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Thiocarbohydrazide as "Diamine" to Construct Macrocyclic and Side-Off Compartmental Ligands

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Abstract

New dinuclear complexes of macrocycles/macroacycles/oximes having a reactive peripheral thioketo functional group were synthesized using 2,6-diformyl-*p*-cresol as parent compound and thiocarbohydrazide/various diamines as side arms. Thioenolization and subsequent coordination to metal ion of the thio-keto sulfur is observed in asymmetric macrocycles and oxime complexes, while it is kept away from the coordination sphere in symmetric macrocycles. Magnetic susceptibility measurements over the range 70–300 K confirm that the copper(II) centers of the symmetric and asymmetric macrocycles are antiferromagnetically coupled, with values for the exchange coupling constant J through the phenolate oxygens of -610 to -580 cm^{-1}, respectively. The ligands and their complexes are found to be excellent fungistatic agents.

Introduction

A bimetallic core is versatile at the active site of many metalloenzymes and plays an essential role in biological systems by the interplay of a pair of metal ions. Synthetically simple binuclear metal complexes are important to understand the mutual influences of two metal centers on the structural, electronic, magnetic, and electrochemical properties of such bimetallic cores. Compartmental macrocyclic ligands having two phenolic oxygens as an endogenous bridge have been developed for this purpose, because they bind two metal centers in close proximity relevant to the active sites of bimetallic enzymes. Recent X-ray crystallographic studies have indicated that most bimetallic biosites are asymmetric with respect to the donor atoms about the metal centers, the nature of the metal ions, the coordination number, and the geometric arrangement of the donor atoms [1–6].

Thus the design of side-off compartmental ligands and asymmetric and symmetric macrocyclic ligands capable of providing a discrete homo/hetero dinuclear core is of particular interest.

One of the objects of studying the bimetallic complexes of thiocarbohydrazones was to investigate whether coordination to metal ion occurs through the sulfur or advantage is taken of the available nitrogen donors to form a coordination sheath consisting of only nitrogen atoms. Thiocarbohydrazide in the present investigation was used as the diamine with 2,6-diformyl-*p*-cresol to construct a compartmental binucleating ligand, hoping that the toxophoric functional group [–C=S] will be away from the coordinating site so that these free functional groups could provide "points of attachment", a system which mimics certain classes of biological systems (similar to the Jager macrocycle) [7] and in addition such groups could be toxic to microbes when used as drugs.

The use of macrocyclic ligands in studies on polydentate metal complexes has great advantages because macrocyclic complexes are thermodynamically stabilized and kinetically retarded towards metal dissociation or substitution relative to complexes of the corresponding non-cyclic ligands (macrocyclic effect) [8].

Experimental

Physical measurements

The complexes were analyzed for their metal content by EDTA titration after decomposition with a mixture of HCl and $HClO_4$. C, H and N were estimated on a Thermoquest CHN analyzer. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. The magnetic susceptibility of powdered samples of the complexes were measured in the temperature range 77–300 K using a PAR model 155 vibrating sample magnetometer and the instrument was calibrated with the use of metallic nickel. Electronic spectra were recorded on a Hitachi 2001 in DMF solution. IR spectra were recorded in the 4000–400 cm^{-1} region (KBr disc) on a Nicolet 170 SX FT-IR. Far IR spectra were recorded in the 500–100 cm^{-1} region on a Bruker IFS66V (Polyethylene disc). The ^{1}H NMR spectra were obtained in D_6-DMSO using TMS as an internal reference on a JEOL AMX-400 NMR spectrometer. Conductance measurements

