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Article

Synthesis, Characterization and Biological Activity of Symmetric Dinuclear Complexes Derived from a Novel Macrocyclic Compartmental Ligand

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Um novo ligante macrocíclico binucleador, *N,N*-bis(2,6-diiminometil-1-hidroxifenil)malonoildicarboxamida, foi preparado. Seus complexos metálicos foram preparados pelo método da moldagem por metal, através das reações de 2,6-diformil-4-metilfenol, malonoil diidrazida com os cloretos metálicos de Cu(II), Ni(II), Co(II), Cd(II), Zn(II) e Hg(II), em methanol, que levaram à formação de uma série de complexos dinucleares. Os complexos foram caracterizados por análises elementares, medidas de conductividade, dados de susceptibilidade magnética, IR, UV-Vis, EPR, RMN e dados de espectrometrica de massas-FAB. A natureza dinuclear dos complexos foi confirmada pelas análises elementares e dados de susceptibilidade magnética, EPR e de espectrometria de massas-FAB. O ligante e os complexos de Cu(II), Ni(II), Co(II) e Zn(II) tiveram suas atividades antibacteriana e antifúngica testadas contra *Escherichia coli, Staphyloccocus aureus, Aspergillus niger* e *Fusarium oxysporum*. As medidas de susceptibilidade magnética dos complexos de Cu(II), Ni(II) e Co(II) revelaram que estes complexos exibem acoplamento antiferromagnético devido à presença de dois íons metálicos próximos um do outro. O espectro de massas-FAB do complexo de Cu(II) forneceu evidencia clara da sua natureza dinuclear. O ligante e os complexos exibiram atividade muito fraca contra as bactérias testadas, entretanto, o ligante mostrou-se ativo contra o fungo *Fusarium oxysporum.*

A phenol based novel macrocyclic binucleating compartmental ligand *N,N*-bis(2,6-diiminomethyl-4-methyl-1-hydroxyphenyl)malonoyldicarboxamide was prepared. The complexes were prepared by template method by reacting 2,6-diformyl-4-methylphenol, malonoyl dihydrazide and the metal chlorides of Cu(II), Ni(II), Co(II), Cd(II), Zn(II) and Hg(II) in methanol to get a series of dinuclear complexes. The complexes were characterized by elemental analyses, conductivity measurements, magnetic susceptibility data, IR, UV-Vis, ESR, NMR and FAB mass spectral data. The dinuclear nature of the complexes was confirmed on the basis of elemental analyses, magnetic susceptibility, ESR and FAB mass spectral data. The ligand as well as Cu(II), Ni(II), Co(II) and Zn(II) complexes were tested for their antibacterial and antifungal properties against *Escherichia coli, Staphyloccocus aureus, Aspergillus niger and Fusarium oxysporum*. Magnetic susceptibility measurements of Cu(II), Ni(II) and Co(II) complexes reveal that these complexes exhibit antiferromagnetic coupling behavior due to the presence of two metal ions in close proximity. FAB mass spectrum of the Cu(II) complex gave a clear evidence for the dinuclear nature. The ligand and the complexes were found to be less active against the tested bacteria, but the ligand alone was found active against the fungus *Fusarium oxysporum*.

Keywords: 'macrocyclic' compartmental ligand, dinuclear complexes, 2,6-diformyl-4-methylphenol, malonoyl dihydrazide

Introduction

Efforts have been made in the last decades to the design and synthesis of macrocyclic or macroacyclic complexes and to study their physico-chemical properties.[1,2] These investigations emphasized the great relevance of these systems in basic and applied chemistry. Several synthetic strategies are now a days available for the preparation of well organized molecular systems or molecular devices, which exhibit peculiar physico-chemical properties or have well defined properties.[1-4] Many macrocyclic or macroacyclic systems containing an appropriate set of donor atoms and a suitable structural configuration are capable of producing new macromolecules which have been used in numerous chemical processes and technologies. Based on this concept many macrocyclic

