the results of elemental analyses, electrical conductance and spectral studies, the bonding in the metal complexes may, therefore, be represented as shown in Figure 4.

¹H NMR Spectra

Table 4 shows ¹H NMR spectral data of the ligands and their metal complexes. An important feature of the ¹H NMR spectra of HIMH and its complexes is the absence of the signal due to the =NOH proton. This indicates that the complexation results by the replacement of the proton of the oxime group by the metal atom. A signal due to water molecules present in the



FIG. 4. O^* = the oxygen atom of neighbouring molecule; M = Fe(II), Cu(II) and Hg(II).

complexes appears in the range 7.069-7.75 ppm and sharp signals due to $2CH_3$, CH_3 , CH shows a downfield shift relative to the free ligand. This indicates coordination through the oximino nitrogen. $[Cu(IMH)_2] \cdot H_2O$ complex was paramagnetic in nature, so it does not show the multiplets properly. The ¹H NMR spectra of the complexes show broad signals due to their paramagnetic nature. However, an important and easily discernible feature of the spectrum of the complexes is the presence of the proton signal due to the ==NOH group of H₂MHDDO, observed at 10.54 ppm in the spectrum of H₂MHDDO.

Thermal Analysis

The thermal analysis of the complexes shows that they are thermally stable to a varying degree in the range $280-530^{\circ}$ C. The complexes of HIMH show a gradual but significant loss in weight in the temperature range $60-170^{\circ}$ C. This observation suggests the presence of water of crystallisation. The complexes of H₂MHDDO do not show such significant loss indicating absence of any lattice water or water of crystallisation. With further increase in temperature in the range investigated, most of the complexes show decomposition by fragmentation and thermal degradation of the organic part of the metal complexes, finally resulting in the corresponding metal oxides FeO and CuO in Fe(II) and Cu(II) cases, respectively (Table 5).

The thermogram of $[Hg(IMH)_2] \cdot 2H_2O$ shows decomposition of water of crystallisation at 60–170°C and in the temperature range 170–360°C simultaneous decomposition of reagent as well as metal atom to metal oxide. While Hg(II) complex of H₂MHDDO shows a single-step simultaneous decomposition. The decomposition starts at 140°C and ends at 300 °C, accompanied by a complete mass loss (Table 6).

ESR Spectra

The ESR spectra of a microcrystalline samples of [Cu(IMH)₂] · H₂O and [Cu(HMHDDO)₂] at room temperature did not show any hyperfine splitting, possibly due to the strong dipolar and exchange interactions between copper(II) ions in the unit cell. The single broad signal that was observed gave g_{π} and g_{\perp} values of Cu(II), indicating esentially a d_{x2-y2} ground state. A value of approximately 3.8 for the ratio $G = (g_{\pi} - 2)/(g_{\perp} - 2)$, (i.e., G < 4) indicates considerable exchange interaction in the solid complexes (Proctor et al., 1968). It has been reported that (Kivelson and Neiman, 1961) g_{π} is a sensitive function of covalency; for an ionic environment, g is greater than 2.3 and for a covalent environment g is less than 2.3. In the present complexes, g < 2.3 indicates their covalent nature. The ESR spectra of present Cu(II) complexes are not well resolved to allow the calculations of hyperfine splitting constants A_{π} and A_{\perp} . However, a good estimate of A_{π} and A_{\perp} values can be obtained (Ramchandraiah et al.,