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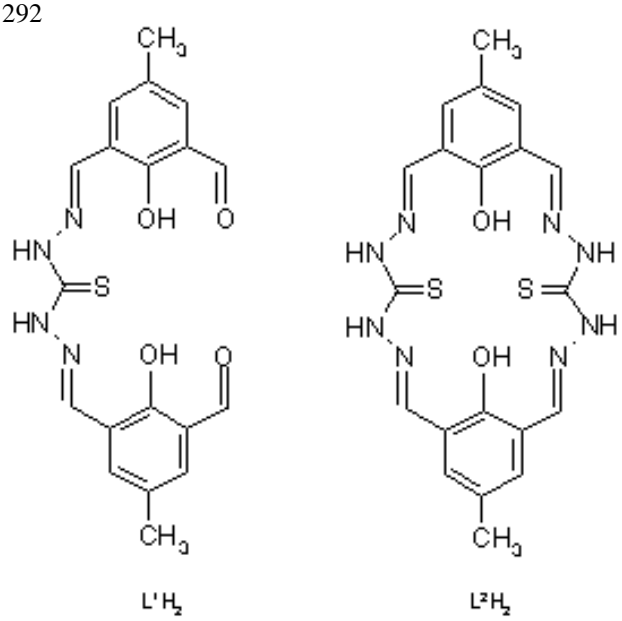


Figure 1. Structures of the ligands.

were made in DMF (10^{-3} M) using a ELICO-CM82 Conductivity bridge. TG-DTG studies were carried out in the 25–800 °C range using a Rigaku TAS-100 model thermal analyzer with a heating rate of 10 °C per min in a N_2 atmosphere. The FAB mass spectrum was recorded on a JEOL EX 102/DA-6000 mass spectrometer using Ar as the FAB gas and m-nitrobenzyl alcohol (NBA) as the matrix.

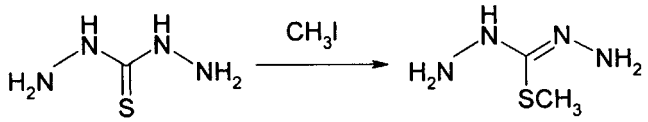
Preparation of ligands

2,6-Diformyl-*p*-cresol was prepared by a slight modification of a literature method [9].

L^1H_2. To a hot ethanolic solution of 2,6-diformyl-*p*-cresol (3.28 g, 0.02 mol) a hot suspension of thiocarbohydrazide (1.06 gm, 0.01 mol) also in ethanol was added dropwise, with stirring. The pale yellow precipitate that separated was refluxed for 1 hr, filtered, washed with ethanol and dried. M.p. 180 °C, Yield 75%. ^{1}H NMR in $CDCl_3$; (2.5, 6H, $-CH_3$), (7.4–7.6, 4H, –Ph), (8.1, 2H, azomethine), (12.8, 2H, –OH), (12.3, 2H, –NH), (10.1, 2H, –CHO)

L^2H_2. The procedure for the synthesis of this ligand is as described for L^1H_2 with a 1:1 stoichiometric ratio of the reactants (Figure 1). M.p. 191 °C, yield 70%. ^{1}H NMR in $CDCl_3$; (2.49, 6H, $-CH_3$), (7.4–7.6, 4H, Ph), (8.2, 4H, azomethine), (12.1–12.4, 4H, –NH), (12.7, 2H, –OH).

Like analogous thioamide compounds, such as thiourea, thiosemicarbazide and thiocarbohydrazide can be S-alkylated readily by the usual methods [10]. 3-Methyl isothiocarbohydrazide is rapidly formed from thiocarbohydrazide and CH_3I in ethanol, which reacts with 2,6-diformyl-*p*-cresol. This compound is prepared in order to decide unambiguously the ν(NH) and thioamide bands (I–IV) in the IR and the $n \rightarrow \pi^*$ absorption of the thioamide chromophore in ultraviolet spectroscopy.



Preparation of complexes (C1–C3 and C13–C15)

To an ethanolic solution of L^1H_2 or L^2H_2 (0.01 mol) the respective metal chloride (0.02 mol) [Cu(II), Ni(II) and Co(II)] also in ethanol was added with stirring. The complexes, which separated immediately, were refluxed for 2 hr, filtered, washed with ethanol and dried. M.p. > 250 °C, Yield 65%.

Complexes C10–C12 (oxime complexes). A successful attempt was made to synthesize binuclear oxime complexes in one step. L^1H_2 (0.01 mol) in ethanol and hydroxylamine hydrochloride (0.02 mol), in the presence of dil NaOH or triethylamine, were refluxed for 1 h. The pale orange precipitate that separated was again refluxed with 0.02 mol of the respective metal chloride [Cu(II), Ni(II) and Co(II)] in ethanol. It was found essential to keep the reaction mixture sufficiently basic in order to achieve the complete transformation of >C=O to >C=NOH which probably also helps to force two metal ions into the N_4O_2 cavity, which otherwise was found to be not possible.

