Architecture of a Novel Binucleating SNONS Compartmental Ligand: Physico-Chemical Investigation of Its Metal Complexes

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The preparation of a novel pentadentate binucleating compartmental ligand, 2-hydroxy-5-methylisophthalaldehyde bis(*p*-methoxy thiobenzoylhydrazone), is described together with the corresponding chloro-bridged cobalt(II), nickel(II), copper(II) and zinc(II) complexes, which were characterized based on spectral, magnetic, thermal and electrochemical studies. Cryomagnetic investigations (77–296 K) reveal a strong antiferromagnetic spin-exchange between the copper(II) ions (J based on $H = -2J\hat{S}_1 . \hat{S}_2$ is 305 cm^{-1}). An electrochemical study of the copper(II) complex shows two distinct quasi-reversible redox peaks ($E^1{}_{1/2} = -0.4$ and $E^2{}_{1/2} = -0.69$ V vs saturated calomel electrode), indicating a stepwise reduction of the copper centers ($Cu^{II}Cu^{II} \rightarrow Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I} \rightarrow Cu^{I}Cu^{I}$). The EPR spectrum is typical of a "rhombic compressed local molecular environment". The ligand and its copper and zinc complexes exhibit fluorescence at room temperature in DMF. All of the compounds under study were screened for antimicrobial action.

Accelerated progress and developments in the field of bioinorganic chemistry have stimulated the study of model systems for copper protein. A number of multicopper proteins have proven to contain pairs of copper atoms, which in the copper(II) ion form are strongly antiferromagnetically coupled. The better known examples include tyrosinase, hemocyanin, laccase, ceruloplasmin, and ascorbate oxidase. The copper(II) ions bound in this manner within the protein are commonly referred to "type 3" coppers. There may be significant differences between the structural details of "type 3" coppers from one metallo enzyme to another, as evidenced by differences in the chemical reactivity of the resting oxidation state of the deoxyenzymes.[1–6]

It is clear that low-molecular-weight copper(II) complexes are not adequate models for the reactivity and specificity of enzymes. However, as mimics for certain chemical and physical properties, they may be able to furnish useful clues to the origin of the metal-based enzyme activity. In mimicking the properties of the "type 3" coppers, most obviously the low-molecular-weight compounds should contain two strongly coupled copper(II) ions, preferably exhibiting no EPR signal at or near room temperature. They should also undergo two-electron reversible reduction at relatively high potentials.[7]

The active sites in a number of metalloproteins have been proposed or demonstrated to be (μ-oxo) bimetal units. A set of model complexes has been developed containing a bridging oxygen atom in these species, which facilitates cooperation between the two metal centers by maintaining them in close, but nonbonded, proximity. Alkoxide or phenoxide bridges are particularly advantageous in these model complexes, since they can be incorporated into a large polydentate ligand, which then inhibits dissociation of the two metal centers. Robson's Schiff-base ligands are one such a class of phenolate-bridged, polydentate ligands, which were developed to provide three chelating coordination sites per metal in their nonmacrocyclic form. Although bimetallic complexes of these ligands were initially designed for N_2 fixation, their ability to bind and activate a variety of small substances was quickly recognized and exploited.[8–11]

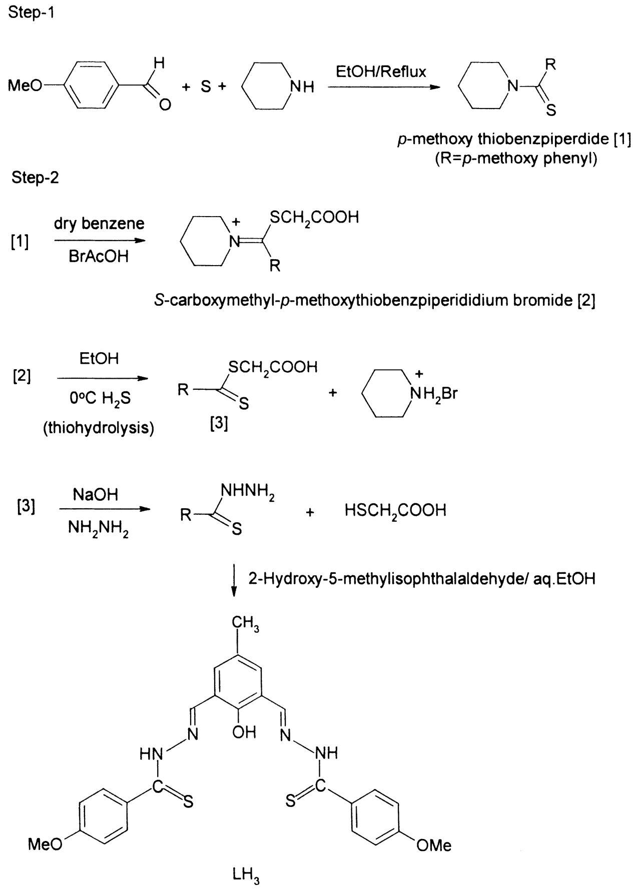
In a continuation of our work[12] on a novel class of binucleating ligands, termed "thiobenzolyhydrazone", based on a 2-hydroxy-5-methylisophthalaldehyde head unit and thiohydrazide side arms, we present here a new analogous binucleating ligand and its few 3d metal chelates which exhibit interesting spectral, magnetic and redox properties and display significant antimicrobial action.

