Dimeric Mixed-ligand Copper(II) Complexes with Di-imines and Salicylaldehydate†

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The variable-temperature (2—298 K) magnetic susceptibility, electrochemical, and spectral properties of three binuclear copper(II) complexes $[\{CuL(sal)\}_2][ClO_4]_2$ are reported. Each copper(II) ion of the binuclear complex is co-ordinated to a di-imine molecule L [bis(2-pyridyl)amine, 2,2′-bipyridine, or 1,10-phenanthroline], and a salicylaldehydate anion (sal) bridging the two metal ions through the phenoxide oxygen atom. At room temperature the complexes show a normal magnetic moment, μ = 1.8—1.9. However, antiferromagnetic interactions are found when susceptibility data are taken at temperatures down to *ca.* 2 K. Magnetic, electrochemical, and spectral properties are discussed in relation to the known solid-state geometry of the complexes.

There has been considerable research activity aimed at correlating the structural and magnetic properties of dimeric copper(II) complexes, with great emphasis placed in the earlier studies, by Hatfield, Hodgson and co-workers,[1–6] on systems in which the bridging atoms are oxygen atoms. For the case of planar di-μ-hydroxo complexes it has been possible to demonstrate a correlation between the magnetic exchange parameter, J, and the bridging angle Cu–O–Cu.[7] Square-planar phenoxide oxygen-bridged complexes show a correlation between the value of J and the dihedral angle, τ, between the planes formed by Cu_2O_2 and $Cu_2N_2X_2$.[8,9] However, the binuclear phenoxide oxygen-bridged copper(II) complexes, with centrosymmetric axial and basal-edged square-pyramidal geometry, show a normal paramagnetic behaviour at room temperature.[10,11]

X-Ray studies of the following mixed-ligand copper(II) complexes, [bis(2-pyridyl)amine]salicylaldehydato copper(II) perchlorate, $[Cu(bipyam)(sal)][ClO_4]$, (2,2′-bipyridine) salicylaldehydato copper(II) perchlorate, $[Cu(bipy)(sal)][ClO_4]$, and (1,10-phenanthroline) salicylaldehydato copper(II) perchlorate, $[Cu(phen)(sal)][ClO_4]$, have shown that they are dimeric with phenoxide oxygen atoms, from salicylaldehydate anions, bridging the two copper atoms.[12–14] The two copper atoms are separated by a distance intermediate between 3 and 4 Å and each metal atom has a tetragonally distorted octahedral geometry.

To continue with the study of magnetic properties of oxygen-bridged copper(II) dimers, we were interested in measuring the magnetic susceptibility of these copper(II) complexes, in order to detect possible intramolecular antiferromagnetic interactions between the two metal centres, and to correlate these with structural parameters.

Experimental

The preparation of the complexes has been previously reported.[12–14] U.v.–visible absorption spectra were recorded on a Carl Zeiss DMR 22 spectrophotometer with a ZR21 accessory for reflectance measurements. Voltammetric data were obtained by cyclic voltammetry using a PAR 370 electrochemistry system in a glass cell with a glassy carbon working electrode, a platinum auxiliary electrode and an aqueous saturated calomel reference electrode (s.c.e.). All measurements were performed under an argon atmosphere. Tetraethylammonium perchlorate was used as background electrolyte (0.1 mol dm^{-3}). All potentials were recorded in freshly distilled acetonitrile, at room temperature.

Magnetic susceptibility measurements were performed in the temperature range 2—298 K using a SHE Corp. VTS variable-temperature magnetometer (model 906). Crystalline samples weighing approximately 100 mg were employed. A metallic sample holder with a known temperature-independent paramagnetism (t.i.p.) signal was used. Magnetization at low temperatures was shown to be linear with applied field from 1 to 10 kG. Susceptibility measurements were carried out at 1 kG. The magnetometer was calibrated with $Hg[Co(SCN)_4]$. The data were corrected to compensate for the diamagnetism of the constituent atoms (Pascal constants) and for the t.i.p. of copper(II).[15]

Exchange interactions between the copper ions are given in terms of the isotropic spin Hamiltonian, $H = -2J\,S_1 \cdot S_2$. The values of $2J$ and the theoretical molar susceptibilities χ_M were calculated from a non-linear least-square fit of the Bleaney–Bowers equation (1)[16] to the experimental data. Observed and

$$\chi_M = \left[\frac{2Ng^2\mu_B^2}{3kT}\right][1 + \tfrac{1}{3}\exp(-2J/kT)]^{-1} \qquad (1)$$

calculated values of χ_M for the three complexes are reported in SUP 56750.

Results and Discussion

The structure of all three mixed complexes consists of isolated dimeric units. The geometry at each copper(II) centre is a significantly distorted octahedron, with the basal plane made up of the two heterocyclic nitrogen atoms and the two oxygen atoms of the salicylaldehyde anion. Two apical copper–oxygen distances complete the 4 + 2 co-ordination. They correspond to one of the oxygen atoms of the perchlorate anion and the oxygen atom of the nearest salicylaldehyde molecule. The structure determinations by *X*-ray crystallography have been

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† *Supplementary data available* (No. SUP 56750, 8 pp.): observed and calculated magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non. S.I. unit employed: G = 10^{-4} T.

