

Synthesis and Characterization of Copper(II) Metal(II) Binuclear Complexes of *N,N'*-Bis(8-hydroxyquinoline-7-carboxaldene)-1,3-diaminopropane

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Abstract

The magnetic, spectral and electrochemical properties of the homobinuclear copper(II) complex of *N,N'*-bis(8-hydroxyquinoline-7-carboxaldene)-1,3-diaminopropane (H_2L) and its binuclear complexes, Cu–Co, Cu–Ni, Cu–Cu, Cu–Zn, Cu–Cd and Cu–Hg are reported. The electronic spectral data show that the d–d transitional bands of the CuN_2O_2 chromophore in $[CuLM](ClO_4)_2 \cdot nH_2O$ are blue shifted in the order, $M = Ni^{2+} > Co^{2+} > Zn^{2+} > Cd^{2+} > Hg^{2+}$, relative to the mononuclear $[CuL] \cdot 3H_2O$. This suggests that the CuN_2O_2 chromophore becomes more planar when $[CuL] \cdot 3H_2O$ is coordinated to the second metal ion M. IR data suggests that H_2L acts as tetradentate in $[CuL] \cdot 3H_2O$ and $[CuLM(OAc)_2] \cdot nH_2O$ but hexadentate in $[CuLM](ClO_4)_2 \cdot nH_2O$. Thermal analysis indicates that the water molecules are of crystallization in $[CuLM](ClO_4)_2 \cdot nH_2O$ but of crystallization and hydrogen bonded in the other complexes. Magnetic data in the temperature 5–300 K range show a strong antiferromagnetic interaction in $[CuLM](ClO_4)_2 \cdot nH_2O$, $M = Co^{2+}$ or Cu^{2+} with $-J = 112$ and 229 cm^{-1} , respectively. The redox potentials of Cu(II)/Cu(I) in the heterobinuclear complexes are found to be around 1.055 V versus NHE which is almost the same as in the mononuclear complex. This behaviour has been discussed in terms of electronic and structural effects.

Introduction

There is growing interest in electrochemical, magnetic and spectroscopic studies on multimetallic complexes [1–17]. This is because of their importance in inorganic chemistry. They are ubiquitous in nature as active sites in a variety of metalloenzymes and are playing a significant role in industrial catalysis. Furthermore, these types of metal

complexes can provide interesting cases for the study of magnetic interaction. In addition, they may also serve as models in certain cases for some metalloproteins for which the biological function is associated with the occurrence of the metal centers in pairs. In this work, we report the synthesis and characterization of the new binucleating agent, *N,N'*-bis(8-hydroxyquinoline-7-carboxaldene)-1,3-diaminopropane and its homobinuclear copper complex as well as some heterobinuclear Cu–Co, Cu–Ni, Cu–Zn, Cu–Cd and Cu–Hg complexes.

Experimental

All reagents were purchased from commercial sources and used without further purification. *N,N'*-Dimethylformamide (DMF) was distilled over molecular sieves and anhydrous $MgSO_4$ prior to use.

Preparation of the Organic Compound

8-Hydroxyquinoline-7-carboxaldehyde was prepared as previously reported [18]. *N,N'*-bis(8-hydroxyquinoline-7-carboxaldene)-1,3-diaminopropane (H_2L) was prepared as follows. To a methanolic solution of 1,3-diaminopropane (0.01 mol), solid 8-hydroxyquinoline-7-carboxaldehyde (0.02 mol) was added. The resulting solution was stirred for 30 min at $-5 \pm 2^\circ C$. The reaction mixture was then kept at room temperature for another hour and the solid formed was filtered and recrystallized from methanol. Yield 83%, melting point (m.p.) $208 \pm 1^\circ C$.