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 the calibrant. The magnetic susceptibility on powdered samples of the complexes was measured over the temperature range 77–300 K using a PAR model 155 vibrating sample magnetometer; the instrument was calibrated using metallic nickel. Electronic spectra were recorded on a Hitachi 2001 spectrophotometer in a DMF solution. IR spectra were recorded in the 4000–400 cm^{-1} region (KBr disc) on a Nicolet 170 SX FT-IR spectrometer. Far IR spectra were recorded in the 500–100 cm^{-1} region (polyethylene disc) on a Bruker IFS66V spectrometer. ^{1}H NMR spectra were obtained in d_6-DMSO using TMS as an internal reference on a JEOL GX-400 NMR spectrometer. Conduc-

Table 1. Analytical Data of Ligand and Its Metal Complexes

Compound	Empirical formula	Found (Calculated)/%					
		C	H	N	S	M	Cl
LH_3	$C_{25}H_{24}N_4O_3S_2$	60.99 (60.95)	4.88 (4.91)	11.39 (11.37)	13.09 (13.02)	—	—
$[Co_2ClL(H_2O)_4]$	$[Co_2Cl(C_{25}H_{21}N_4O_3S_2)$-$(H_2O)_4]$	42.07 (42.00)	4.11 (4.09)	7.89 (7.84)	8.95 (8.97)	16.52 (16.49)	4.92 (4.96)
$[Ni_2Cl_2LH](H_2O)_3$	$[Ni_2Cl_2(C_{25}H_{22}N_4O_3S_2)]$-$(H_2O)_3$	40.88 (40.97)	3.81 (3.85)	7.59 (7.64)	8.77 (8.75)	16.08 (16.02)	9.60 (9.67)
$[Cu_2ClL(H_2O)_2](H_2O)_2$	$[Cu_2Cl(C_{25}H_{21}N_4O_3S_2)]$-$(H_2O)_4$	41.55 (41.46)	4.10 (4.04)	7.78 (7.74)	8.89 (8.86)	17.52 (17.55)	4.82 (4.90)
$[Zn_2ClL]$	$[Zn_2Cl(C_{25}H_{21}N_4O_3S_2)]$	45.82 (45.79)	3.27 (3.23)	8.48 (8.54)	9.72 (9.78)	19.91 (19.94)	5.47 (5.41)



Scheme 1.

Table 2. Magnetic and Electronic Spectral Data

Compound	λ_{max}/nm	μ_{eff}[a] (B. M)
LH_3	480, 292, 262	—
$[Co_2ClL(H_2O)_4]$	476, 300, 262	3.02
$[Ni_2Cl_2LH](H_2O)_3$	435, 311, 257	2.21
$[Cu_2ClL(H_2O)_2](H_2O)_2$	450, 315, 258	0.99
$[Zn_2ClL]$	444, 312, 260	—

a) per metal ion.

tance measurements were made in DMF (10^{-3} M) using an 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 an N_2 atmosphere. The EPR spectrum of a polycrystalline sample was recorded at room temperature on a Varian E-4 X-band spectrometer using TCNE as a $<g>$ marker. The FAB mass spectrum was recorded on a JEOL EX 102/DA-6000 mass spectrometer using Ar as the FAB gas. *m*-Nitrobenzyl alcohol (NBA) was used as the matrix. Electrochemical measurements were performed at room temperature in DMSO under O_2-free conditions using an Optoprecision potentiostat. A three-electrode assembly comprising a graphite-working electrode, a Pt auxiliary electrode and a saturated calomel reference electrode (SCE) were used. The supporting electrolyte was $N(Et)_4Cl$ with a 0.1 M concentration and a sample concentration of 0.001 M. A fluorescence study was carried out on an F-2000 Hitachi Fluorescence spectrometer.