		, 2		1 11		
Compound	$2 \times CH_3$	m-CH	s-CH ₃	d-CH ₂	H ₂ O	NOH
HIMH	0.869–0.870 d (0.5 Hz)	1.948-2.016 m	2.320 s	2.450–2.473 d (11.5 Hz)	—	10.490
$[Fe(IMH)_2] \cdot H_2O$	0.882–0.901 d (9.5 Hz)	1.672–1.820 m	1.960 s	2.341–2.365 d (12 Hz)	7.505	—
$[Cu(IMH)_2] \cdot H_2O$	0.880–0.898 d (9 Hz)	1.800-1.910 m	1.930 s	2.340–2.358 d (9 Hz)	7.650	—
$[Hg(IMH)_2] \cdot 2H_2O$	0.881–0.894 d (6.5 Hz)	2.190-2.250 m	2.352 s	2.450–2.476 d (13 Hz)	7.095	—
H ₂ MHDDO	0.856–0.879 d (11.5 Hz)	1.990-2.060 m	1.972 s	2.520-2.530 d (5 Hz)	_	10.540
[Fe(HMHDDO) ₂]	0.868–0.876 d (4 Hz)	1.826–1.933 m	1.820 s	2.199–2.216 d (8.5 Hz)	—	11.267
[Cu(HMHDDO) ₂]	1.256–1.278 d (11 Hz)	1.820-2.050 m	2.068 s	2.232–2.259 d (13.5 Hz)	—	10.590
[Hg(HMHDDO) ₂]	0.878–0.902 d (12 Hz)	1.790–1.973 m	2.074 s	2.543–2.558 d (7.5 Hz)	—	10.560

TABLE 4 ¹H NMR data of HIMH, H₂MHDDO and their metal complexes in δ ppm

s-singlet, d-doublet, m-multiplet.

1989), by taking one-third of the line widths at half maximum and A_{av} as $1/3 (A_{\pi} + 2A_{\perp})$. The in-plane covalency parameter, α^2 was calculated (Dutta and Syamal, 1993). This quantity is a function, which depends upon the nature of the Cu-ligand

bond. For Cu(II) complexes $\alpha^2 = 0.5$ indicating complete covalent bonding, but $\alpha^2 = 1.0$ suggests complete ionic bonding. The smaller the value of α^2 , the more covalent is the bonding. The values of the Cu(II) complexes fall in the

	Temp. ir	n °C	Wt. lo	oss in %		Metal oxide residue $(MO)^a$		
Complex	Commencement of decomp.	Completion of decomp.	Observed	Calculated	Group/moiety lossed	Observed	Calculated	
$[Fe(IMH)_2] \cdot H_2O$	70	110	4.89	5.02	-H ₂ O	20.97	20.05	
	110	240	39.21	39.64	$-C_7H_{12}NO_2$			
	240	450	34.93	35.17	$-C_7H_{12}NO$			
$[Cu(IMH)_2] \cdot H_2O$	70	90	5.33	4.92	-H ₂ O	22.88	21.74	
	90	190	38.09	38.81	$-C_7H_{12}NO_2$			
	190	450	34.92	34.48	$-C_7H_{12}NO$			
$[Hg(IMH)_2] \cdot 2H_2O$	60	170	6.20	6.91	-2H ₂ O	_	_	
	170	380	91.62	93.08	$-C_{14}H_{24}N_2O_3Hg$	19.19	19.42	
[Fe(HMHDDO) ₂]	170	260	42.88	42.45	$-C_7H_{13}N_2O_2$	19.19	19.42	
	260	530	37.93	38.12	$-C_7H_{13}N_2O$			
[Cu(HMHDDO) ₂]	190	280	79.25	78.93	$-C_{14}H_{26}N_4O_3$	20.75	21.07	
[Hg(HMHDDO) ₂]	140	300	97.02	100	$-C_{14}H_{26}N_4O_4Hg$	—	—	

TABLE 5Thermoanalytical data of the complexes

^aMetal oxide residue is in the form of FeO and CuO.

Electron spin resonance data of copper complexes at liquid nitrogen temperature

Complex	g_{π}	g⊥	g _{av}	G	$A_{\pi}^{\ a}$	${\rm A_{\perp}}^a$	$A_{av}{}^a$	α^2
$[Cu(IMH)_2] \cdot H_2O$	2.069	2.033	2.060	2.091	60	35	53.34	0.286
[Cu(HMHDDO) ₂]	2.134	2.034	2.060	4.15	20	15	18.3	0.35

 $^{a} \times 10^{4}$.

range 0.2-0.3, which are less than unity, suggesting the covalent nature of metal-ligand bonding in the complexes.

CONCLUSION

Based on spectroscopic investigations and their correlations with the available data of known compounds, the proposed structures of metal complexes have been illustrated in Figures 3 and 4.

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