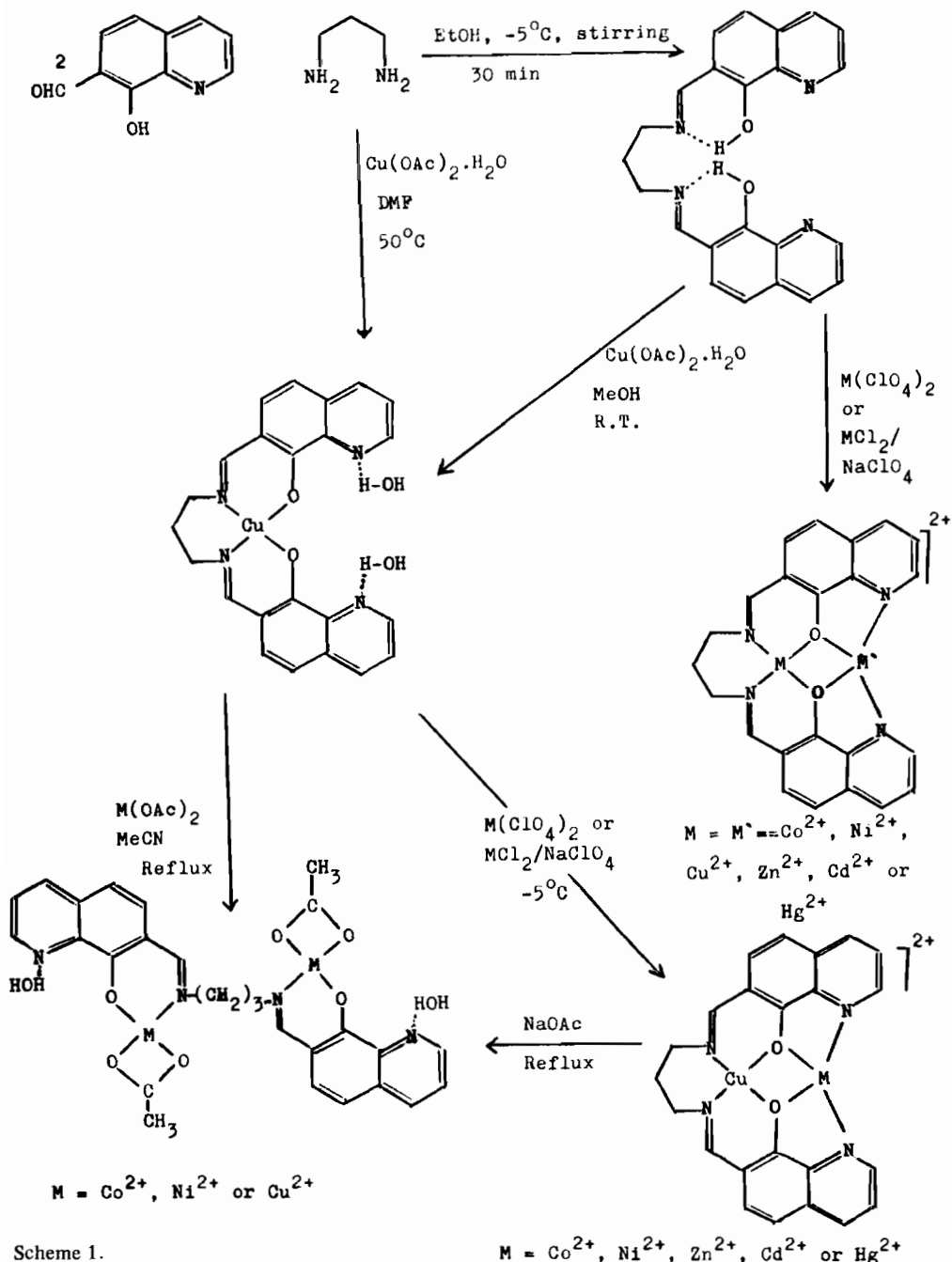
Preparation of the Complexes

All complexes were prepared either by using a template synthesis without previous separation of the ligand (H_2L) or by using the separated pure ligand (H_2L). In both methods, the mononuclear copper(II) complex was isolated first as shown in Scheme 1.

$[CuL] \cdot 3H_2O$

Method A. To a warm solution of 8-hydroxyquinoline-7-carboxaldehyde (0.01 mol) in DMF (50 ml) was added 1,3-diaminopropane (0.005 mol)

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Scheme 1.

dropwise with stirring followed by the addition of solid $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$ (0.005 mol). The solution was maintained hot at 50°C and stirred until all the $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$ had dissolved. The stirring was continued at the same temperature for a further 2 h. After this period and on cooling to room temperature, the olive green crystalline solid formed was filtered, washed several times with ethanol and dried *in vacuo*. Yield 72%.

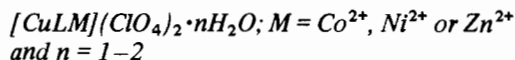
Method B. To the methanolic solution of H_2L (0.001 mol) a solution of $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$ (0.001

mol) in methanol was added. The reaction mixture was stirred at room temperature for 3 h. Then the solvent was removed under reduced pressure and the resulting olive green solid was washed several times with water, filtered and washed with diethyl ether and dried *in vacuo*. Yield 84%.

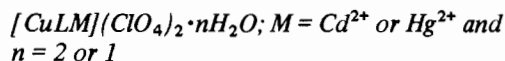


Solid $[\text{CuL}] \cdot 3\text{H}_2\text{O}$ (0.005 mol) was added to an ethanolic solution of $\text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.005 mol). The reaction mixture was stirred at 60°C for

30 min. After cooling to room temperature, the green crystalline solid formed was filtered off, washed with ethanol followed by diethyl ether and dried *in vacuo*. Yield 92%.