Preparation of Ligand. 2-Hydroxy-5-methylisophthalaldehyde was prepared by a slight modification of a literature method.[13] A number of potential methods for preparing thiobenzoylhydrazine are available in the literature. The reaction between carboxymethyl dithioate and hydrazine has proved to be most convenient.[14] The thiohydrolysis of *S*-carboxymethyl-*p*-methoxythiobenzpiperidinium bromide in abs EtOH provides a 60% yield of carboxymethyl *p*-methoxydithiobenzoate, which with diluted hydrazinehydrate in NaOH gave the required thiohydrazide. The sequence of steps for its synthesis is shown in Scheme 1.

2-Hydroxy-5-methylisophthalaldehyde Bis(*p*-methoxy thiobenzoylhydrazone). Thiobenzolyhydrazine (3.28 g, 0.02 mol) and *2-hydroxy-5-methylisophthalaldehyde* (1.64 g, 0.01 mol) in 50% EtOH (50 cm^3) were refluxed for 1 h. The pale-yellow precipitate, which separated, was collected by filtration, washed with EtOH and dried. Mp 180 °C, Yield 85%, MS *m*/*z* 491, ^{1}H NMR (DMSO-d_6) δ 2.25 (s, 3H, $-CH_3$), 6.9–8.2 (m, 10H, aromatic), 3.8 (s, 6H, $-OCH_3$), 8.46 (s, 2H, H–C=N), 12.5 (s, OH, D_2O exchange), 13.5 (s, NH, D_2O exchange).

Preparation of Complexes. An EtOH solution (30 cm^3) of metal chloride (20 mmol) was added dropwise with stirring to an EtOH solution (50 cm^3) of the ligand (10 mmol) and the mixture was refluxed for 2 h. The resulting complexes were filtered off, washed with EtOH and dried in vacuo. Mp > 250 °C, Yield 80–85%. ^{1}H NMR for Zn complex (DMSO-d_6) δ 2.2 (s, 3H, $-CH_3$), 6.7–8.3 (m, 10H, aromatic), 3.85 (s, 6H, $-OCH_3$), 8.9 (s, 2H, H–C=N).

Results and Discussion

All of the complexes have a $[M_2L]$ stoichiometry in which the ligand has lost two/three protons. They are insoluble in H_2O, EtOH and MeOH, but soluble in organic solvents, such as DMF, DMSO and MeCN. Analytical data are presented in Table 1. The molar conductivities in DMF suggest that all of the complexes are nonelectrolytes.

Magnetic and Electronic Spectral Studies. Magnetic

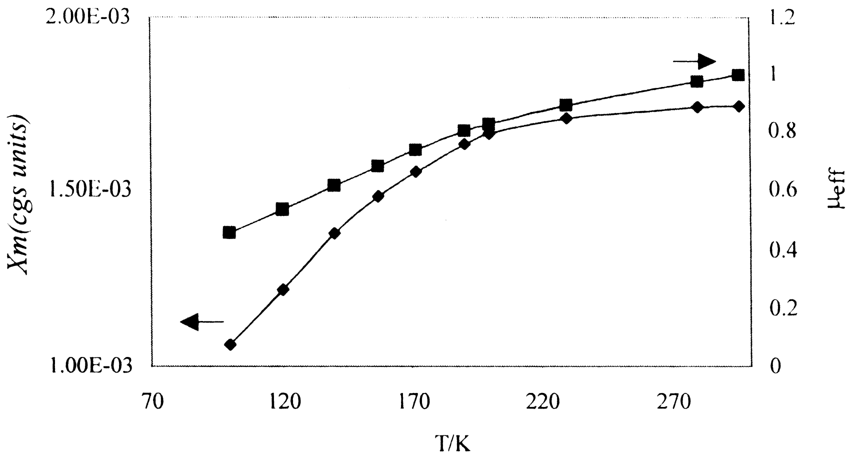


Fig. 1. Molar paramagnetic susceptibility per binuclear copper(II) and effective magnetic moment per copper(II) ion vs temperature. The solid line results from least squares fit to the theoretical Eq. 1 given in the text.