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systems are available and are already applied in the fields of activation and catalysis, molecular materials, microelectronics, sensors, and so on.[4] Bimetallic cores have been recognized at the active sites of many metalloenzymes.[5] Studies on the geometry around the metal by electronic spectra and magnetic properties of the metal ions present in the active sites of the metalloenzymes are rather difficult owing to the fact that the metal ions in active sites are embedded in protein polymer back bone.[6] Hence, design and synthesis of model compounds that mimic the physical and chemical properties of the active sites present in metalloenzymes is very essential and the studies on such compounds is becoming increasingly important in understanding biological functions of the bimetallic cores.[5] Dinuclear complexes with two metal ions in close proximity show interesting magnetic, catalytic and electron transfer properties. Efforts to synthesize ligands capable of generating such dinuclear complexes have resulted in a large number of dinuclear ligands.[7] One of such ligand systems was obtained from "2+2" condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane.[8] Macrocyclic ligands derived by template condensation of 2,6-diformyl-4-methylphenol with simple diamines such as 1,2-ethylenediamine, 1,3-propanediamine, 1,4-butanediamine etc., generally produce 2:2 macrocyclic rings, encompassing two metal atoms, bridged by two phenoxide groups and each bound terminally by two imine nitrogen donors. Such complexes particularly in the case of copper are strongly antiferromagnetically coupled and exhibit well-defined one electron redox processes.[9] A literature survey reveals that, for the synthesis of macrocyclic dinuclear complexes, the ligands employed were generally synthesized by the template condensation of 2,6-diformyl-4-methylphenol with various diamines. There are only a few references wherein the 2,6-diformyl-4-methylphenol has been condensed with aroyl hydrazones,[4,10] but there are no reports on the complexes of macrocycles obtained by the reaction of 2,6-diformyl-4-methylphenol with dicarboxylic acid dihydrazides. In view of these observations, we report here the synthesis, characterization and biological activity of a novel macrocyclic ligand obtained by "2+2" condensation of 2,6-diformyl-4-methylphenol with malonoyl dihydrazide and its dinuclear complexes.

Experimental

Materials

All chemicals used were of reagent grade. Solvents were distilled and dried before use according to standard procedures.[11] 2,6-Diformyl-4-methylphenol[12] and malonoyl dihydrazide[13] were prepared by the literature methods. The metal salts used were generally in their hydrated form.

Methods

Elemental analyses for C, H, and N were obtained from Heraeus CHN-O rapid analyzer, IR spectra were recorded on Perkin-Elmer 1000 IR spectrometer using KBr pellets. Conductance measurements were carried out in DMF solution ($1x10^{-3}$ mol dm^{-3}) using an Elico-CM 82 conductivity bridge. Electronic spectral measurements were carried out using Elico SL 159 spectrophotometer in the range 200-1000 nm. ^{1}H NMR spectra were recorded on Bruker AMX 400 MHz spectrometer, ESR spectrum of Cu(II) complex was recorded on X-band ESR spectrometer (Varian Associates). Magnetic measurements were made on a Cahn 2000 electro balance by Faraday Method using $Hg[Co(SCN)_4]$ as calibrant. FAB mass spectrum of Cu(II) complex was recorded on a JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon as the FAB gas.

Preparation of ligand H_2L

The ligand was prepared by refluxing 2,6-diformyl-4-methylphenol (0.33 mol dm^{-3}) with malonoyl dihydrazide (0.33 mol dm^{-3}) in methanol for 5 h. The pale yellow amorphous solid obtained was filtered, washed with little amount of hot methanol (5 cm^3) and dried in vacuo (mp 270 °C, yield 68%).

Preparation of the complexes

Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) complexes of ligand, H_2L, were prepared adapting template method owing to the insolubility of the ligand in common organic solvents. 2,6-diformyl-4-methylphenol (0.33 mol dm^{-3}), malonoyl dihydrazide (0.33 mol dm^{-3}) and respective metal chloride (0.33 mol dm^{-3}) in methanol were refluxed for 5-6 h. The separated complexes were collected by filtration, washed with hot methanol and dried under vacuum over $CaCl_2$ (yield 58-75%).

Biological activity

The *in vitro* biological screening of the ligand H_2L and its Cu(II), Ni(II), Co(II) and Zn(II) complexes was undertaken against the bacteria *Escherichia coli* and *Staphyloccocus aureus* by the cup-plate method using nutrient agar as medium. In a typical procedure, molten nutrient agar kept at 45 °C was then poured into Petri dishes and allowed to solidify. Then holes of 6 mm diameter were punched carefully using a sterile cork borer and these were completely filled with test solutions (1000 μg cm^{-3} in DMF). The plates were incubated for 24 h at 37 °C. The diameter of the zones of inhibition for all the test compounds was measured and the results were compared with the standard drug Ciprofloxacin of the same concentration as that of the test compound under identical conditions.

The antifungal activity of the test compounds was evaluated against the *Aspergillus niger* and *Fusarium oxysporum* by cup-plate method cultured on potato-dextrose agar medium adapting similar procedure described above. The plates were incubated at 37 °C for 48 h. The diameters of the zone of inhibition for all the test compounds were measured and the results were compared with the standard drug Griseofulvin of the same concentration as that of the test compound under identical conditions.