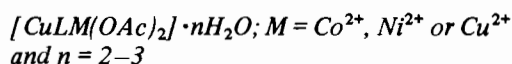


These complexes were prepared by the general method, viz. to an ethanolic solution of hydrated $\text{M}(\text{ClO}_4)_2$ (0.005 mol) at $-5 \pm 2^\circ\text{C}$, was added $[\text{CuL}] \cdot 3\text{H}_2\text{O}$ (0.005 mol) under N_2 (in the case of Ni^{2+} and Co^{2+}). The solution was stirred at the same temperature for no more than 25–30 min and the formed solid in each case was filtered off, washed with ethanol followed by diethyl ether and dried *in vacuo*. Yield 82–68%.



To absolute dry ethanol (50 ml) at $-5 \pm 3^\circ\text{C}$ was added MCl_2 , $M = \text{Cd}^{2+}$ or Hg^{2+} (0.005 mol). To this solution, solid $[\text{CuL}] \cdot 3\text{H}_2\text{O}$ (0.005 mol) and NaClO_4 (0.01 mol) were added with stirring for 5–10 min. The immediately formed crystalline solid in each case was filtered, washed with ethanol followed by diethyl ether and dried *in vacuo*. Yield 77–68%.

All binuclear complexes could be prepared by the addition of the appropriate metal(II) salt to the solution containing the aldehyde, diamine and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ keeping the temperature at -5°C . In this case the product was very low and not pure. By application of column chromatograph separation to the product mixture, compounds of the formulae $[\text{CuLM}]^{2+}$, $[\text{M}_2\text{L}]^{2+}$ and other unknown compounds were obtained.



These were prepared by the addition of solid hydrated $\text{M}(\text{OAc})_2$ (0.005 mol) to 100 ml of MeCN solution of $[\text{CuL}] \cdot 3\text{H}_2\text{O}$ (0.005 mol). The reaction mixture was heated to reflux for 3–4 h, then left to cool at room temperature. The product was filtered off, washed thoroughly with diethyl ether and dried *in vacuo*. Yield 68–87%.

The same products could be obtained on boiling $[\text{CuLM}](\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ in ethanol in the presence of NaOAc as given in Scheme 1.

Elemental analyses were performed by the Mikro-analytisches Labor Pascher, Busch-Strasse 54, F.R.G. Electronic spectra were measured by using a Pye Unicam SP8-400 spectrophotometer. IR spectra were taken as KBr discs by using a Pye Unicam SP3-300 spectrophotometer. Magnetic susceptibilities were measured by the Faraday method at room temperature and in the temperature 5–300 K range as given before [19–21]. The molar conductivity

was measured for 10^{-3} M DMF solutions at 25°C as reported previously [19–21]. Thermal analysis was carried out as described before [21]. Electrochemical data were taken with a Par Model 174 polarographic analyzer connected to a X-Y Omni-graphic Model 2000 recorder. Differential pulse polarography (DP) and cyclic voltammetry (CV) were recorded in a cell containing a platinum working electrode. DMF was used as solvent in all measurements and all redox potentials were corrected by the use of ferrocene as internal standard [22], where the ferrocene/ferricinium(+1) oxidation wave occurs at 0.400 V versus the normal hydrogen electrode (NHE) [23] and is considered solvent independent [22]. All solutions were saturated with pure dry nitrogen gas for 30 min prior to electrochemical measurements.

Results and Discussion

The complexes under investigation were prepared according to the reactions given in Scheme 1. It is shown that a good yield and pure products could be obtained by the reaction of the mononuclear copper(II) complex with the appropriate metal(II) salt in the preparation of the heterobinuclear complexes. Trials were made to prepare these heterobinuclear complexes by replacement of the second copper(II) in $[\text{Cu}_2\text{L}]^{2+}$ with the appropriate metal ion (Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} or Hg^{2+}). This method was only successful in the case of Co^{2+} , Ni^{2+} and Hg^{2+} . As given in the preparation section, a low temperature and short reaction time are necessary to isolate pure heterobinuclear complexes otherwise the dissociation reaction, $2[\text{CuLM}]^{2+} \rightleftharpoons [\text{Cu}_2\text{L}]^{2+} + [\text{M}_2\text{L}]^{2+}$, will take place and can easily be observed. These were isolated chromatographically and identified. The complexes are air stable and insoluble in most organic solvents except Lewis bases.

The molar conductivity values in DMF at 25°C (Table 1) indicate a non-electrolytic nature of $[\text{CuLM}(\text{OAc})_2] \cdot n\text{H}_2\text{O}$ and $[\text{CuL}] \cdot 3\text{H}_2\text{O}$ but the other complexes are 1:2 electrolytes [24].

The IR spectrum of H_2L displays a strong broad band at 3480 cm^{-1} with band width of 144 cm^{-1} . This band could be assigned to hydrogen bonded OH. The presence of a broad weak band at 1922 cm^{-1} can be taken as an evidence for the presence of intramolecular hydrogen bonding of the type $\text{O}-\text{H} \cdots \text{N}$ as shown in Scheme 1. This also was proved by the appearance of $\nu(\text{C}-\text{O})(\text{phenolic})$ at 1282 cm^{-1} . Upon complex formation the bands at 3480 and 1922 cm^{-1} disappeared and that due to $\nu(\text{C}-\text{O})(\text{phenolic})$ is shifted to higher wavenumber by c. $30-44\text{ cm}^{-1}$. This indicates the bonding of the phenolic oxygen to the metal ion in all complexes.