Complexes C4–C9 (asymmetric macrocycles). Achieving binuclearity was unsuccessful in the asymmetric macrocycles by the procedure employed for the preparation of C1–C3 and C13–C15. A mixture of L^1H_2 in ethanol (0.01 mol) and the respective metal chloride (0.01 mol) [Cu(II), Ni(II) and Co(II)] was refluxed for 1 hr. To the thus formed mononuclear complex, metal chloride (0.01 mol) was added followed by 0.01 mol of diamine (ethylene diamine [C4–C6] or propylene diamine [C7–C9]). The mixture was stirred for 30 min, with dropwise addition of dil NaOH, and refluxing continued for another 30 min. The filtered complexes were washed thoroughly with distilled water, followed by ethanol and dried *in vacuo*. M.p. > 250 °C, yield 90% (Figure 2).

Results and discussion

All the complexes are non-hygroscopic. They are formed by the loss of two, three or four protons. They are insoluble in water, EtOH and MeOH but soluble in DMF, DMSO and MeCN. Analytical data are presented in Table 1. Molar conductivities in DMF suggest that the complexes are non-electrolyte (16–19 mho cm^2 mol^{-1}).

Electronic spectral studies

Electronic absorption spectra of all the compounds were recorded in DMF solution over the range 200–1200 nm. These regions encompass, to lower energies, the $d--d$ transitions and to higher energies, some of the charge transfer bands, the $n \rightarrow \pi^*$ transitions of the thioamide and azomethine chromophores and the $\pi \rightarrow \pi^*$ intraligand transitions. The absorption maxima for L^1H_2 at 272, 379 and 450 nm were

Table 1. Analytical data of the ligands and complexes

Compound	Empirical formula	Found % (Calc. %)			
		C	H	N	M
L^1H_2	$C_{19}H_{18}N_4O_4S$	57.21(57.28)	4.51(4.55)	14.10(14.06)	–
L^2H_2	$C_{20}H_{20}N_8O_2S_2$	51.23(51.27)	4.32(4.30)	23.88(23.91)	–
C1	$[Cu_2(C_{19}H_{16}N_4O_4S)Cl_2]$	38.40(38.39)	2.68(2.71)	9.47(9.43)	21.40(21.38)
C2	$[Ni_2(C_{19}H_{16}N_4O_4S)Cl_2]$	39.05(39.03)	2.77(2.76)	9.51(9.58)	20.10(20.08)
C3	$[Co_2(C_{19}H_{16}N_4O_4S)Cl_2]$	39.10(39.00)	2.78(2.76)	9.52(9.57)	20.17(20.14)
C4	$[Cu_2(C_{21}H_{20}N_6O_3S)]2H_2O$	42.09(42.07)	4.08(4.03)	14.11(14.02)	21.25(21.26)
C5	$[Ni_2(C_{21}H_{20}N_6O_3S)]2H_2O$	46.79(46.76)	4.15(4.10)	14.21(14.25)	19.82(19.90)
C6	$[Co_2(C_{21}H_{20}N_6O_3S)]2H_2O$	42.77(42.72)	4.49(4.10)	14.22(14.24)	19.81(19.96)
C7	$[Cu_2(C_{22}H_{22}N_6O_3S)]2H_2O$	43.10(43.06)	4.29(4.27)	13.71(13.70)	20.72(20.71)
C8	$[Ni_2(C_{22}H_{22}N_6O_3S)]2H_2O$	43.80(43.75)	4.44(4.34)	13.88(13.92)	19.47(19.44)
C9	$[Co_2(C_{22}H_{22}N_6O_3S)]2H_2O$	43.68(43.72)	4.39(4.34)	13.85(13.90)	19.55(19.50)
C10	$[Cu_2(C_{19}H_{16}N_6O_4S)]2H_2O$	38.98(38.84)	3.47(3.43)	14.31(14.30)	21.67(21.63)
C11	$[Ni_2(C_{19}H_{16}N_6O_4S)]2H_2O$	39.52(39.49)	3.54(3.49)	14.57(14.54)	20.40(20.41)
C12	$[Co_2(C_{19}H_{16}N_6O_4S)]2H_2O$	39.44(39.46)	3.50(3.48)	14.55(14.53)	20.41(20.38)
C13	$[Cu_2(C_{20}H_{18}N_8O_2S_2)Cl_2]$	36.22(36.15)	2.77(2.73)	16.77(16.86)	19.17(19.12)
C14	$[Ni_2(C_{20}H_{18}N_8O_2S_2)Cl_2]$	36.70(36.68)	2.79(2.77)	17.27(17.11)	17.99(17.93)
C15	$[Co_2(C_{20}H_{18}N_8O_2S_2)Cl_2]$	36.71(36.66)	2.80(2.77)	17.17(17.10)	17.81(17.99)

