Transition metal complexes of oximes derived from natural aldehydes : Synthesis, spectroscopic characterization and antimicrobial activities

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Abstract : A series of complexes of Co^{II}, Zn^{II}, Cd^{II} and Hg^{II} have been synthesized by the reactions of the metal chlorides with the sodium salt of oximes of citral (L_1H) and citronellal (L_2H) in 1 : 2 stoichiometry in anhydrous dichloromethane. The oximes have been derived by the condensation reaction of hydroxylamine hydrochloride and citral or citronellal in 1 : 1 molar ratio in ethanol. The plausible structure of these newly synthesized complexes has been proposed on the basis of elemental analysis, molar conductance and various spectral (IR, UV-Vis, ^1H and $^{13}C\{^1H\}$ NMR) studies and four coordinated geometries have been assigned to these complexes. FAB mass spectra of 1 and 3 revealed the monomeric nature of these complexes. The powder XRD studies confirm the crystalline nature of the complexes. Studies were conducted to assess the growth inhibiting potential of the complexes and oximes against three bacterial strains, *S. aureus*, *B. subtilis* Gram +ve and *E. coli* Gram –ve bacteria and two fungal strains, *F. moniliformae* and *M. phaseolina*. All complexes and oximes possess strong inhibitory action against microorganism. The results of antibacterial activity show that the Gram +ve bacteria *S. aureus* and *B. subtilis* are more susceptible than the Gram –ve bacteria *E. coli*. The antimicrobial activities of the complexes are found to be more than those of free oximes.

Keywords : Condensation reaction, growth inhibiting potential, bacterial strains, microorganism, antimicrobial activities.

Introduction

Oximes are versatile chelating ligands, the metal complexes of which have been widely studied[1,2]. Owing to the diverse application of oximes in chemistry and technology, the interest in oximes containing transition metal compounds is continuously increasing in connection with the biological implication of oximes (especially as intermediate in the biological synthesis of NO)[3] and the marked and versatile bioactivities exhibited by different oximes and their metal complexes[4]. Among the numerous organic reagents capable of coordinating to the metal ions, special attention is given to the natural compounds. The interest in the study of the reactivity of some substances originating from plants such as terpenoids (citral, citronellal) and their derivatives might be explained by the numerous applications of these natural compounds and their derivatives (in medicine, perfumery and cosmetics industry, and food and flavoring industry)[5-8]. Studies of metal complexation with terpenoids and their derivatives[9] are of interest for a number of reasons, first the metal compounds with these reagents can exhibit biological activity[10,11], second the data available[12] confirm that plants liberates some metals (Ni, Cu, Cd, Mo) in the form of volatile complexes with terpenes to the atmosphere and third by reacting the metal ions with optically active terpenoids, one can obtain complexes in optically active forms[13,14]. Attempts to synthesize coordination compounds of transition metals based on terpenoid oxime were made.

In continuation of our previous work on the synthesis, spectroscopic characterization and biological activity of some binary complexes[15] and mixed ligand transition metal complexes[16] with semicarbazone and thiosemicarbazone derivatives of citral and citronellal, it seemed desirable to investigate the coordination ability of the citral oxime and citronellal oxime, for comparison purpose. The structures of oximes used for the present study are shown in Fig. 1.

Experimental

Materials and methods :

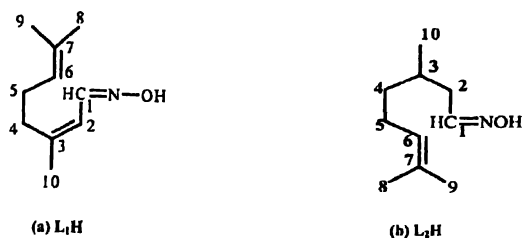All the chemicals used were of AR grade. Solvents were dried by conventional methods and distilled prior to

Fig. 1. Ligand structure : (a) citral oxime (L_1H) and (b) citronellal oxime (L_2H).

use. Elemental analyses were carried out on Elemental Varia EL III Carlo Erba 1108 analyzer. The IR spectra were recorded with KBr pellets in the 4000–400 cm^{-1} range on SHIMADZU FT-IR 8400 spectrometer. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in DMSO-d_6 solution using TMS as internal standard on JEOL FX 300 FT-NMR spectrometer at 300.4 and 75.45 MHz frequencies for ^1H and $^{13}C\{^1H\}$ NMR, respectively. FAB mass spectra of some of the complexes were recorded on a Jeol SX 102/Da-600 mass spectrometer using m-nitrobenzyl alcohol matrix and electronic spectra were recorded on a Varian Cary 50 Bio UV/Visible spectro-meter. Powder X-ray diffraction analysis was carried out on a diffractometer (Zydus Research Center, Ahmedabad) operating with Cu-Kα radiation. Magnetic moments were measured by Gouy method. Molar conductivities of 10^{-4} M DMF solutions were measured on a microprocessor based conductivity meter model 1601/E.