TABLE 1. Elemental analysis, conductivity^a, yield and colour

Compound	Yield (%)	Colour	Λ_M	Analytical data: calc. (found) (%)				
				C	H	N	Cu	M
H ₂ L	83	pale yellow		71.9(70.1)	5.2(5.3)	14.6(14.5)		
[CuL]·3H ₂ O	84 ^b	olive green		55.3(54.9)	5.2(5.2)	11.2(11.0)	12.7(12.8)	
[CuLCo](ClO ₄) ₂ ·1.5H ₂ O	72	green	155.90	37.8(37.9)	2.9(2.8)	7.7(7.5)	8.7(8.7)	8.1(8.0)
[CuLNi](ClO ₄) ₂ ·H ₂ O	82	yellow green	160.03	38.3(37.9)	2.8(2.8)	7.8(7.7)	8.8(8.9)	8.1(8.3)
[CuLCu](ClO ₄) ₂ ·2H ₂ O	92	green	151.86	37.1(36.8)	3.0(2.9)	7.5(7.5)	17.1(17.0)	
[CuLZn](ClO ₄) ₂ ·2H ₂ O	68	green	162.24	37.0(36.6)	2.9(3.0)	7.5(7.6)	8.5(8.6)	8.8(9.0)
[CuLCd](ClO ₄) ₂ ·2H ₂ O	68	green	160.80	34.8(34.5)	2.8(2.8)	7.1(7.0)	8.0(7.8)	14.2(14.1)
[CuLHg](ClO ₄) ₂ ·2H ₂ O	77	green	165.20	31.3(31.0)	2.5(2.4)	6.4(6.3)	7.2(7.0)	22.8(22.5)
[CuLCo(OAc) ₂]·3H ₂ O	68	bluish green	3.08	47.9(47.3)	4.4(4.5)	8.3(8.1)	9.4(9.3)	8.7(8.8)
[CuLNi(OAc) ₂]·3H ₂ O	80	green blue	2.92	47.9(47.6)	4.4(4.4)	8.3(8.1)	9.4(9.1)	8.7(8.8)
[CuLCu(OAc) ₂]·2H ₂ O	87	dark green	1.88	48.9(48.7)	4.5(4.4)	8.5(88.6)	19.2(19.0)	

^aMolar conductivity of 10⁻³ M solutions in DMF at 25 ± 1 °C. ^bPrepared by method B.

The bands at 1638 and 1586 cm⁻¹ in the spectrum of H₂L, could be assigned to $\nu(\text{C}=\text{N})$ of the azomethine and quinoline, respectively. The first band is shifted to lower wavenumber whereas the second is shifted to higher wavenumber in the complexes [CuLM]²⁺, M = Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ or Hg²⁺. This suggests the participation of both groups in complex formation. This was proved by the bands at 322–334, 500–516 and 478–486 cm⁻¹ which are not present in the spectrum of H₂L. These were assigned to $\nu(\text{M}-\text{N})$ of quinoline and azomethine and $\nu(\text{M}-\text{O})$, respectively. Furthermore, the spectra of these complexes display very strong bands at 1072–1130 cm⁻¹ characteristic of ionic ClO₄⁻. The bands at 3400–3520 cm⁻¹ in the spectra of these complexes are assigned to water of crystallization. This is because of the absence of the characteristic bands of coordinated water in the spectra. This was also proved from the thermal analysis where the data showed mass loss characteristic of one or two molecules of water at 120–133 °C. Accordingly, the organic compound acts as a hexadentate coordinated to the metal ions via two azomethine nitrogen, two quinoline nitrogen and two phenolic oxygen atoms in [CuLM](ClO₄)₂·*n*H₂O, Scheme 1. On the other hand, the spectra of [CuL]·3H₂O and [CuLM(OAc)₂]·*n*H₂O, showed that the band at 1586 is not greatly affected upon complex formation whereas the bands due to $\nu(\text{C}=\text{N})$ (aromatic) and $\nu(\text{C}-\text{O})$ (phenolic) are greatly

affected (Table 2) indicating their bonding to the metal ions in these complexes. Accordingly, the ligand is tetradentate in these complexes. Furthermore, the spectra exhibit strong bands at 1555–1562 and 1408–1418 cm⁻¹ characteristic of ν_{as} and ν_{s} of the acetato group. Furthermore, $\Delta\nu = 147-144$ cm⁻¹ indicates its bidentate nature. The presence of water in these complexes was confirmed from the presence of broad medium bands at 3220–3452 cm⁻¹. The nature of these water molecules was identified by thermal analysis. The data showed weight loss characteristic of two water molecules at 288–292 °C and another weight loss characteristic of one water molecule at 116–123 °C. These are due to hydrogen bonded water molecules and water of crystallization [25], respectively. The absence of IR bands characteristic of coordinated water molecules could be taken as evidence for this assumption.