Since all test compounds and standard drugs were prepared in freshly distilled DMF, its zone of inhibition was found to be very negligible and taken as zero mm.

Results and Discussion

All the complexes were sparingly soluble in common organic solvents but soluble in DMF, DMSO, and acetonitrile. The analytical data (Table 1) indicate that the complexes are dinuclear in nature. The molar conductance (Table 1) values measured in DMF solution (1x10^{-3} mol dm^{-3}) fall in the range 50-62 ohm^{-1} cm^{2} mol^{-1}. These observed values of the molar conductance are well within the expected range for non-electrolytes.[14]

IR spectra

The important bands in the IR spectra of the ligand as well as complexes together with their assignments are listed in Table 2. The free ligand showed a broad band at 3432 cm^{-1} due to ν_{OH} in case of ligand has disappeared in all the complexes indicating its involvement in the coordination with the metal ions via deprotonation.[15] The free ligand showed a medium intensity band at 3210 cm^{-1} assigned to ν_{NH} vibrations,[16] which has been observed in the 3203-3207 cm^{-1} region in the case of the complexes. It can be observed that there is no considerable shift in the ν_{NH} vibrations in the case of the complexes compared to the ligand, indicates non-involvement of amide NH function in the coordination. A strong intensity band observed at 1675 cm^{-1} and a medium intensity band at 1630 cm^{-1} in the case of the ligand are assigned to $\nu_{C=O}$ and $\nu_{C=N}$ functions respectively. In the case of complexes the band due to $\nu_{C=O}$ was observed in the 1670-1676 cm^{-1} region, indicating its non-involvement in the complexation.[17] The band due to $\nu_{C=N}$ observed at 1630 cm^{-1} in the case of the ligand has shown a negative shift of 14-3 cm^{-1} in the complexes which suggests the involvement of azomethine group (C=N) in the coordination with the metal ions and bonded through the nitrogen atom.[18] The band due to phenolic C-O observed at 1240 cm^{-1} in the case of the ligand has shifted towards higher wave number and this positive shift of the band suggests the coordination of the phenolate anions with the metal ions via deprotonation.[15] Further, the appearance of new bands in the 1536-1555 cm^{-1} region in all the complexes suggest phenoxide bridging with the metal ions.[19] The presence of broad stretching vibrations in the 3444-3401 cm^{-1} region can be

Table 1. Physical, analytical, magnetic susceptibility and molar conductivity data of Ligand H_2L and its complexes

Ligand/ Complex	Empirical Formula	Mol.Wt. % (Colour)	mp / °C (yield / (%))	Elemental analysis (%): Found (Calc.)					μ_{eff}. (B.M)	λ_M (S)
				M	C	H	N	Cl		
H_2L	$C_{24}H_{24}N_8O_6$	520 (Yellow)	270 (70)	—	55.32 (55.38)	4.60 (4.62)	21.56 (21.53)	—	—	—
Cu-comp.	$Cu_2[LCl_2].3H_2O$	770.08 (Brown)	>300 (68)	16.46 (16.50)	37.42 (37.39)	3.65 (3.63)	14.51 (14.54)	9.20 (9.21)	1.42	60
Ni-comp.	$Ni_2[LCl_2(H_2O)_2].H_2O$	742.38 (Brown)	>300 (62)	15.84 (15.81)	38.77 (38.79)	3.45 (3.50)	15.11 (15.08)	9.50 (9.56)	2.77	58
Co-comp.	$Co_2[LCl_2].2H_2O$	742.86 (Brown)	>300 (63)	15.78 (15.86)	38.75 (38.76)	3.50 (3.49)	15.10 (15.07)	9.53 (9.55)	4.21	61
Zn-comp.	$Zn_2[LCl_2].2H_2O$	755.78 (Yellow)	247 (58)	17.39 (17.30)	38.11 (38.10)	3.42 (3.44)	14.80 (14.81)	9.36 (9.39)	dia*	53
Cd-comp.	$Cd_2[LCl_2].2H_2O$	849.82 (Yellow)	283 (75)	26.38 (26.45)	33.85 (33.88)	3.10 (3.05)	13.21 (13.17)	8.38 (8.35)	dia*	62
Hg-comp.	$Hg_2[LCl_2].2H_2O$	1026.1 (Yellow)	268 (64)	39.67 (39.09)	28.04 (28.06)	2.51 (2.53)	10.90 (10.91)	6.93 (6.91)	dia*	50

*Diamagnetic, S-ohm^{-1}cm^{2} mol^{-1}.