Synthesis of ligands :

Citral oxime (cis-3,7-dimethyl-2,6-octadienoxime) :

Citral (3,7-dimethyl-2,6-octadienal) (3.44 ml, 20 mmol), hydroxylamine hydrochloride (1.39 g, 20 mmol) and sodium acetate (2.72 g, 20 mmol) were added to absolute alcohol (75 ml). The reaction mixture was stirred for ~ 15 h at 40 °C and then precipitated NaCl was filtered off. Excess of solvent in the filtrate was removed by evaporation on water bath to get brown coloured oil, which was dried over P_2O_5. Yield : 87% (2.91 g); IR (cm^{-1}) : 3365 (O–H), 1627 (C=N), 1607 (C=C); ^1H NMR (DMSO-d_6, δ ppm) : 1.60 and 1.68 (6H, 2s, $(CH_3)_2C=CH$), 1.83 (3H, s, CH_3 in C-3), 1.86–1.91 (2H, m, CH_2 in C-5), 2.10–2.27 (2H, m, CH_2 in C-4), 5.08 (1H, t, CH-C(CH_3)$_2$), 5.92 (1H, d, CH=C in C-2), 7.37 (1H, d, CH=N), 8.65 (1H, br s, C=NOH); ^{13}C

NMR (δ ppm) : 17.7 (C-9), 24.7 (C-5), 26.0 (C-10), 26.7 (C-8), 40.3 (C-4), 120.4 (C-2), 123.0 (C-6), 133.1 (C-7), 147.7 (C-3), 153.9 (C-1) (Found : C, 71.74; H, 10.31; N, 8.32. Calcd. for $C_{10}H_{17}NO$ (167.25) : C, 71.82; H, 10.25; N, 8.37%).

Citronellal oxime (3,7-dimethyl-6-octeneoxime) :

Citronellal (3,7-dimethyl-6-octenal) (4.5 ml, 25 mmol), hydroxylamine hydrochloride (1.74 g, 25 mmol) and sodium hydroxide (1 g, 25 mmol) were added to a mixture of ethanol (75 ml) and water (25 ml) and the reaction mixture was stirred at 60 °C for 20 h, subsequently ethanol was evaporated, the water-layer was acidified with 2 M HCl and extracted with diethyl ether (2 × 100 ml) and evaporation of the solvent yielded a colourless oil. Yield : 92% (3.89 g); IR (cm^{-1}) : 3387 (O–H), 1603 (C=N and C=C); ^1H NMR (DMSO-d_6, δ ppm) : 0.96 (3H, dd, CHCH_3), 1.14–1.26 and 1.29–1.33 (2H, 2m, CH_2 in C-4, H_α + H_β), 1.36–1.42 (1H, m, CHCH_3), 1.59 and 1.67 (6H, 2s, $(CH_3)_2C=CH$), 1.73–1.78 (1H, m, CH_2 in C-2, H_β), 2.0–2.09 (2H, m, CH_2 in C-5), 2.16–2.40 (1H, m, CH_2 in C-2, H_α), 5.10 (1H, t, CH=C(CH_3)$_2$), 6.76 and 7.44 (1H, 2t, CH=N *trans* and *cis*), 9.60 (1H, br s, C=NOH); ^{13}C NMR (δ ppm) : 17.6 (C-9), 19.7 (C-10), 25.4 (C-5), 25.7 (C-8), 30.9 (C-3), 32.0 (C-2), 36.8 (C-4), 124.4 (C-6), 131.4 (C-7), 151.6 (C-1) (Found : C, 70.72; H, 11.23; N, 8.35. Calcd. for $C_{10}H_{19}NO$ (169.26) : C, 70.96; H, 11.31; N, 8.28%).

Synthesis of metal(II) complexes :

Synthesis of $[Co(L_1)_2]$ (1) :

To a methanolic solution of sodium salt of citral oxime [prepared from sodium metal (0.23 g, 10 mmol) dissolved in methanol (~ 20 ml) and citral oxime (1.67 g, 10 mmol)], a solution (~ 30 ml) of CoCl$_2$.6H$_2$O (1.19 g, 5 mmol) in dichloromethane was added with constant stirring. The reaction mixture was refluxed for 4 h. The solvent was evaporated under vacuum and the residue was extracted with dichloromethane (2 × 20 ml) and filtered through G-3 filtration unit. The excess solvent was stripped off *in vacuo* to give solid complex.