The nujol mull electronic spectrum of H₂L displays intense bands at 44 250, 39 060, 32 790 and 26 480 cm⁻¹. These could be assigned to Ph–Ph*, $\pi-\pi^*$ (phenyl), $n-\pi^*$ (quinoline) and $n-\pi^*$ (azomethine) transitions, respectively. The disappearance of the bands at 26 480 cm⁻¹ in all complexes indicates the bonding of the azomethine-N to the metal ion. The band at 32 790 cm⁻¹ also disappeared in the spectra of [CuLM](ClO₄)₂·*n*H₂O but strongly blue shifted in the spectra of the others. This could be taken as evidence for the coordination of

TABLE 2. Main IR bands ($\bar{\nu}$ cm⁻¹) with their tentative assignments

Compound	ν CN -CH=N-	ν CN aromatic	ν M-O	ν M-N -CH=N-	ν M-N aromatic	Others
H ₂ L	1638	1586				3480(OH), 1282(C-O)
[CuL]·3H ₂ O	1608	1588	480	508		3460(H ₂ O)
[CuLCo](ClO ₄) ₂ ·1.5H ₂ O	1605	1600	478	500	322	1088, 1118(ClO ₄), 3430(H ₂ O)
[CuLNi](ClO ₄) ₂ ·H ₂ O	1602	1598	486	516	328	1080, 1122(ClO ₄), 3446(H ₂ O)
[CuLCu](ClO ₄) ₂ ·2H ₂ O	1602	1596	482	506	332	1090, 1130(ClO ₄), 3430(H ₂ O)
[CuLZn](ClO ₄) ₂ ·2H ₂ O	1604	1598	478	504	334	1078, 1124(ClO ₄), 3462(H ₂ O)
[CuLCd](ClO ₄) ₂ ·2H ₂ O	1605	1600	480	516	330	1072, 1128(ClO ₄), 3458(H ₂ O)
[CuLHg](ClO ₄) ₂ ·2H ₂ O	1606	1600	484	515	330	1086, 1116(ClO ₄), 3446(H ₂ O)
[CuLCo(OAc) ₂]·3H ₂ O	1600	1590	485	510		1558(ν_{as})OAc, 1418(ν_s)OAc, 3442(H ₂ O), 3238(H ₂ O)
[CuLNi(OAc) ₂]·3H ₂ O	1604	1585	482	508		1562(ν_{as})OAc, 1412(ν_s)OAc, 3450(H ₂ O), 3266(H ₂ O)
[CuLCu(OAc) ₂]·2H ₂ O	1608	1590	486	512		1555(ν_{as})OAc, 1408(ν_s)OAc, 3462(H ₂ O), 3240(H ₂ O)

TABLE 3. Magnetic and electronic spectral data

Compound	μ_{eff}^a (BM)	$-J$ (cm ⁻¹)	g	d-d transition (cm ⁻¹) (log ϵ)
[CuL]·3H ₂ O	1.83			18450(2.65)
[CuLCo](ClO ₄) ₂ ·1.5H ₂ O	4.06	116	2.760	14880(3.08), 15385(3.89), 18900(2.43)
[CuLNi](ClO ₄) ₂ ·H ₂ O	1.83		2.080	22350(2.08), 19180(2.36)
[CuLCu](ClO ₄) ₂ ·2H ₂ O	1.14	229	2.068	18600(2.33), 16490(2.01)
[CuLZn](ClO ₄) ₂ ·2H ₂ O	1.79		2.074	18700(2.29)
[CuLCd](ClO ₄) ₂ ·2H ₂ O	1.82		2.070	18636(2.56)
[CuLHg](ClO ₄) ₂ ·2H ₂ O	1.82		2.076	18570(2.60)
[CuLCo(OAc) ₂]·3H ₂ O	4.98			12160, 16650, 17020, 18060 ^c
[CuLNi(OAc) ₂]·3H ₂ O	1.82			17450, 14630, 20890 ^c
[CuLCu(OAc) ₂]·2H ₂ O	1.67 ^b			17890, 22380 ^c

^aEffective magnetic moment/mol. ^bEffective magnetic moment/Cu. ^cMeasured as saturated solution.

quinoline-N in [CuLM](ClO₄)₂·*n*H₂O and not in the others.