Table 2. IR spectral assignments of the ligand H_2L and its complexes

Ligand/Complex	ν_{OH}/ν_{H_2O}	ν_{NH}	ν_{CH_3}	$\nu_{C=O}$	$\nu_{C=N}$	Phenolic ν_{C-O}	ν_{M-O}	ν_{M-N}	ν_{M-Cl}
H_2L	3432	3210	2919	1675	1630	1240	—	—	—
Cu-comp.	3427	3203	2919	1674	1627	1540	515	464	320
Ni-comp.	3427	3207	2920	1672	1618	1536	571	466	320
Co-comp.	3401	3203	2906	1670	1626	1550	579	479	316
Zn-comp.	3412	3203	2920	1676	1616	1548	568	476	339
Cd-comp.	3444	3207	2920	1674	1627	1555	568	417	313
Hg-comp.	3417	3205	2920	1674	1620	1552	568	417	317

attributed to coordinated or lattice water molecules in all the complexes.[15] The low frequency skeletal vibrations due to M-O and M-N stretching provide direct evidence for the complexation. In the present investigation, the bands in the 579-515 cm^{-1} region have been assigned to ν_{M-O} and the bands observed in the 479-417 cm^{-1} region for ν_{M-N} vibrations respectively.[20,21] The bands due to ν_{M-Cl} were observed in the 339-313 cm^{-1} region and are characteristic of chloro-bridged binuclear complexes.[22]

Magnetic susceptibility

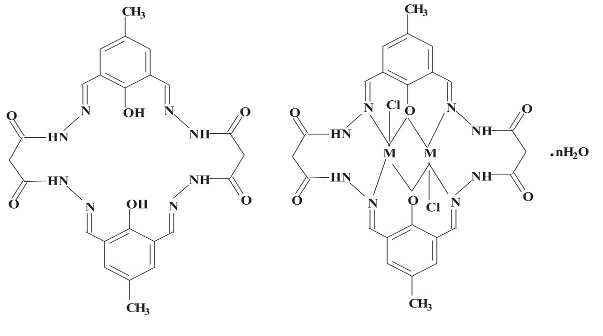
The room temperature magnetic susceptibility values are recorded in Table 1. Cu(II) complex of ligand H_2L showed a magnetic moment of 1.42 B.M. which is considerably lower than the spin only value for Cu(II) complexes. The low value of the magnetic moment is attributed for the antiferromagnetic coupling interaction between two metal ions. This fact suggests the dinuclear nature of the Cu(II) complex.[23] On the other hand, Ni(II) and Co(II) complexes have shown magnetic moment values 2.77 and 4.21 B.M. respectively which are lower than the respective spin only values and indicate weak antiferromagnetic coupling interaction[24] between the metal ions which further confirm the dinuclear nature of the complexes.

Electronic spectra

The Cu(II) complex of ligand H_2L exhibited a high intensity band at 380 nm in the UV-region. Appearance of this band is due to $\pi \rightarrow \pi^*$ transition associated with the azomethine linkage and ligand to metal charge transfer transition.[22] The charge transfer may be from *p*-orbital of the phenolic oxygen to the vacant *d*-orbital of the Cu(II) ion. The electronic spectrum of Cu(II) complex showed three bands at 950 nm (ε = 40 dm^3 mol^{-1} cm^{-1}), 685 nm (ε = 54 dm^3 mol^{-1} cm^{-1}) and 540 nm (ε = 44 dm^3 mol^{-1} cm^{-1}), these bands have been assigned to the transitions $^2B_1 \rightarrow {}^2A_1(\nu_1)$, $^2B_1 \rightarrow {}^2B_2\ (\nu_2)$ and $^2B_1 \rightarrow {}^2E(\nu_3)$ respectively. These transitions are characteristic of square pyramidal geometry.[25] The band observed at 685 nm is indicative of Cu(II) d-d transition.[26] Ni(II) complex showed absorption bands at 980 nm (ε = 30 dm^3 mol^{-1} cm^{-1}), 615 nm (ε = 60 dm^3 mol^{-1} cm^{-1}), 398 nm (ε = 84 dm^3 mol^{-1} cm^{-1}) and these bands can be assigned to $^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F) (ν_1), $^3A_{2g}$ (F)$\rightarrow$ $^3T_{1g}$ (F) (ν_2) and $^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (P) (ν_3) transitions respectively suggesting octahedral geometry.[27] The band around 980 nm is expected for the Nickel(II) d-d transition.[26] Co(II) complex displayed three bands at 905 (ε = 43 dm^3 mol^{-1} cm^{-1}), 585 nm (ε = 52 dm^3 mol^{-1} cm^{-1}) and 503 (ε = 61 dm^3 mol^{-1} cm^{-1}) which can be assigned to the transitions $^4A_2 + {}^4E \rightarrow {}^4B_1$, $^4A_2 + {}^4E \rightarrow {}^4E(P)$ and $^4A_2 + {}^4E \rightarrow {}^4A_2(P)$ respectively which are characteristic of square pyramidal geometry.[27]