The same method was used for the preparation of the other complexes (2-8).

[Zn(L₁)₂] (3) :

^1H NMR (DMSO-d_6, δ ppm) : 1.58 and 1.65 (6H, 2s,

$(CH_3)_2C=CH)$, 1.79 (3H, s, CH_3 in C-3), 1.81–1.91 and 2.01–2.37 (4H, 2m, CH_2 in C-4 and C-5), 5.02 (1H, m, $CH=C(CH_3)_2$), 5.95 (1H, d, $CH=C$ in C-2), 7.26 (1H, d, $CH=N$); ^{13}C NMR (δ ppm) : 17.3 (C-9), 24.2 (C-5), 25.9 (C-10), 26.8 (C-8), 39.8 (C-4), 120.2 (C-2), 121.2 (C-6), 131.4 (C-7), 147.7 (C-3), 150.7 (C-1).

[Zn(L₂)₂] (4) :

^1H NMR (DMSO-d_6, δ ppm) : 0.93 (3H, m, $CHCH_3$), 1.10–1.27 and 1.28–1.30 (2H, 2m, CH_2 in C-4), 1.32–1.45 (1H, m, $CHCH_3$), 1.58 and 1.65 (6H, 2s, $(CH_3)_2C=CH$), 1.76–2.56 (4H, 2m, CH_2 in C-2 and C-5), 5.06 (1H, t, $CH=C(CH_3)_2$), 6.61 and 7.31 (1H, 2t, $CH=N$ *trans* and *cis*); ^{13}C NMR (δ ppm) : 17.5 (C-9), 19.6 (C-10), 25.3 (C-5), 25.6 (C-8), 30.6 (C-3), 31.7 (C-2), 36.6 (C-4), 123.5 (C-6), 130.5 (C-7), 148.8 (C-1).

[Cd(L₁)₂] (5) :

^1H NMR (DMSO-d_6, δ ppm) : 1.60 and 1.68 (6H, 2s, $(CH_3)_2C=CH$), 1.78 (3H, s, CH_3 in C-3), 1.83–1.93 and 1.99–2.63 (4H, 2m, CH_2 in C-4 and C-5), 5.09 (1H, m, $CH=C(CH_3)_2$), 5.89 (1H, d, $CH=C$ in C-2), 7.23 (1H, d, $CH=N$); ^{13}C NMR (δ ppm) : 17.6 (C-9), 24.5 (C-5), 25.7 (C-10), 26.8 (C-8), 40.1 (C-4), 120.9 (C-6), 131.0 (C-7), 147.9 (C-3), 150.5 (C-1).

[Cd(L₂)₂] (6) :

^1H NMR (DMSO-d_6, δ ppm) : 0.93 (3H, m, $CHCH_3$), 1.12 and 1.28 (2H, 2m, CH_2 in C-4), 1.30–1.40 (1H, m, $CHCH_3$), 1.58 and 1.66 (6H, 2s, $(CH_3)_2C=CH$), 1.85–2.04 (2H, m, CH_2 in C-2), 2.11–2.26 (2H, m, CH_2 in C-5), 5.07 (1H, t, $CH=C(CH_3)_2$), 6.63 and 7.33 (1H, 2t, $CH=N$ *trans* and *cis*); ^{13}C NMR (δ ppm) : 16.4 (C-9), 18.5 (C-10), 24.1 (C-5), 24.5 (C-8), 29.6 (C-3), 31.6 (C-3), 35.5 (C-4), 122.9 (C-6), 129.7 (C-7), 148.5 (C-1).

[Hg(L₁)₂] (7) :

^1H NMR (DMSO-d_6, δ ppm) : 1.59 and 1.66 (6H, 2s, $(CH_3)_2C=CH$), 1.81 (3H, s, CH_3 in C-3), 1.83–1.89 and 2.01–2.27 (4H, 2m, CH_2 in C-4 and C-5), 5.03 (1H, t, $CH=C(CH_3)_2$), 5.89 (1H, d, $CH=C$ in C-2),7.29 (1H, d, $CH=N$); ^{13}C NMR (δ ppm) : 17.6 (C-9), 24.4 (C-5), 25.6 (C-10), 26.7 (C-8), 39.7 (C-4), 120.5 (C-2), 121.3 (C-6), 131.6 (C-7), 147.7 (C-3), 151.1 (C-1).