The electronic spectra of the complexes as (CH₂Cl)₂ solutions are given in Table 3. The spectrum of [CuL]·3H₂O exhibits a band at 18 450 cm⁻¹ as has been reported for square planar copper(II) complexes. On the other hand, the spectrum of [Cu₂L]²⁺ displays two bands at 18 600 cm⁻¹ due to d-d transitions of copper(II) in two different N₂O₂ sites. The lower energy band could also be taken as evidence for the distortion of one CuN₂O₂ from the planar configuration [26]. The spectrum of [CuLNi]²⁺ exhibits bands at 22 350 and 19 180

cm⁻¹ which are consistent with those reported for square planar nickel(II) and copper(II) complexes, respectively. The spectrum of [CuLCo]²⁺ shows bands at 15 385 and 14 880 cm⁻¹ in addition to another one at 18 900 cm⁻¹. The first two bands are certainly due to the cobalt(II) ion, and judging from the band positions intensities, the configuration around the cobalt(II) is nearly tetrahedral. The third band could be attributed to the CuN₂O₂ chromophore. The spectra of [CuLM]²⁺, M = Zn²⁺, Cd²⁺ or Hg²⁺ show d-d bands at 18 570–18 070 cm⁻¹ characteristic of CuN₂O₂. As seen in Table 3, the intensity of the d-d bands characteristic of

Cu^{2+} is decreased as it blue shifted. Such a blue shift was observed by Sinn *et al.* [27]. The extent of the blue shift and intensity loss in this work were found to be in the order $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+}$, in the reverse order of their ionic radii of 0.70, 0.74, 0.78, 0.98 and 1.10 Å, respectively [28]. This behaviour could be explained on the basis that CuN_2O_2 becomes more planar in the heterobinuclear complexes relative to that in $[\text{CuL}] \cdot 3\text{H}_2\text{O}$, as it is bonded to M. The planarity increases with increasing the ionic radius of the second metal M. The electronic spectra of $[\text{CuLM}(\text{OAc})_2] \cdot n\text{H}_2\text{O}$ (Table 3) exhibit a broad band with maximum at 17890 cm^{-1} and a shoulder at 22380 cm^{-1} in the case of $\text{M} = \text{Cu}^{2+}$, characteristic of square planar copper(II) complexes. The spectrum also exhibits a strong band at 25860 that could be attributed to $d-\pi^*$ charge transfer. In the case of $\text{M} = \text{Ni}^{2+}$, the spectrum exhibits a series of bands at 17450 , 14630 and 20890 cm^{-1} . The first one could be attributed to the CuO_3N chromophore, whereas the latter two bands could be due to NiO_3N in square planar formation. The bands at 12160 , 16650 and 17020 cm^{-1} in the case of $\text{M} = \text{Co}^{2+}$ are characteristic of distorted tetrahedral cobalt(II). The band at 18060 cm^{-1} could be attributed to the CuO_3N chromophore.

The room temperature magnetic moments of $[\text{CuLM}(\text{OAc})_2] \cdot n\text{H}_2\text{O}$ of $1.67/\text{Cu}$, $1.82/\text{mol}$ and $4.98/\text{mol}$ BM for $\text{M} = \text{Cu}^{2+}$, Ni^{2+} and Co^{2+} , respectively, suggest either an uncoupled system or one involving weak spin exchange. Also, the value in the case of $\text{M} = \text{Ni}^{2+}$ is quite reasonable since nickel(II) has no unpaired electron and the value for the cobalt containing complex is a normal value for complexes containing copper(II) and tetrahedral cobalt(II) [29]. The data for $[\text{CuLM}]^{2+}$, $\text{M} = \text{Ni}^{2+}$, Zn^{2+} , Cd^{2+} or Hg^{2+} , in the range $5-300 \text{ K}$ corrected for diamagnetism and TIP are well fitted to the Curie-Weiss law, $\chi_M^{\text{corr}} = C/T - \theta$, where $C = 0.32-0.41^\circ \text{ cm}^3 \text{ mol}^{-1}$ and $\theta = 0.5 \pm 0.2 \text{ K}$. Extrapolation of the data to infinite temperature gives $\chi_{\text{TIP}} = 110-120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The values of g and μ_{eff} (Table 3) are typical of copper(II). The non-zero value of θ may indicate that a very weak intramolecular interaction is operative in the solid. The room temperature magnetic moment of $[\text{Cu}_2\text{L}]^{2+}$ of 1.14 BM/mol is consistent with that reported for high coupled paramagnetism CuN_2O_2 [1, 19, 28-31]. A plot of χ versus T for this complex is represented in Fig. 1. The susceptibility passes through a maximum at 38 K and then decreases. This behaviour is typical of an antiferromagnetically coupled system. The absence of a Curie tail in the low temperature region indicates that the sample is free of mononuclear impurities. Therefore, χ_M values are fitted to the Bleaney-Bower expression [9, 30, 32] for isotropic exchange in copper(II)