Table 3. Major IR Bands

Compound	ν(NH)	ν(C=N)	Thioamide bands I	II	III	IV	ν(C–S)
LH_3	3296*m*	1601*s*	1505*s*	1458*s*	1308*s*	961*br*	—
$[Co_2ClL(H_2O)_4]$	—	1602*s*	1507*s*	1481*m*	1307*m*	950*br*	610*m*
$[Ni_2Cl_2LH](H_2O)_3$	3250*w*	1618*s*	1505*s*	1449*m*	1308*m*	962*br*	608*w*
$[Cu_2ClL(H_2O)_2](H_2O)_2$	—	1597*s*	1510*s*	1440*m*	1307*m*	960*br*	606*s*
$[Zn_2ClL]$	—	1596*s*	1512*s*	1444*m*	1310*m*	955*m*	612*m*

and electronic spectral 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.

A variable-temperature magnetic-susceptibility measurement was performed on a powdered sample of copper complex in the temperature range 77–300 K. The best fit of the data to the Bleaney–Bowers Eq. 1[15] (using isotropic (Heisenberg) exchange Hamiltonian, $H = -2J\hat{S}_1 . \hat{S}_2$; $S = 1/2$), for exchange-coupled pairs of copper(II) ions was obtained with two variable nonlinear regression analyses:

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

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 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 Fig. 1 for $-2J = 610$ cm^{-1} and $g = 2.09$. This X_mT vs T curve is typical of a strongly antiferromagnetically coupled system, as expected for a phenoxo-bridged Cu_2 dimer.[16–20] The magnetic moment decreases noticeably as the temperature decreases. Because of the proximity of the two metal centers in the SNONS compartment, we describe this magnetic behaviour in large part as being an intramolecular antiferromagnetic exchange interaction. This interaction is likely to be propagated by the endogenous bridging oxygen atom, and to a lesser extent by exogenous bridging chloride, but not via a direct metal–metal interaction.[21–24] The discrepancy factor,

$$\sigma = \left[\sum(\chi_{obs} - \chi_{calc})^2 / \sum \chi_{obs}\right]^{1/2},$$

in the least-square fits was 1.6×10^{-3}.

In the electronic spectrum of ligand, bands below 257 nm are due to intra-ligand transitions. These bands are almost unchanged in all complexes. The maxima at 298 and 480 nm are due to n–π* transitions associated with the azomethine linkage and the thioamide chromophore, respectively. The band due to azomethine linkage has undergone a bathochromic shift in all of the complexes due to the donation of a lone pair of electrons to the metal, and hence the coordination of azomethine. The thioamide band suffers a blue shift in the complexes due to thioenolization; this band broadens considerably, probably due to the overlap of the S→M(II) ligand-to-metal charge-transfer transition (LMCT). The ligand absorption tails into the visible region, and tends to obscure contiguous weaker d–d transitions.[25–31]

Fluorescence Study. Generally, phenolic derivatives, or molecules having highly conjugated chromophores, show fluorescence. The ligand LH_3 (λ_{max} 415; λ_{emis} 520; emission intensity 265) shows enhanced fluorescence intensity upon complexation with copper (emission intensity, 870) and zinc (emission intensity, 4300) ions. The emission is neither MLCT (metal-to-ligand charge transfer) nor LMCT in nature. We ten-

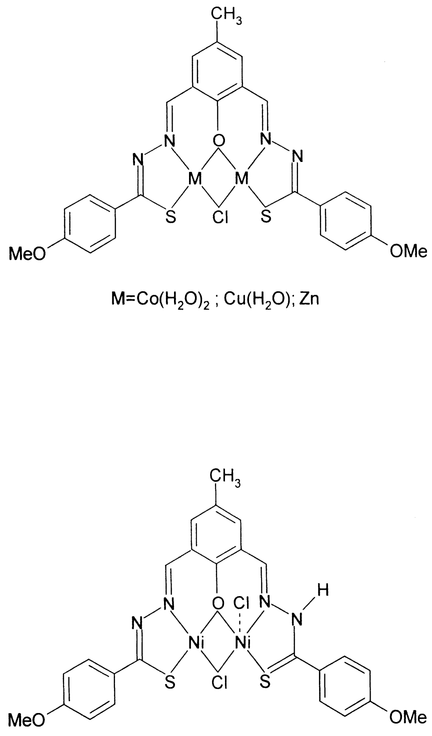


Fig. 2. Structures of the complexes.