^1H NMR spectra

The ^1H NMR spectrum of ligand H_2L recorded in DMSO-d_6 showed a peak at δ 2.09 (s, 6, 2×$ArCH_3$) due to methyl group at 4-position on the phenol rings. Four methylene protons have resonated at δ 3.61 (s, 4, 2×CH_2) as a singlet and the four azomethine protons have resonated as a singlet at δ 8.51 (s, 4, 4×CH=N-) and protons due to the amide function have appeared as a singlet at δ 11.70 (s, 4, 4×NH). Two protons due to phenolic –OH have appeared at δ 12.06 (s, 1H) as a singlet whereas the four aromatic protons have resonated at δ 7.23 (s, 4, 2×ArH_2) as a singlet.



M= Cu(II), Ni(II).H_2O, Co(II), Zn(II), Cd(II) and Hg(II)
n= 1-3

Figure 1. Structures of the ligand H_2L and its complexes.

The ^1H NMR spectrum of Cd(II) complex of ligand H_2L scanned in DMSO-d_6 showed a peak at δ 2.24 (s, 6, 2×ArCH_3) due to six methyl protons at 4-position of phenyl rings. Four methylene protons have resonated at δ 3.61 (s, 4, 2×CH_2) and four aromatic protons of the phenyl ring have resonated as a singlet at δ 7.58 (s, 4, 2×ArH_2) respectively. Four azomethine protons have appeared at δ 8.47 (s, 4, CH=N-) as a singlet. The signal observed at δ 12.06 due to the protons of phenolic -OH group, in case of ligand has disappeared indicating coordination of the phenoxide ions to the metal ions via deprotonation.[15] Four -NH protons of amide function have resonated at δ 11.65 (s, 4, 4xNH) as a singlet. These observations reveal that the involvement of phenolic –OH groups in the complexation with the metal ions via deprotonation indicated by the disappearance of the signals due to –OH groups in the Cd(II) complex. Further, the changes in the chemical shifts of azomethine function and aromatic protons in the Cd(II) complex suggest coordination of the azomethine nitrogen with metal ions.

ESR spectrum of Cu(II) complex

The X-band ESR spectrum of the powder Cu(II) complex (Figure 2) was recorded at room temperature using DPPH as a reference standard. The spectrum appeared to be slightly broadened with $g_{\perp}$=2.08 and $g_{||}$ =2.17. Generally, chloro-bridged binuclear Cu(II) complexes give broad ESR signals.[22] The observed ESR spectrum is characteristic of square pyramidal geometry. 'g' values averaged to overall directions and 'G' which is a measure of extent of exchange interaction between the metal ions have been calculated using the relations $g^2_{av} = 1/3(2\, g^2_{\perp} + g^2_{||})$ and $G = (g_{||} - 2)/(g_{\perp} - 2)$. By observing the g-values it is clear that $g_e < g_{\perp} < g_{||}$ (2.0023 < 2.0844 < 2.1719)) which suggest that d_{x2-y2} orbital is in the ground state and the d^9 configuration is $(e_g)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1$. The 'g' values are related to the axial symmetry[22] and $g_{||} > g_{\perp}$ suggests square pyramidal geometry for Cu(II) complex.[27] In the present case the value of 'G' was found to be 2.03. According to Hathaway,[28] if G value is greater than 4, the exchange interaction is negligible whereas G value less than 4 indicates considerable exchange interaction between metal ions in the solid complex. In the present case G=2.03 indicate considerable exchange interaction between the Cu(II) ions in the complex which further supports the dinuclear nature of the complexes.

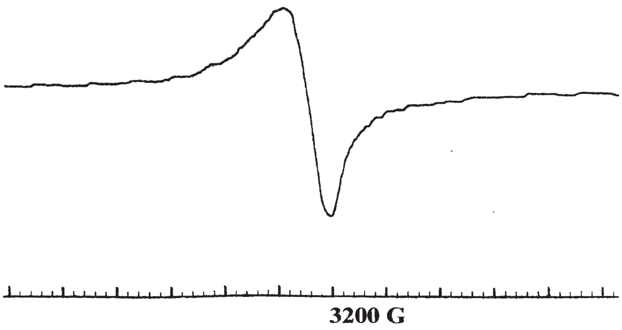


Figure 2. ESR spectrum of the Cu(II) complex.