[Hg(L₂)₂] (8) :

^1H NMR (DMSO-d_6, δ ppm) : 0.94 (3H, m, $CHCH_3$), 1.10 and 1.27 (2H, 2m, CH_2 in C-4), 1.29–1.42 (1H, m, $CHCH_3$), 1.59 and 1.68 (6H, 2s, $(CH_3)_2C=CH$), 1.78–1.98 (2H, m, CH_2 in C-2), 2.04–2.26 (2H, m, CH_2 in C-5), 5.09 (1H, t, $CH=C(CH_3)_2$), 6.59 and 7.30 (1H, 2t, $CH=N$ *trans* and *cis*); ^{13}C NMR (δ ppm) : 17.2 (C-9), 19.2 (C-10), 25.4 (C-5), 25.8 (C-8), 30.8 (C-3), 32.2 (C-2), 35.9 (C-4), 122.7 (C-6), 129.4 (C-7), 148.1 (C-1).

Antimicrobial screening :

(a) Evaluation of antibacterial activity by inhibition zone technique :

The ligands and the complexes were evaluated against three bacterial strains *Staphylococcus aureus*, *Bacillus subtilis*, Gram (+ve) and *Escherichia coli* Gram (-ve), using the paper disc method[17]. For this purpose pure culture of bacteria were dissolved in distilled water and then uniformly seeded on the nutrient agar plate (composition : peptone 0.5%, beaf extract 3%, NaCl 5%, agar-agar 15% and distilled water 1000 ml). The paper discs of Whatman's paper No. 1 of 5 mm diameter were prepared for the purpose of making bacteriostatic slices. *ca.* 2 mg of test compound was dissolved in 10 cm³ DMSO (1%) to make a concentration of 0.2 mg/cm³. The paper discs were soaked in the test solution and then such 5 paper discs were placed on Petri-dish at almost equal distance on the surface of medium preseeded with bacterial strain. One sample was inoculated in parallel on three medium plates. These Petri-dishes were incubated at 35 ± 1 °C. After three days (72 h), the zone of inhibition thus formed around each disc containing the test compound was measured accurately in mm (Table 5).

(b) Evaluation of antifungal activity by food poison technique :

The ligands and complexes were screened for their antifungal activity against two fungal strains, *Fusarium moniliformae* and *Macrophomina phaseolina* using radial growth method[18–20]. In this method the medium used was potato dextrose agar medium (composition : dextrose 15 g, agar-agar 20 g and distilled water 1000 ml). The solution of test compound was prepared by dissolving 1 mg in 1 ml of DMSO and added to known amount of medium so as to get desired concentrations (100 and 400 ppm). The flasks were shaken several times to ensure proper and uniform distribution of the test compound. The warm medium was poured in sterilized Petri-dishes and allowed to solidify. The spores of fungi were placed on the medium with the help of a sterilized inoculum needle and the Petri-dishes were placed in an incubator at 25 ± 1 °C. Medium with DMSO only incubated with pathogen served as control and three replicates were used in each case. The linear growth of the fungus was obtained by measuring the fungal colony after 72 h and percent inhi-

Table 1. Analytical data for metal complexes

Sl. no.	Compd. Empirical formula	Yield (%)	M.p. (°C)	Colour and physical state	Analysis % : Found (Calcd.)			Molar cond.^{a} (Ω^{-1} cm^2 mol^{-1})
					C	H	N	
1.	[Co(L$_1$)$_2$] [Co(C$_{10}$H$_{16}$NO)$_2$]	89	285^d	Brown Solid	61.29 (61.37)	8.20 (8.24)	7.22 (7.16)	1.35
2.	[Co(L$_2$)$_2$] [Co(C$_{10}$H$_{18}$NO)$_2$]	83	255	Brown Solid	60.62 (60.75)	9.33 (9.18)	7.13 (7.08)	1.76
3.	[Zn(L$_1$)$_2$] [Zn(C$_{10}$H$_{16}$NO)$_2$]	87	277	Yellow Solid	60.22 (60.38)	8.02 (8.11)	7.12 (7.04)	1.79
4.	[Zn(L$_2$)$_2$] [Zn(C$_{10}$H$_{18}$NO)$_2$]	84	285^d	Brownish yellow Sticky solid	59.62 (59.77)	8.97 (9.03)	7.09 (6.97)	1.54
5.	[Cd(L$_1$)$_2$] [Cd(C$_{10}$H$_{16}$NO)$_2$]	79	280	Brownish yellow Solid	53.81 (53.99)	7.32 (7.25)	6.23 (6.30)	1.56
6.	[Cd(L$_2$)$_2$] [Cd(C$_{10}$H$_{18}$NO)$_2$]	85	298^d	Yellow Sticky solid	53.42 (53.51)	7.92 (8.08)	6.36 (6.24)	1.98
7.	[Hg(L$_1$)$_2$] [Hg(C$_{10}$H$_{16}$NO)$_2$]	86	292^d	Grey solid	44.98 (45.06)	6.12 (6.05)	5.18 (5.25)	1.72
8.	[Hg(L$_2$)$_2$] [Hg(C$_{10}$H$_{18}$NO)$_2$]	81	287	Grey Sticky solid	44.60 (44.73)	6.81 (6.76)	5.17 (5.21)	1.45