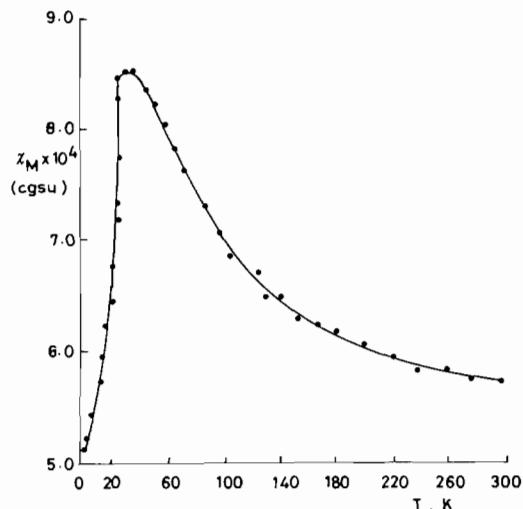


Fig. 1. Molar magnetic susceptibility χ_M vs. temperature for $[\text{CuLCu}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. The solid line represents least-squares fit of the data to the Bleaney-Bower expression.

dimers without including paramagnetic corrections. The resulting values of g and J are 2.068 and -229 cm^{-1} , respectively. The J value of this complex is somewhat small compared to those of the binuclear complexes showing a maximum. The strength of the antiferromagnetic interaction or the magnitude of J is affected by various factors; one of them is the stereochemistry about the oxygen bridges [33]. As has been shown in the electronic spectrum, the distortion of one of the two CuN_2O_2 chromophores from planar towards tetrahedral symmetry leads to the reduction of the superexchange integral through the oxygen bridge, resulting in the smaller absolute value of J .

The susceptibility data for $[\text{CuLCo}]^{2+}$ shown in Fig. 2, indicates the presence of an antiferromagnetic interaction. The μ_{eff} at 298 K of 4.06 BM is further evidence for such an interaction. At 5 K , the magnetic moment is decreased to 1.08 BM

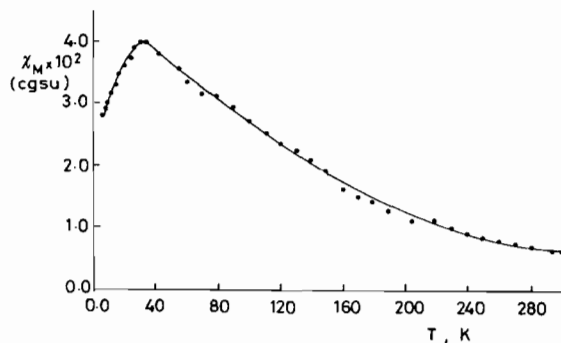


Fig. 2. Molar magnetic susceptibility χ_M vs. temperature for $[\text{CuLCo}](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$. The solid line represents the least-squares fit of the data to the equation derived from the spin Hamiltonian including the zero-field effect.

TABLE 4. Electrochemical data of the reduction of Cu(II)/Cu(I) in [CuLM]²⁺^a

Compound	CV		DP	
	Δ^b (mV)	$E_{1/2}$ (V)	E_p (V) ^c	$E_{1/2}$ (V) ^d
[CuL]·3H ₂ O	100	-1.060	-1.055	-1.059
[CuLCo](ClO ₄) ₂ ·1.5H ₂ O	80	-1.052	-1.049	-1.050
[CuLNi](ClO ₄) ₂ ·H ₂ O	76	-1.060	-1.056	-1.059
[CuLCu](ClO ₄) ₂ ·2H ₂ O	68	-0.950	-0.935	-0.944
	68	-1.360	-1.330	-1.358
[CuLZn](ClO ₄) ₂ ·2H ₂ O	78	-1.058	-1.055	-1.061
[CuLCd](ClO ₄) ₂ ·2H ₂ O	66	-1.054	-1.052	-1.057
[CuLHg](ClO ₄) ₂ ·2H ₂ O	70	-1.058	-1.056	-1.058

^aDMF solutions with 0.1 M tetrabutylammonium perchlorate supporting electrolyte. ^b $\Delta = E_{pa} - E_{pc}$. ^c E_p peak potentials of 1×10^{-4} M solutions in DMF vs. NHE. ^d $E_{1/2} = E_p + PH/2$; PH = pulse height.

compared to 2.87 BM expected for all molecules in the $S = 1$ state. The data were least-squares fit to the equation given by Bencini *et al.* [34]. The best fit is found with $g = 2.76$, $J = -116 \text{ cm}^{-1}$, $D = 2.42$ and $\theta = 30.9 \text{ K}$. The relatively large value of g is somewhat in keeping with the average g values quoted for cobalt(II) and copper(II) complexes in tetrahedral and square planar ligand fields [34–36].