tatively assign it to intra-ligand (π–π^*) fluorescence, since a similar emission is also observed for the free ligand, but with reduced intensity. It is known that lone pairs of electrons on nitrogen and thioamide chromophore can quench the fluorescence of the ligand through photo-induced electron transfer. The draining of electrons out of these pairs onto the metal orbital via complex formation causes a suppression of this fluorescence quenching, and therefore results in an increase in the fluorescence intensity. The formation of metal chelates generally also promotes fluorescence by promoting rigidity and minimizing internal vibrations. That a copper complex is less fluorescent compared to a zinc complex can be explained based on the idea that paramagnetic ions generally quench the fluorescence intensity. At higher concentrations the fluorescence intensity decreases considerably due to self-quenching in all compounds.[32–34]

Infrared Spectra. Pertinent IR absorption bands are listed in Table 3. The spectrum of the free ligand shows a band of medium intensity at 3296 cm^{-1}, which is assigned to ν(NH). The absence of any band in the 2400–2500 cm^{-1} region, due to ν(SH) confirms that the ligand exists in the thioxo form, which is further supported by ^{1}H NMR studies.[35] The broad band due to ν(OH), around 3400 cm^{-1}, for the free ligand is absent in the spectra of the complexes, suggesting deprotonation of the phenolic oxygen upon coordination. The sharp band at 1601 cm^{-1} assigned to ν(C=N) in the free ligand is shifted to higher energy or lower energy in the spectra of complexes, suggesting coordination of both azomethine nitrogens to the metal.

Vibrational coupling among the components of the thioamide chromophore are distributed in the fingerprint region at around 1505, 1458, 1308 and 961 cm^{-1}, and are assigned to I [β(NH) + ν(CN)], II [ν(CN) + β(NH)], III and IV respectively.

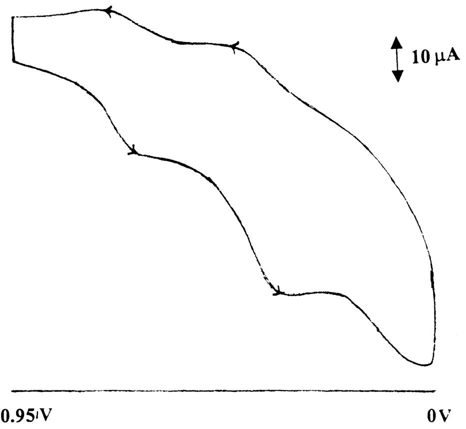


Fig. 3. Cyclic voltammogram of copper(II) complex (in DMSO), at scan rate of 0.075 1/4 V s^{-1}.

The shift of these bands in complexes supports the involvement of the thioamide chromophore in bonding. There has been great uncertainty regarding the assignment of the C=S stretching frequency in nitrogen-containing compounds. The extreme variation in the assignment of the C=S stretching frequency in nitrogen containing thiocarbonyl derivatives is undoubtedly due to vibrational coupling effects. In most systems containing the thioamide group the C=S stretching is not localized. Frequencies ranging from 850 to 1550 cm^{-1} have been attributed to the C=S vibrations in the literature.[36–46]

In the copper complex, the ν(NH) band disappears completely, and there appears a strong band at 606 cm^{-1} assigned to ν(C-S). The thioamide bands III and IV, which have a major contribution from ν(C=S), appear with reduced intensity. These observations indicate the involvement of thioxo sulfur in coordination to metal via thioenolization. A similar observation has also been made for zinc and cobalt complexes. In a nickel complex, there exists thione-thiol tautomerism (Fig. 2). The lowering of the intensity of the ν(NH) band at 3400 cm^{-1} suggests that only one –NH group is deprotonated, and not both. A weak band around 610 cm^{-1} indicates the presence of ν(C–S). Such a type of dibasic nature of the ligand is pH dependent. The broad band around 3510–3455 cm^{-1} in copper(II), nickel(II), and cobalt(II) complexes can be assigned to ν(OH) of lattice or coordinated water molecules. The presence of water molecules has been confirmed by TG studies. The low-frequency bands in the 500–470, 412–350 and 370–292 cm^{-1} regions are assigned to ν(M–N), ν(M–O) and ν(M–S), respectively. The presence of a chloro bridge is evident from the IR band in the 270–240 cm^{-1} region.[47]