assigned to an intraligand transition, the $n \rightarrow \pi^*$ transition of the thioamide chromophore and the $n \rightarrow \pi^*$ transition of the azomethine group respectively. The methylated compound of L^1H_2 does not show the $n \rightarrow \pi^*$ transition of thioamide chromophore.

In the C1–C3 and C13–C15 complexes, the ligand bands remained unchanged except the one around 450 nm, which broadened, probably due to overlap with charge transfer transitions. In all other complexes the absorption around 370 nm due to the thioamide chromophore is destroyed due to thioenolization and subsequent coordination to the metal ion. Visible bands around 810 nm in all copper and cobalt complexes are assigned to the superimposed bands from the d-d transitions. The C2 and C14 nickel complexes exhibit bands at around 820, 765, 615 and 540 nm suggesting square-pyramidal geometry. Nickel(II) complexes C5 and C8 also followed the same spectral trends but with additional bands in the near IR region, indicating that Ni(II) at the thiocarbohydrazide compartment had assumed octahedral geometry. The complex C11 exhibited bands attributable to square-pyramidal geometry with an additional weak shoulder at 570 nm, which is probably associated with the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition of square-planar nickel at the oxime compartment. It is to be noted that in an asymmetric macrocycle complex the band around 450 nm, a combination of the $n \rightarrow \pi^*$ transition of azomethine and the charge transfer transition, splits into two. This suggests that the two metal ions in these complexes assume different geometries owing to the different lateral side chains of the macrocycles [11–13]. The EPR spectra of all the polycrystalline copper complexes at room temperature are essentially same and are typical for an isotropic local molecular environment (Table 2).

IR spectral study

Pertinent IR absorptions are presented in Table 3. The possibility of thione-thiol tautomerism, in L^1H_2 and L^2H_2, has been ruled out, since there is no band around 2500–2600 cm^{-1}, characteristic of the thiol group. The phenolic ν(OH) which is found around 3300 cm^{-1} as a weak broad band, disappears in all the complexes indicating its involvement in coordination. The coupled vibrations among thioamide bands (I, II, III and IV) are distributed around 1523, 1462, 1307 and 974 cm^{-1}. [I β(NH) + ν(C=N); II ν(CN) + β(NH); III ν(CN) + ν(C=S); IV ν(C=S) + α(CNN) + ν(CN)].

Sharp absorptions at 1653 and 1616 cm^{-1} are assigned to free carbonyl and azomethine stretching respectively. The former absorption disappears in L^2H_2 and in all macrocyclic complexes supporting formation of the macrocycle. The ν(NH) is identified at 3209 and 3123 cm^{-1}, which in the 3-methylated L^1H_2 shows only one weak band at 3122 cm^{-1}. The position and intensity of the ν(NH) and thioamide bands is helpful in determining the mode of coordination in the complexes.

The C=N stretch of the new azomethine bond in the oxime fragment of the C10–C12 complexes probably overlap with that of the Schiff base fragment, since only one strong band is observed at around 1628 cm^{-1} in their spectra. Two N–O bands (characteristic of oxime complexes) appear around 1060–1080 and 1097–1115 cm^{-1} in the spectra of complexes after transformation of the aldehyde group to oxime. A weak feature sometimes observed for oxime complexes in the region between 2300 and 2700 cm^{-1} and attributed to the hydrogen bonded fragment O–H–O, is present in the same region in complexes C10–C12.