FAB mass spectrum of Cu(II)-complex of ligand H_2L

FAB mass spectrum of Cu(II)-complex of ligand H_2L has been depicted in Figure 3. The spectrum showed a molecular ion peak M^+ at *m/z* 770, which is equivalent to its molecular weight. The molecular ion by the loss of four hydrogen radicals gave a fragment ion peak A_1 at *m/z* 766. The fragment ion A_1 by the loss of three water molecules, two chloride and two methyl radicals simultaneously gave

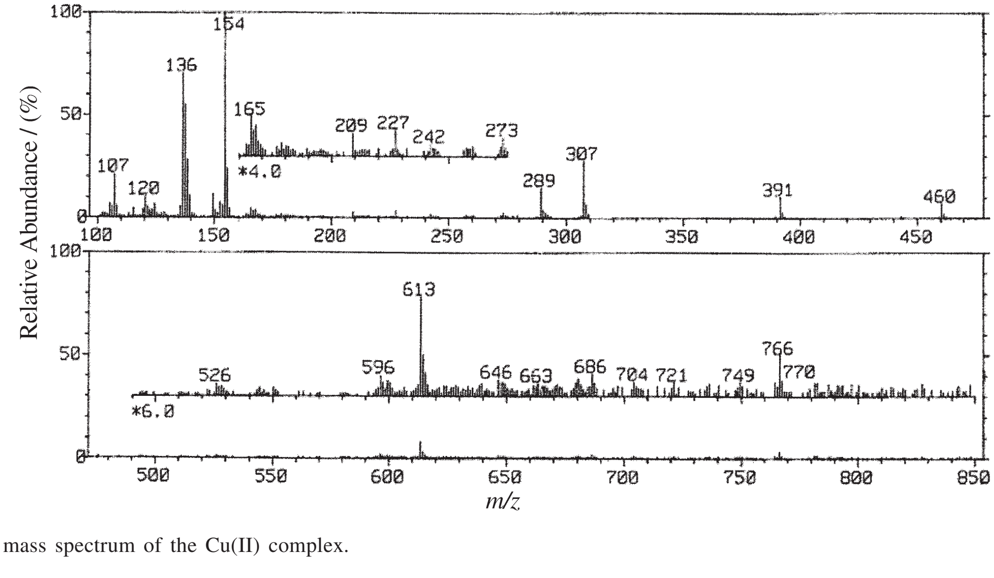
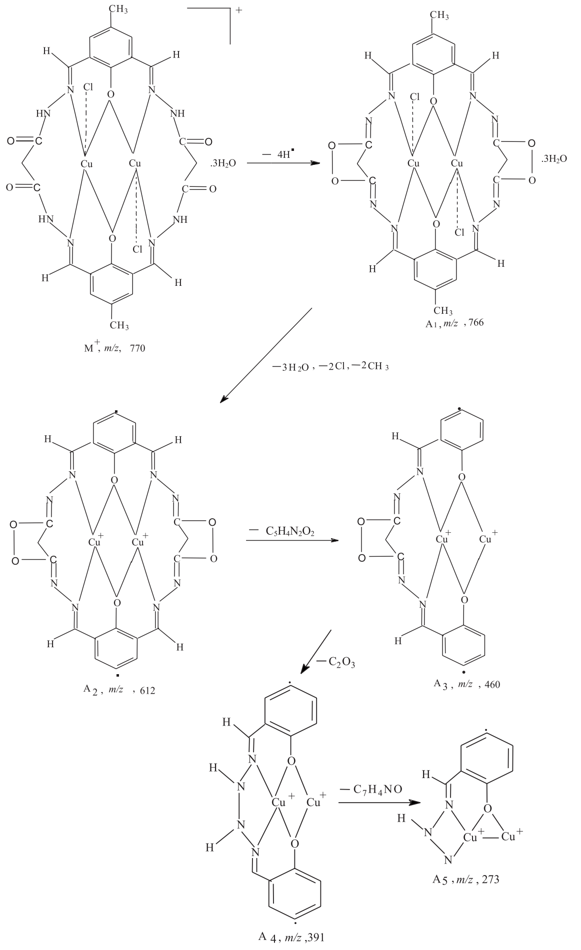


Figure 3. FAB mass spectrum of the Cu(II) complex.