Electrochemistry. The electrochemical behavior of the copper(II) complex was studied over the potential range from 0 to -0.95 V in DMSO containing 0.1 M N(Et)$_4$Cl; the voltammogram is depicted in Fig. 3. Two separate quasi-reversible reduction waves were observed, with half-wave potentials of $E_{1/2}{}^{1} = -0.4$ V for Cu^{II}Cu^{II}/Cu^{II}Cu^{I} couple and $E_{1/2}{}^{2} = -0.69$ V for a Cu^{II}Cu^{I}/Cu^{I}Cu^{I} couple, respectively. Neither the ligand nor its zinc complex shows any electrochemical response over the working potential range. The overall two-electron exchanges appear to be separate one-electron processes, indicating that a reduction at one site induces a steric influence on the

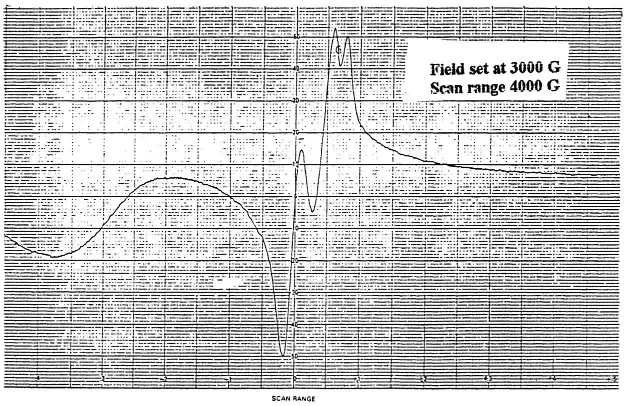


Fig. 4. EPR spectrum of copper(II) complex.

other site. Patterson and Holm compared the reduction potentials of a series of neutral copper(II) chelates with potentials for "blue" copper sites in proteins. Molecules that contain two or more chemically equivalent and reversible redox sites exhibit electrochemistry, which is dictated by the thermodynamic relationships between various molecular redox states. This subject has been examined in the literature both theoretically and experimentally. For the case of a molecule with two sites, the reduction potentials and the conproportionation constant, K_{con}, are related in the following ways:

$$\mathrm{Ox-Ox} + \mathrm{e}^- \xrightleftharpoons{E_1^{\mathrm{f}}} \mathrm{Ox-Red},$$

$$\mathrm{Ox-Red} + \mathrm{e}^- \xrightleftharpoons{E_2^{\mathrm{f}}} \mathrm{Red-Red},$$

$$\mathrm{Ox-Ox} + \mathrm{Red-Red} \xrightleftharpoons{K_{\mathrm{con}}} 2(\mathrm{Ox-Red}),$$

$$E_1^{\mathrm{f}} - E_2^{\mathrm{f}} = 0.0591 \log k_{\mathrm{con}}.$$

The large difference between the observed redox potentials [$\Delta E = E_{1/2}{}^1 - E_{1/2}{}^2$] (290 mV) indicates considerable stability of the mixed-valence species (8×10^4). For dicopper complexes with symmetrical ligands, the conproportionation constant has been suggested to be a measure of the electron delocalization in a mixed-valence complex.

The irreversibility of redox processes in metal complexes in electrochemical experiments is attributable to changes in the coordination geometry or coordination number (e.g. solvent coordination/dissociation) upon a change of the oxidation state, or even to an expulsion of metal ions from the coordination sphere.