^{d}Decompose. ^{a}Molar conductance determined at 278 K in 10^{-4} DMF solution.

bition (Table 5) was calculated according to Vincent's formula (1927)[21].

$$\% \text{ Inhibition} = \frac{(C - T) \times 100}{C}$$

where C = diameter of fungal colony in control plate and T = diameter of fungal colony in test plate.

Results and discussion

The reactions of metal(II) chloride with sodium salt of corresponding oxime in 1 : 2 stoichiometry in refluxing anhydrous dichloromethane afforded the complexes of type [M(L)$_2$] as shown below :

$$MCl_2 + 2NaL \xrightarrow[\text{Reflux}]{\text{CH}_2\text{Cl}_2} [M(L)_2] + 2NaCl \downarrow$$
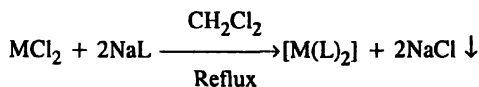
(M = Co^{II}, Zn^{II}, Cd^{II} and Hg^{II}; NaL = sodium salt of L$_1$H and L$_2$H)

All the complexes are solids, insoluble in water as well as in common organic solvents but soluble in DMF, DMSO, THF and dichloromethane. These complexes are non-hygroscopic in nature and decompose at temperature above 250 °C. The molar conductivity values show that these complexes are non-electrolytes. The physical data of these complexes are summarized in Table 1.

IR spectra :

The important IR spectral bands for oximes and metal complexes are summarized in Table 2. Interpretation of IR spectra of these complexes has been carried out by comparison with those of free ligands and other related

Table 2. Main IR spectral vibrations (cm^{-1}) of metal complexes

Sl. no.	Compd.	IR absorption frequencies (cm^{-1})			
		v(C=N)	v(C=C)	v(N–O)	v(M–N)
1.	[Co(L$_1$)$_2$]	1587	1572	1155	483
2.	[Co(L$_2$)$_2$]	1568	1558	1168	467
3.	[Zn(L$_1$)$_2$]	1573	1558	1163	483
4.	[Zn(L$_2$)$_2$]	1562	1545	1187	459
5.	[Cd(L$_1$)$_2$]	1568	1548	1173	495
6.	[Cd(L$_2$)$_2$]	1556	1552	1192	462
7.	[Hg(L$_1$)$_2$]	1568	1554	1168	485
8.	[Hg(L$_2$)$_2$]	1557	1542	1182	462

complexes. Absence of hydroxyl group of oximes (3365–3387 cm^{-1}) in the spectra of these complexes indicates deprotonation of OH group of oximes. The IR spectra of complexes show that the v(C=N) stretching frequency undergoes a shift to lower frequency by 35–59 cm^{-1}. This is indicative of nitrogen coordination of the oximato group[22] to the metal(II) ion, further supported by the appearance of a strong band at 1155–1192 cm^{-1} range corresponds to *N*-coordination of the oximato group[23,24]. The complexes show a band in the 459–495 cm^{-1} range, due to M–N vibration[25]. The downward shifting (31–61 cm^{-1}) of v(C=C) stretching frequency in complexes as

compared to free oxime moieties, indicates the coordination of π-allylic bond[26] of oximes to the metal(II) ion.

Magnetic moments and electronic spectra of cobalt(II) complexes :

The magnetic moment data (Table 1) and electronic spectral data have been found to useful for determining the geometry of complexes. The magnetic moment of cobalt(II) complexes was found 2.2 and 2.5 B.M. for complex 1 and 2 respectively, indicating square-planar configuration[27,28].