a fragment ion A_2, at *m/z* 612. This fragment ion A_2 by the expulsion of $C_5H_4N_4O_2$ species gave another fragment ion A_3 at *m/z* 460. Further, the fragment ion A_3 by the loss of C_3O_2 species gave a fragment ion A_4 at *m/z* 391. Finally, the fragment ion A_4 by the loss of C_7H_4NO species gave a fragment ion A_5 at *m/z* 273. The fragmentation pattern is given in Scheme 1. It clearly indicates dinuclear nature of the complex and two Cu(II) ions are held in the macrocyclic compartment of the ligand H_2L. The metal ions are bonded to two phenoxo bridges which endogenously coordinate to the metal ions and the other coordinating sites in the ligand are the azomethine nitrogen atoms. Both phenoxide and azomethine groups surround the two metal ions which are in close proximity within the ligand molecule to form a square base. A chloride ion coordinates to each metal ion from opposite sides to give square pyramidal configuration to the metal ions. The FAB mass spectrum confirms the dinuclear nature of the metal complex.



Scheme 1. FAB mass fragmentation pattern of the Cu(II) complex.

Table 3. FAB mass spectral data of the Cu(II) complex

Complex	*m/z*	Peak assignments	Relative % abundance
$[Cu_2(L)Cl_2]\ .3H_2O$	770	$\{[Cu_2(L)Cl_2].3H_2O\}^+$	3
	766	$[Cu_2(C_{22}H_{12}N_8O_6)Cl_2]^+$	5
	612	$[Cu_2(C_{22}H_{12}N_8O_6)]^+$	12
	460	$[Cu_2(C_{17}H_8N_4O_4)]^+$	10
	391	$[Cu_2(C_{14}H_8N_4O_2)]^+$	12
	273	$[Cu_2(C_7H_4N_3O)]^+$	2

Biological activity

The ligand H_2L and its Cu(II), Ni(II), Co(II) and Zn(II) complexes were tested for their antibacterial and antifungal activity. The zones of inhibitions of the antimicrobial activity have been presented in the Table 4. The results of the antibacterial activity of the ligand H_2L and its Cu(II), Ni(II), Co(II) and Zn(II) complexes revealed that the ligand as well as its Cu(II), Ni(II), Co(II) and Zn(II) complexes displayed very weak activity against both the bacteria *E. coli* and *S. aureus* with 12-14 mm inhibition compared to the standard drug ciprofloxacin which showed 24 mm and 22 mm inhibition against *E.coli* and *S. aureus* respectively.

The antifungal activity results of the ligand H_2L and its complexes revealed that the ligand showed less activity against *A.Niger* and good activity against *F.oxysporum* with 14 mm and 18 mm inhibition respectively, compared to the standard drug griseofulvin with 24 mm and 23 mm inhibition. Cu(II), Ni(II), Co(II) and Zn(II) complexes were found to be less active with 10-15 mm inhibition against

Table 4. Antibacterial and antifungal activities of the ligand H_2L and its complexes

Test Compound	Antibacterial activity(zone of inhibition in mm)		Antifungal activity(zone of inhibition in mm)	
	E. coli	*S. aureus*	*A. niger*	*F. oxysporum*
(Ligand) H_2L	12	12	14	18
Cu-complex	13	11	15	14
Ni- complex	12	14	14	12
Co- complex	12	12	14	15
Zn- complex	12	13	10	13
Ciprofloxacin	24	22	—	—
Griseofulvin	—	—	24	23
DMF* (Control)	0	0	0	0

* Freshly distilled DMF.

A.niger and *F.oxysporum* respectively compared to the standard drug.

A comparative study of the ligand and its complexes indicates that some of the metal chelates exhibit higher antimicrobial activity than the free ligand. The increase in the antimicrobial activity of metal chelates is due to the presence of metal ions in the complexes.

Conclusions

The ligand *N,N*-bis(2,6-diiminomethyl-4-methyl-1-hydroxylphenyl)malonoyl dicarboxamide behaved as a binegative octadentate chelating agent coordinating through two deprotonated phenoxo groups and four azomethine nitrogen atoms. The ligand was so designed that it can secure two metal ions in the close proximity. Analytical data, electronic spectra, magnetic susceptibility, IR, ^{1}H NMR, ESR, FAB mass spectral data reveal dinuclear nature of all the complexes. The dinuclear nature of the complexes was confirmed on the basis of ESR and FAB mass spectral data, it is further confirmed on the basis of considerable low value of magnetic moments in the case of Cu(II), Ni(II), and Co(II) complexes, which indicate antiferromagnetic coupling interaction between the two metal centers in the complexes. The ligand and its Cu(II), Ni(II), Co(II) and Zn(II) complexes were tested for antimicrobial activity and the compounds were found to be less active against the bacteria *E.coli* and *S.aureus* and the fungi *A.niger* and *F.oxysporum,* but the ligand alone was found to be active against the fungus *F.oxysporum*.