Due to the different preferred coordination polyhedra by $\mathrm{Cu^I}$ and $\mathrm{Cu^{II}}$, it is further expected that considerable changes in the coordination geometry would occur due to a redox process. The association of solvent (DMSO) is not unlikely because of its high binding tendency towards $\mathrm{Cu^I}$. On the whole, it can be postulated that the structure of the $\mathrm{Cu^ICu^I}$ species (or even the $\mathrm{Cu^ICu^{II}}$ species) differs notably from that of the original $\mathrm{Cu^{II}Cu^{II}}$ complex. Considerable structural changes occur again upon reoxidation. However, a reassociation to the original chloro bridged copper(II) complex is most unlikely. Therefore, the chance for a combination of reoxidised $\mathrm{Cu^{II}Cu^{II}}$ species with the previously dissociated chloro bridge within the cyclic voltammetric experiment is extremely low. This assumption has been confirmed by the fact that in a second scan the shape and position of the reduction peak changed. The structural reorganization accompanying a redox change should essentially affect the kinetics of the heterogeneous electron-transfer process. According to the Marcus theory, inner-sphere rearrangements, enhancing the activation barrier of the electron transfer, slow down the rate of process, thus causing a departure from electrochemical reversibility. However, Gray has elegantly pointed out that the lower is the reorganization following a redox change in copper complexes, the more positive is its thermodynamic redox potential.[48–56]

EPR Studies. The EPR spectrum (Fig. 4) of a polycrystalline sample at room temperature exhibits absorption typical of a rhombic compressed local molecular environment ($g_1 = 1.96$; $g_2 = 2.09$; $g_3 = 2.22$; $g_{\mathrm{av}} = 2.09$). The spectrum shows evidence of magnetic exchange coupling between the metal centers. The broad band at 1500 G is assigned to the $\Delta M_{\mathrm{s}} = \pm 2$ transition arising from the coupling between $s = 1/2$ metal ions ($g = 4.35$).

FAB Mass Spectral and Thermal Studies. The elemental and analytical data of the copper complex suggests the empirical formula [$\mathrm{Cu_2ClL}$], which is supported by the FAB mass spectrum. Although the peaks at the highest m/z value cannot always be assigned with certainty, the isotopic pattern is consistent with a binuclear complex. A peak at m/z 593 was observed, corresponding to the mass of the entire dehydrated binuclear complex.

In the copper complex, two lattice and two coordinated water molecules are lost in the initial decomposition stage between 25–160 °C. The dehydrated complex then decomposes in one step with three different rates, leaving behind a stable CuO residue above 540 °C. The cobalt complex follows the same type of decomposition pattern after an initial loss of four coordinated water molecules between 110–175 °C; the residue obtained above 520 °C was analyzed as $\mathrm{Co_3O_4}$. In the nickel complex, the initial weight loss occurs up to 135 °C, which corresponds to a loss of three lattice water molecules. The complex is stable after the expulsion of chloride at 135–225 °C. The complex then completely decomposes in two steps. A residue obtained above 600 °C was found to be NiO. The weight losses from the TG agree well with theoretical calculations.

Biological Activity. The antimicrobial activities of compounds were assessed by the cup-plate method.[57] The results concerning the inhibitory activity of the ligand and its complexes on few species of bacteria (*Pseudomonas auregenosa* and *Bacillus cirroflagellous*) and fungi (*Aspgergillus niger* and *Candida albicana*) show that the free ligand and its copper and zinc complexes have a pronounced inhibitory effect on fungi.

Conclusion

There has recently been considerable discussions about the desirability of copper sites in proteins being able to accommodate both Cu(II) in its preferred square-planar and Cu(I) in its preferred tetrahedral environments. It is thought that intermediate or flexible geometries would facilitate electron transfer in

Cu(II)-Cu(I) processes. Therefore, it is possible that the molecule distorts upon going from Cu(II)-Cu(II) to Cu(I)-Cu(I). The designed ligand is flexible enough to accommodate these geometries.

While the magnetic property of our newly designed complexes has shown relevance to biological systems, there are a few differences. The reduction potentials of the "type 3" copper determined by chemical redox titrations are quite positive, and are single-potential two-electron transfers. Although the binuclear copper(II) complex discussed in our present study displays a quite positive reduction potential, it involves sequential one-electron reductions, and displays a well-defined EPR signal with a magnetic moment of 0.99 B.M at room temperature. As a result of these differences, the copper complex of the LH_3 ligand may not be a good mimic for the reactivity of the enzymatic copper. Part of our emphasis in future research will be to design complexes with the same/similar ligand(s) with varied substituents on the phenyl ring, enforcing both geometrical and electronic constraint so that we might end up with highly coupled system(s), hopefully exhibiting multielectron transfer at a single more positive reduction potential. Obviously, such complexes would be much better mimics for "type 3" coppers.

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