The electronic spectra of these complexes have been recorded in DMF solution, which exhibit three bands in the 8362–8525, 9512–9640 and 15578–15652 cm^{-1} ranges and the first and third bands may be assigned to $^2A_{1g} \rightarrow$ ^2E_g and $^2A_{1g} \rightarrow {}^4E_{2g}$ transitions, respectively in square-planar stereochemistry. The band in the range 9512–9640 cm^{-1} is considered as a characteristics band for cobalt(II) in a square-planar environment[27,29] (Fig. 2).
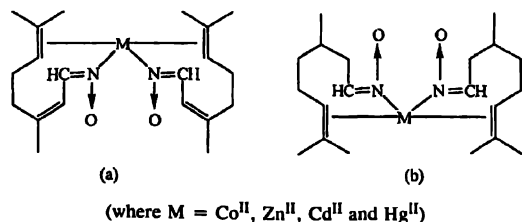

(where M = Co^{II}, Zn^{II}, Cd^{II} and Hg^{II})

Fig. 2. Proposed structural formula for complexes : (a) [M(L$_1$)$_2$] and (b) [M(L$_2$)$_2$].

NMR spectra :

The characteristics signals in ^{1}H and ^{13}C{^{1}H} NMR spectra of oximes and their Zn^{II}, Cd^{II}, Hg^{II} complexes are given in experimental section. A comparison of the spectra of the free oximes with the spectra of the corresponding complexes show the absence of -OH signals, indicating the deprotonation of the hydroxyl group of the oxime moieties and the azomethine proton is shielded as compared to the free oximes, which suggests that there may be coordination of metal ion through nitrogen atom as evinced by IR spectra also.

In the ^{13}C{^{1}H} NMR spectra of the complexes the C-6 and C-7 carbon signals of oxime moieties shows appreciable shifting and appeared at δ 120.9–123.5 and 129.4–131.6 ppm, respectively. This shifting provides support for the coordination of oxime moieties through the π-allylic bond to the metal(II) ion. The C=N carbon resonance of ligands is shielded on complexation as compared to free oximes, which suggests that there may be

coordination of metal through nitrogen atom as evinced by IR spectra. The other carbon signals of ligand moieties have been observed at their expected position and do not show any appreciable shift.

FAB mass spectra :

FAB mass spectral studies of two of the representative complexes [Co(L$_1$)$_2$] (1) and [Zn(L$_1$)$_2$] (3) (Table 3) indicates monomeric nature. The molecular ion peak of (1) appears at *m/e* 391, which is equivalent to its molecular weight, thus confirming the formation of a metal complex in 1 : 2 ratio.

Table 3. Fragmented molecular ions vs *m/e* values of [Co(C$_{10}$H$_{16}$NO)$_2$] (1) and [Co(C$_{10}$H$_{16}$NO)$_2$] (3)

Complex	Fragmented ions	*m/e* value
[Co(C$_{10}$H$_{16}$NO)$_2$] (1)	[Co(C$_{10}$H$_{16}$NO)$_2$]$^+$	391
	[Co(C$_{10}$H$_{16}$NO)(C$_{10}$H$_{10}$N)]$^+$	369
	[Co(C$_{10}$H$_{16}$NO)(C$_5$N)]$^+$	299
	[Co(C$_{10}$H$_{16}$NO)(C$_2$N)]$^+$	263
	[Co(C$_{10}$H$_{16}$NO)(N)]$^+$	239
	[Co(C$_8$H$_{10}$NO)(N)]$^+$	209
	[Co(C$_6$H$_{10}$NO)(N)]$^+$	185
	[Co(C$_2$H$_4$NO)]$^+$	117
	[Co(H$_4$NO)]$^+$	93
	[Co(OH)]$^+$	76
[Zn(C$_{10}$H$_{16}$NO)$_2$] (3)	[Zn(C$_{10}$H$_{16}$NO)$_2$(H$_2$O)]$^+$	415
	[Zn(C$_{10}$H$_{16}$NO)(C$_5$H$_8$NO)]$^+$	329
	[Zn(C$_{10}$H$_{16}$NO)(C$_3$H$_4$NO)]$^+$	301
	[Zn(C$_{10}$H$_{16}$NO)(C$_2$H$_4$NO)]$^+$	289
	[Zn(C$_{10}$H$_{16}$NO)(CH$_2$O)]$^+$	261
	[Zn(C$_{10}$H$_{16}$NO)(O)]$^+$	247
	[Zn(C$_{10}$H$_{15}$NO)(O)]$^+$	246
	[Zn(C$_7$H$_{11}$NO)]$^+$	190
	[Zn(C$_6$H$_9$NO)]$^+$	176
	[Zn(C$_2$H$_4$NO)]$^+$	123
	[Zn(CNO)]$^+$	107
	[Zn(CN)]$^+$	91
	[Zn(C)]$^+$	77

Although in the absence of crystal structure analyses of at least one of the representative compound, it is difficult to comment on the solid state structure, yet on the basis of above studies following tentative structures may be proposed for all these complexes (Fig. 2).