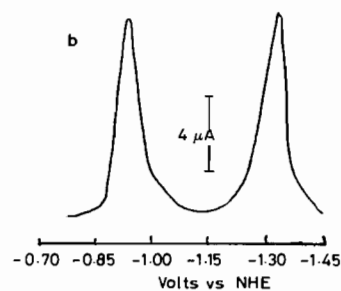
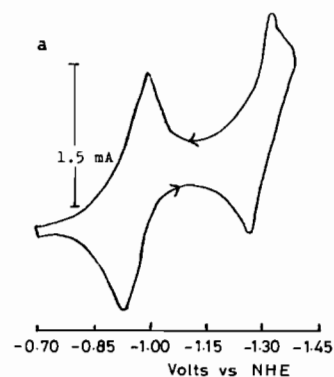


Fig. 3. (a) Cyclic voltammogram of Cu(II)Cu(II) in DMF. Successive one electron reduction waves are seen at a scan rate of 20 mV/s. (b) Differential pulse voltammogram of Cu(II)Cu(II) complex in DMF at a scan rate of 2 mV/s.

The electrochemical properties of the complexes [CuLM]²⁺ were investigated by CV and DP in DMF solvent. The data are given in Table 4 and illustrated in Figs. 3 and 4. The CV and DP of [Cu₂L]²⁺ exhibit two sequential reductions from [Cu(II)LCu(II)]²⁺ to [Cu(II)LCu(I)]¹⁺ and [Cu(I)LCu(I)]⁰ at -0.985 and -1.340 V versus NHE, respectively. In all heterobinuclear complexes, only one Cu(II)/Cu(I) reduction wave was observed, indicating the presence of only one copper species. The absence of shoulders at the potentials observed for the heterobinuclear complexes indicate that all complexes are pure. The electrochemical behaviour of the second metal ion in [CuLM]²⁺ was shown at -1.45 to -0.46 V versus NHE with a $E_{pa} - E_{pc}$ (anodic and cathodic peak, respectively) value of 112 and 200 mV for Ni(II)/Ni(I) and Hg(II)/Hg(I), respectively. It was found that Zn²⁺ and Cd²⁺ are electroinactive in Cu–Zn and Cu–Cd systems. The polarogram of [CuLCo]²⁺ could not be analysed because of the overlapping redox waves of Cu(II) and Co(II). From the electrochemical data, it was found that the potential difference $\Delta E = E_1 - E_2 = 355 \text{ mV}$ in

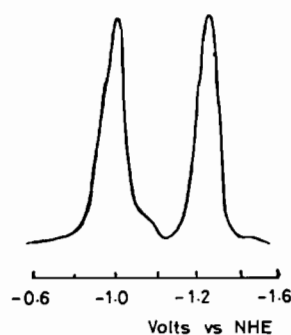
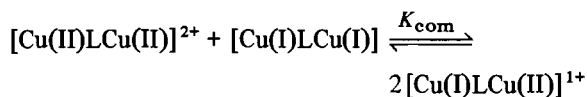


Fig. 4. Differential pulse polarogram for Cu(II)Ni(II) complex at a scan rate of 10 mV/s.

the case of $[\text{Cu}_2\text{L}]^{2+}$ is ten times larger than that observed for the non-interacting copper centers (36 mV) [11–39].

Of greater interest was the determination of the relative stability of the mixed valent species Cu(II)-LCu(I)^+ in the equilibrium mixture $[\text{Cu(II)LCu(II)}]^{2+}$ and Cu(I)LCu(I) as given by the comproportionation constant (K_{com}) for



using the relation, $\Delta E = (RT/nF)\ln K_{\text{com}}$, where $n = 1$. The value of K_{com} of 3.36×10^6 indicates that (i) there is a considerable interaction between the two copper centers, (ii) the magnetic superexchange effects between the two copper ions lead to the stabilization of $[\text{Cu(I)LCu(II)}]^{1+}$ over $[\text{Cu(II)LCu(II)}]^{2+}$ and $[\text{Cu(I)LCu(I)}$ in a mixture, (iii) the reduction of Cu(II) to Cu(I) is easier than Cu(I) to Cu(0) .

The electrochemical data of $[\text{CuLM}]^{2+}$ and $[\text{CuL}] \cdot 3\text{H}_2\text{O}$ showed that the reduction potentials of Cu(II)/Cu(I) always occur around 1.055 V versus NHE except in the case of $\text{M} = \text{Cu}^{2+}$. This appeared to be abnormal because there is structural change between the mononuclear and heterobinuclear complexes as shown from the electronic spectra. According to Patterson and Holm [40], the redox potential of copper(II) shifts to more negative values when the geometrical shape becomes more planar. Therefore, the geometrical change is not the only factor effecting the redox potential of copper(II) in these complexes. Another difference between the mononuclear and heterobinuclear complexes is the bonding mode of the phenoxide oxygen. The bonding of this group is simple in the former and bridging in the latter. Therefore, the electron donation of the phenoxide oxygen to copper is small in $[\text{CuLM}]^{2+}$ relative to $[\text{CuL}] \cdot 3\text{H}_2\text{O}$. The charge density on copper in the first will therefore be decreased leading to the positive shift of the reduction potentials. Accordingly, the geometrical change and the electronic effects compensate one another.

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