In the C1–C3 and C13–C15 complexes the thioamide bands I, II, III and IV and ν(NH) at 3209 and 3123 cm^{-1}, remain essentially at the same position and show no change

Table 2. Electronic, EPR spectral and magnetic data

Compound	λ_{max} (nm)				EPR (g_{av})	μ_{eff} (BM)
	$\pi \rightarrow \pi^*$ (intraligand)	$n \rightarrow \pi^*$ (thioamide)	$n \rightarrow \pi^*$ (azomethine)	*d–d*		
L^1H_2	272	379	450	–	–	–
L^2H_2	270	380	444	–	–	–
C1	271	375	461	805	2.04	0.91
C2	273	374	462	820, 765, 615, 540	–	2.10
C3	270	371	454	816	-	2.70
C4	266	–	451	810	2.03	0.80
C5	267	–	455	866, 765, 615, 540, 570 sh	–	2.30
C6	262	–	452	815	–	2.60
C7	261	-	455	814	2.04	0.80
C8	265	–	450	1023, 960, 815, 766, 620, 541	–	2.20
C9	264	–	452	811	–	2.60
C10	266	–	451	806	2.04	0.80
C11	261	–	451	1021, 965, 811, 763, 619, 543	–	2.40
C12	265	–	450	815	–	2.80
C13	270	380	455	811	2.03	1.11
C14	271	381	451	822, 768, 620, 551	–	2.40
C15	273	380	454	816	–	2.72

in the intensity which rules out the possibility of the involvement of the thioamide chromophore in bonding. In the rest of the complexes, C4–C12, the thioamide bands III and IV, which have a major contribution from ν(C=S) suffer a reduction in intensity and a shift in position. A weak band replaces the two medium intensity ν(NH) bands. The thioenolization and subsequent coordination to metal ions is also supported by the absence of bands due to ν(SH) and the appearance of a new band around 610 cm^{-1} due to ν(C–S). The basic medium maintained during the preparation of these complexes might be responsible for its thioenolization process. The hydroxy bridged complexes exhibit a sharp band in the range 3480–3600 cm^{-1} which is assigned to the bridging O–H stretch on the basis of previous observations. The bridging O–H stretching band is readily distinguished from the O-H stretching bands for waters of hydration, which occurs at 3200–3300 cm^{-1}. Because of the appearance of a large number of bands due to ligands in the far-IR region, no attempts have been made to identify the M-L frequencies [14–23].

Magnetochemistry

Magnetic data are summarized in Table 2. The room temperature magnetic moments of all the complexes are far below the spin only value indicating a high degree of antiferromagnetic interaction between the metal centers.

For planar Robson-type dicopper complexes strong antiferromagnetic interactions have usually been reported. However, in several cases, especially for complexes with asymmetric ligands of distorted geometry, only weak/moderate antiferromagnetic interactions were observed. Cryomagnetic investigation down to 77 K was carried out for the complexes C4 and C13 in order to ascertain whether or not the asymmetric nature of the complexes affect the exchange coupling between the metal centers. The dominant exchange pathway, through the two oxygen bridge atoms involves interaction of the two copper $d_{x^2-y^2}$ orbitals and a 's' and 'p' orbital on the oxygen with a predominantly σ overlap. Out of plane distortions at the copper centers will, no doubt, lead to some reduction in σ overlap and hence exchange, but the effect on the exchange is likely to be small.

The best fit of the data to the Bleaney–Bowers equation (1) (using the isotropic (Heisenberg) exchange Hamiltonian, $H = -2J\hat{S}_1.\hat{S}_2$; $S = 1/2$) for exchange-coupled pairs of copper (II) ions was determined with two variable non-linear regression analyses.

$$\chi_m = \frac{N\beta^2 g^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-\rho) + \left[\frac{N\beta^2 g^2}{4kT}\right]\rho + N\alpha. \quad (1)$$