Powder X-ray diffraction study :

Powder X-ray diffraction pattern of the complexes [Co(L$_1$)$_2$] (1) and [Zn(L$_1$)$_2$] (3) and [Hg(L$_1$)$_2$] (7) were recorded over the 2θ = 0–40 range. The principal inter-

space lines and their intensities are represented in Table 4 and shown in Fig. 3. All the complexes are crystalline solid. The complexes [Zn(L$_1$)$_2$] and [Hg(L$_1$)$_2$] have similar crystallinity which is higher than the [Co(L$_1$)$_2$] com-
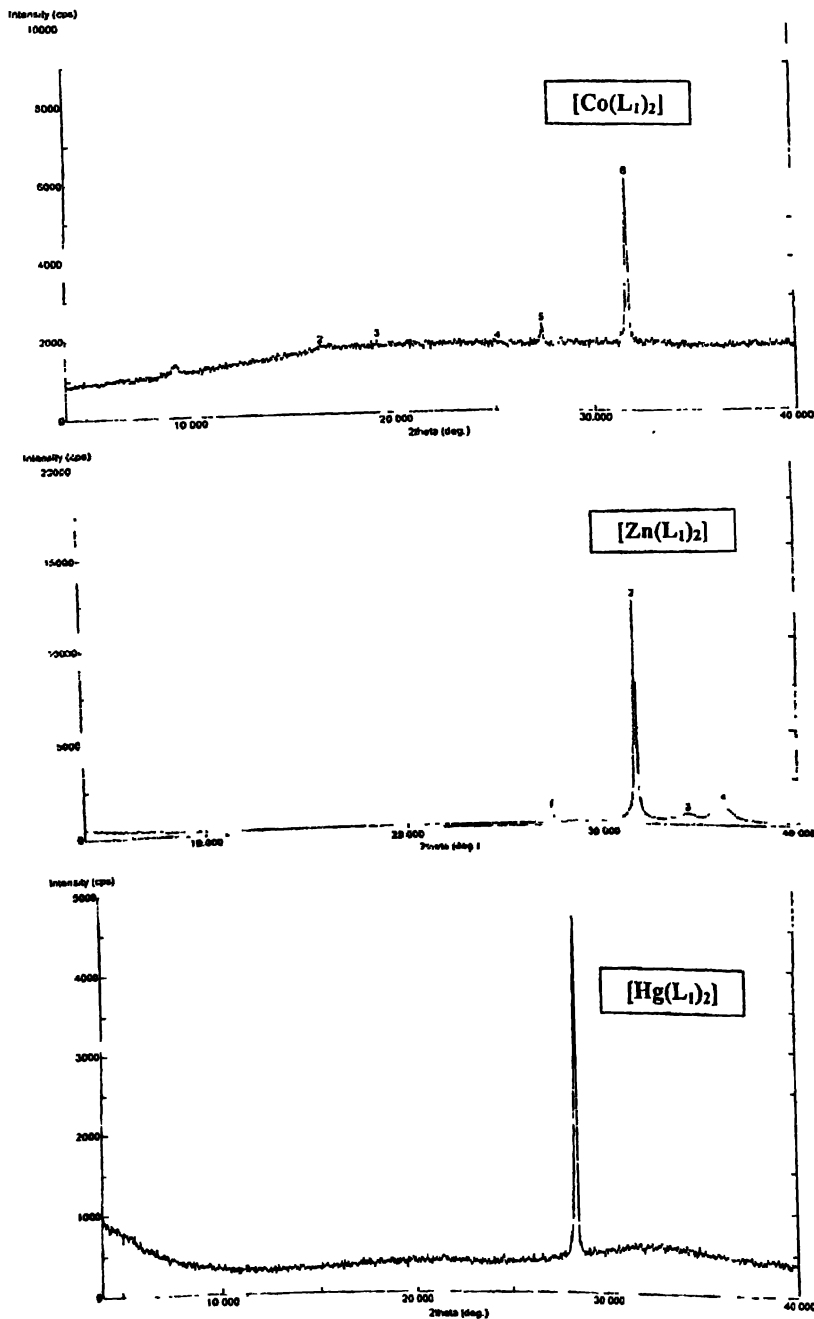

Fig. 3. Powder X-ray diffraction patterns of the metal complexes.