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References

1. Fenton, D. E. In *Advances in Inorganic and Bioorganic Mechanisms;* Sykes, A. G., ed.; Academic: London, 1983, vol. 12B, p. 187.
2. Fenton, D. E.; Casellato, U.; Vigato, P.A.; Vidali, M.; *Inorg. Chim. Acta* **1984**, *95*, 187.
3. Zanello P.; Tamburini S.; Vigato P.A.; Mazzocchin, G. A.; *Coord. Chem. Rev*. **1987,** *77*, 165.
4. Lehn, J. M.; *Pure Appl. Chem*. **1978**, *50*, 871.
5. Fenton D.E.; Okawa, H.; *Perspectives on Bioinorganic Chemistry*, JAI Press: London, 1993, p. 8.
6. Karthikeyan, S.; Rajendiran, T.M.; Kannappan, R.; Mahalakshmy, R.; Venkateshan,R.; Sambasiva Rao, P.; *Proc. Indian Acad. Sci. (Chem. Sci.)* **2001,** *113*, 245.
7. Casellato, U.; Vigato P.A.; Vidali, M.; *Coord. Chem. Rev*. **1977,** *23*, 31.
8. Pilkington, N. H.; Robson, R.; *Aust. J. Chem*. **1970**, *23*, 2225.
9. Okawa, H.; Kida, S.; *Bull. Chem. Soc. Japan* **1972,** *5*, 1759.
10. Ullas Shetty, N.; Revankar, V.K.; Mahale, V. B.; *Proc. Indian Acd. Sci., (Chem. Sci.)* **1997,** *109*, 7.
11. Brian, S.F.; Hannaford, A.J.; Smith, P.W.G.; Tatchell A.R.; *Vogel's Text Book of Partical Organic Chemistry,* ELBS Publishers: Singapore, 1989, p. 395.
12. Denton D. A.; Suschitzky, H.; *J. Chem. Soc.* **1963,** 4741.
13. Sangapure, S.S.; Raga B.V.; *Asian J. Chem.* **1997,** *9*, 663.
14. Geary, W.J.; *Coord. Chem. Rev.* **1972**, *1***,** 81.
15. Malhotra, R; Sudhir, K.; Jyoti; Singal, H. R.; Dhindra, K. S.; *Indian J. Chem.* **2000**, *39A*, 421.
16. Singh N.K.; Singh S.B.; *Indian J. Chem.* **2001**, *40A*, 1047.
17. Warad, D.U.; Satish, C.D.; Kulkarni, V.H.; Bajgur, C.S.; *Indian J. Chem.* **2000**, *39A*, 418.
18. Sashidhara, G. M.; Goudar, T.R.; *J. Indian Chem. Soc*. **2001**, *78*, 360.
19. Srinivas, B.; Arulsamy, N.; Zacharias, P. S.; *Polyhedron* **1991,** *10*, 731.
20. Choudhary, C. K.; Choudhary, R.K.; Mishra, L. K.; *J. Indian Chem. Soc.* **2003**, *80*, 693.
21. Mohapatra, B.B.; Saraf, S.K.; *J. Indian.Chem. Soc.* **2003**, *80,* 696.
22. Annigeri, S.M.; Naik, A.D.; Gangadharmath,U. B.; Revankar,V.K; Mahale,V.B.; *Trans. Met .Chem.* **2002**, *27*, 316.
23. Kannappan, R.; Mahalakshmy, R.; Rajendiran, T.M.; Venkateshan, R.; Sambashiva Rao, P.; *Proc. Indian Acad. Sci. (Chem. Sci.)* **2003**, *115*, 1.
24. Naik, A.D.; Annigeri, S.M.; Gangadharmath,U. B.; Revankar,V.K.; Mahale,V.B.; Reddy,V.; *Indian J. Chem***. 2002**, *41A*, 2046.
25. Sengottuvelan, N.; Manonmani, J.; Kandaswamy, M.; *Polyhedron* **2002**, *21***,** 2767.
26. Koji, A.; Matsfuji, K.; Ohba, M.; Okawa, H.; *Inorg. Chem.* **2002**, *41***,** 4461.
27. Satyanarayana, D.N.; *Electronic Absorption Spectroscopy and Related Techniques*, Universities Press: Hyderabad, 2001.
28. Hathaway, B.J.; Billing, D.E.; *Coord. Chem. Rev.* **1970,** *6*, 143.

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