In this expression $-2J$ is the singlet-triplet splitting or exchange integral and the other terms have their usual meaning. ρ represents the fraction of a possible magnetically dilute monomeric Cu(II) impurity. The temperature independent paramagnetism $N\alpha$ was taken as 60×10^{-6} cgs units/mol for copper, and ρ was treated as a floating parameter. A typical experimental variable temperature susceptibility data and magnetic moment including the best-fit theoretical line is shown in Figure 3 for $-2J = 610(6)$ cm^{-1}, $g = 2.09$ and 580(5) cm^{-1}, 2.2 respectively. This X_mT vs T curve is typical of a strongly antiferromagnetically coupled system, as expected for a phenoxo-bridged Cu_2 dimer. The magnetic moment decreases noticeably as the temperature decreases. Because of the proximity of the two metal centers in the N_4O_2 compartment, we ascribe this magnetic behavior to an intramolecular antiferromagnetic exchange interaction propagated by the endogenous bridging oxygen atoms. The

Table 3. IR spectral data

Compound	ν(NH)	ν(C=N)	Thioamide bands				ν(C=S)
			I	II	III	IV	
C1	3209m, 3122m	1615s	1523s	1462s	1309m	975m	–
C2	3210m, 3120m	1609s	1524s	1459s	1308m	977m	–
C3	3211m, 3120m	1610s	1521s	1463s	1310m	973m	–
C4	3122w	1628br	1510m	1458m	1300w	968w	606m
C5	3120w	1629br	1515m	1455m	1301w	969w	605m
C6	3121w	1627br	1516m	1450m	1302w	968w	610m
C7	3120w	1630s	1519m	1451m	1301w	967w	612m
C8	3122w	1628s	1515m	1452m	1302w	967w	608m
C9	3123w	1631s	1516m	1453m	1301w	968w	611m
C10	3123w	1628s	1510m	1451m	1300w	969w	613m
C11	3124w	1630s	1512m	1452m	1305w	965w	608m
C12	3120w	1634s	1513m	1451m	1302w	968w	619m
C13	3213m, 3123m	1618s	1525m	1464s	1311m	969m	–
C14	3214m, 3122m	1615s	1520s	1463s	1314m	968m	–
C15	3213m, 3120m	1613s	1524s	1465s	1312m	973m	–

s = strong; m = medium; w = weak.

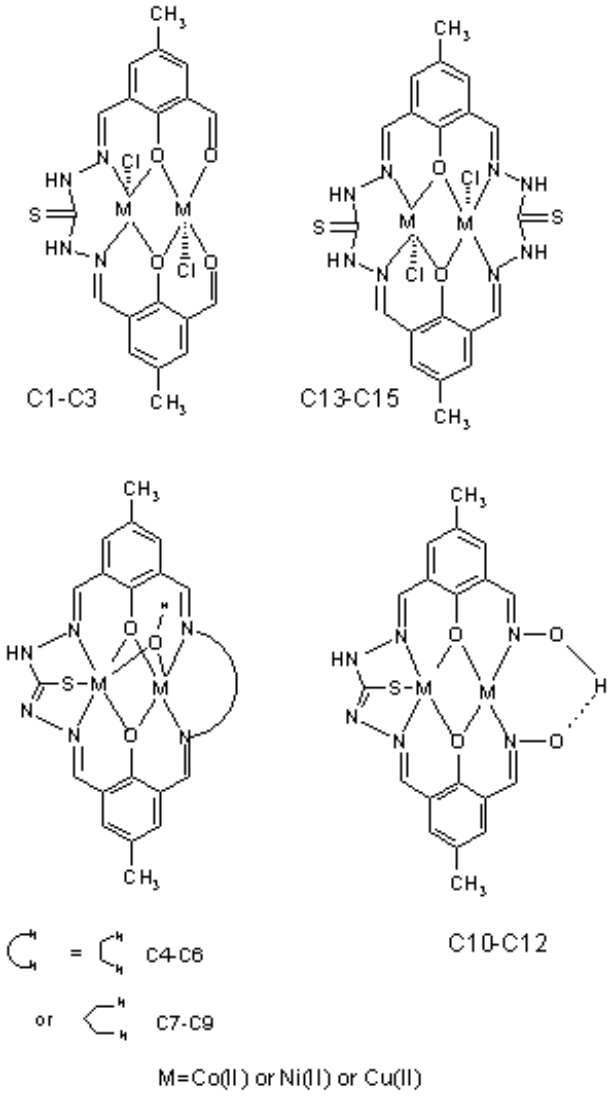


Figure 2. Structures of the complexes.