Table 4. Powder X-ray diffraction data of the [Co(L₁)₂], [Zn(L₁)₂] and [Hg(L₁)₂] complexes

Complex	n	2 theta	d-value	Intensity	(I/I_0)
[Co(L₁)₂]	1	9.310	9.4914	1305	22
	2	16.340	5.4203	1711	29
	3	19.120	4.6380	1816	31
	4	25.130	3.5408	1724	29
	5	27.330	3.2605	2173	37
	6	31.680	2.8220	5975	100
[Zn(L₁)₂]	1	27.350	3.2582	1342	12
	2	31.700	2.8203	11984	100
	3	34.340	2.6093	622	6
	4	36.180	2.4807	1147	10
[Hg(L₁)₂]	1	28.340	3.1466	4643	100

plex. Each complex has specified values which can be used for its characterization[30,31].

Antimicrobial activity :

The antibacterial and antifungal activity results, presented in Table 5, show clearly that all the newly synthesized ligands and metal complexes possess good antimi-

The susceptibility of bacteria towards complex compounds were tested by measuring the bacteriostatic diameter (*d*) and compared with parent ligands with a concentration of 2.0 µg/disc. The antibacterial activity data show that Gram +ve bacteria, *S. aureus* and *B. subtilis* are more susceptible to test compounds than the Gram −ve bacteria, *E. coli*, which is in accordance with previous studies. The weak antibacterial activity against Gram −ve bacteria was ascribed to the presence of an outer membrane[32], which possessed hydrophilic polysaccharide chains as a barrier to hydrophobic test compound.

All the complexes show high activity against such fungi at the lower concentration and the inhibition of fungal growth has been found to be dependent on the concentration of compound. The antifungal activity data of test compounds against *F. moniliformae* and *M. phaseolina*, indicate that the test compounds are more active against *M. phaseolina* than the *F. moniliformae*. It is observed from these tests that metal chelates have a higher activity than the free ligands. Such increased activity of the metal chelates can be explained on the basis of Overtone's con-

Table 5. Antimicrobial activity data for oximes and complexes

Compd.	Average value of bacteriostatic diameter (*d*) (mm)ᵃ			Average % inhibition after 72 h			
	S. aureus	*B. subtilis*	*E. coli*	*F. moniliformae* (conc. in ppm)		*M. phaseolina* (conc. in ppm)	
				100	400	100	400
L₁H	10.0	11.2	9.6	34.1	49.17	43.47	62.17
L₂H	9.6	10.2	9.2	32.13	48.73	42.02	60.12
[Co(L₁)₂]	11.2	11.8	10.2	40.15	57.12	48.57	68.19
[Co(L₂)₂]	10.6	11.2	9.8	39.87	54.54	46.43	66 68
[Zn(L₁)₂]	11.8	12.0	10.8	43.48	61.72	52.48	70.18
[Zn(L₂)₂]	11.5	11.8	10.5	41.13	58.33	50.14	69.13
[Cd(L₁)₂]	14.8	15.2	12.7	48.53	65.18	58.68	75.12
[Cd(L₂)₂]	13.6	14.9	12.3	45.12	62.47	54.67	74.17
[Hg(L₁)₂]	16.2	17.6	14.8	55.40	66.19	61.13	78.80
[Hg(L₂)₂]	15.8	17.0	14.5	53.19	64.65	67.69	77.95

$d \geq 20$ mm = high sensitivity, $14 \leq d < 20$ mm = medium sensitivity and $9 \leq d \leq 13$ = slight sensitivity; ᵃAverage value from three experiments.

crobial activity. New derivatives were screened for their antibacterial activity against *S. aureus*, *B. subtilis* and *E. coli* and for antifungal activity against *F. moniliformae* and *M. phaseolina* which exhibited a markedly enhancement of activity on further coordination with the metal(II) ions against all the test bacteria/fungal strains.

cept[33] and Tweedy's chelation theory[34]. These complexes also disturb the respiratory processes of the cell and thus block the synthesis of protein, which restricts further growth of the organism.

Conclusion :

The metal(II) complexes isolated during the present

study demonstrated that the interaction of metal(II) chloride with oxime of citral or citronellal leads to complexes with 1 : 2 stoichiometry and are found to be mononuclear. The bidentate nature of both ligand have been suggested on the basis of spectral evidences. All the complexes showed enhanced antimicrobial activity than the parent ligands.

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