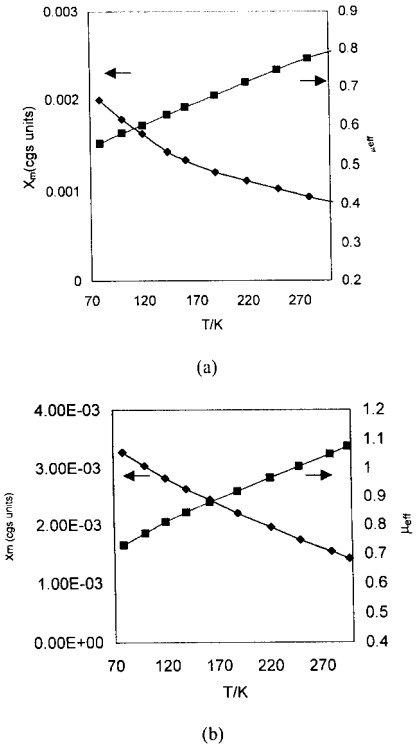


Figure 3. Molar paramagnetic susceptibility per binuclear Cu(II) and effective magnetic moment per Cu(II) ion vs. temperature for (a) C4 (b) C13. The solid line results from least squares fit to the theoretical equation (1) given in the text.

discrepancy factor $\sigma = [\sum(\chi_{obs} - \chi_{calc})^2 / \sum \chi_{obs}]^{1/2}$ in the least-squares fits was 1.9×10^{-3} [24-29].

FAB mass spectral and thermal studies

The molecular ion peak at around *m/z* 598 and 586 in the FAB mass spectra of the complexes C1 and C10 suggests the formation of dinuclear complexes.

Table 4. Results of antimicrobial activity screening[a]

Compound	Zone of Inhibition (mm)			
	Antibacterial		Antifungal	
	Pa[b]	Ba	An	Ca
L^1H_2	32	31	>40	>40
L^2H_2	30	30	>40	>40
C1	31	32	>40	>40
C2	32	33	>40	>40
C3	30	33	>40	>40
C4	33	35	30	37
C5	30	33	30	38
C6	33	31	31	33
C7	35	32	29	35
C8	30	32	28	35
C9	33	35	28	31
C10	31	26	27	33
C11	35	31	30	32
C12	32	35	30	32
C13	22	34	>40	>40
C14	20	25	>40	>40
C15	21	24	>40	>40
Norfloxin	32	32	–	–
Miconazole nitrate	–	–	30	30

[a]Concentration of compound is 1 mg/mL in DMF.
[b]Organisms; Pa = *Pseudomonas auregenosa*; Bc = *Bacillus cirroflagellosus*; An = *Aspergillus niger*; Ca = *Candida albicana*.

Thermal studies have been carried out in the 25 to 800 °C temperature range under a N_2 atmosphere in order to ascertain whether or not the water molecules are coordinated. The complexes under study, C7 and C10, initially lose weight between 50 to 100 °C, which corresponds to two water molecules, confirming the presence of non-coordinated water molecules. The dehydrated complexes decompose in a single step leaving behind a stable CuO residue above 600 °C.

Biological activity

The antimicrobial activities of compounds were assessed by the cup-plate method [30]. The results of the inhibitory activity of the ligand and its complexes on a few species of bacteria (*Pseudomonas auregenosa* and *Bacillus cirroflagellous*) and fungi (*Aspergillus niger* and *Candida albicana*) show that the free ligands and their complexes have a pronounced inhibitory effect on fungi (Table 4).

Conclusion

In order to develop certain classes of models for biological systems, it is highly useful to have access to functional groups appended to macrocyclic ligands. These functional groups (like $>NH_2$, >C=O, >C=S etc.) provide points of attachment for a ligand designed to facilitate certain biomimetic properties in the complexes of the product ligands. Keeping toxophoric functional groups out of the coordination sphere was probably responsible for the striking fungistatic action observed in the present investigation of the C1–C3 and C13–C15 complexes. The fungistatic action was so high, that a zone of inhibition could not be measured as the fungus was completely destroyed. The strong antiferromagnetic interaction observed is promising towards its applicability as biomimics for the 'type 3' copper proteins.

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