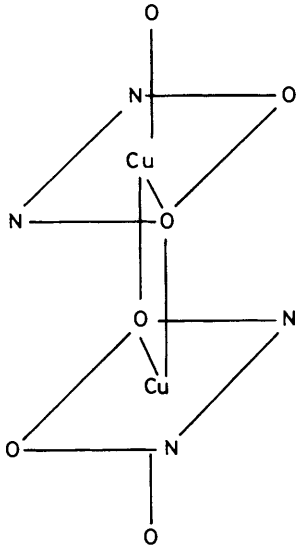

Figure 1. Geometrical arrangement in the binuclear oxygen-bridged complexes

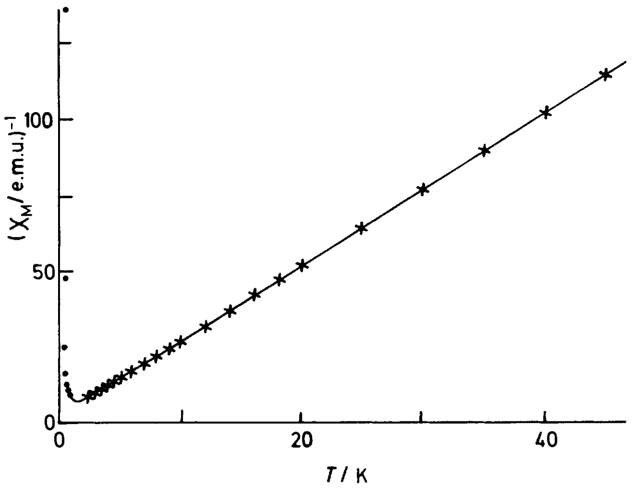

Figure 2. Variation with temperature of the molar susceptibility of $[\{Cu(bipy)(sal)\}_2][ClO_4]_2$. (×) Experimental points, (●) calculated points from Bleaney–Bowers equation; χ_m (c.g.s.) = $4\pi \times 10^{-6}$ m^3 mol^{-1}

previously described.[12–14] Figure 1 shows the octahedral geometry around the copper atoms.

The important bond distances and angles are listed in Table 1. Comparison of these parameters shows a few differences between the three structures. The two copper–nitrogen distances in each complex are similar in value [bipyam, 2.005(3), 2.007(2); bipy, 1.981(3), 1.983(3); phen, 1.995(3), 1.993(3) Å]. However, the two Cu–O(bridging) distances are markedly different [bipyam, 2.436(2), 1.932(3); bipy, 2.690(3) 1.897(2); phen, 2.622(2), 1.900(2) Å], a trait observed in the binuclear copper(II) complex, with bridging phenoxide oxygens, $[Cu_2(OPh)_4(en)_2]{\cdot}2\,PhOH$ (en = ethylenediamine).[10] For the short copper–phenoxide oxygen distances, the bis(2-pyridyl)amine complex shows the longer Cu–O bond [bipyam, 1.932(3); bipy, 1.897(2); phen, 1.900(2) Å].

The copper–copper distance is 3.343(0), 3.452(0), and 3.369(1) Å for the bis(2-pyridyl)amine, 2,2′-bipyridine, and 1,10-phenanthroline mixed-ligand complexes, respectively. Therefore, any direct magnetic interaction between the two metal centres is considered negligible; spin coupling must therefore take place by a superexchange interaction.[17]

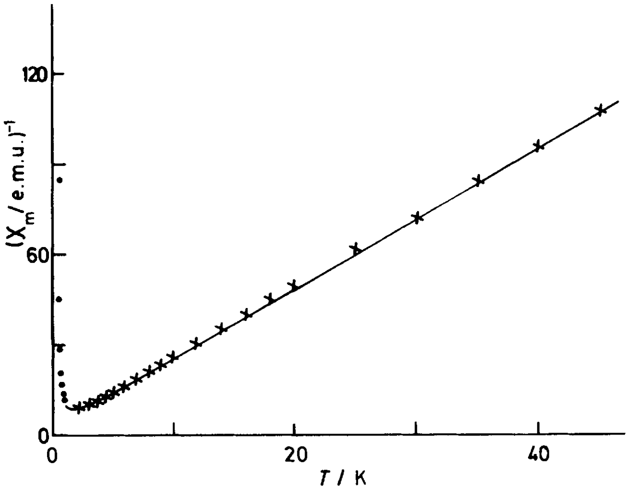

Figure 3. Variation with temperature of the molar susceptibility of $[\{Cu(phen)(sal)\}_2][ClO_4]_2$. (×) Experimental points, (●) calculated points from Bleaney–Bowers equation

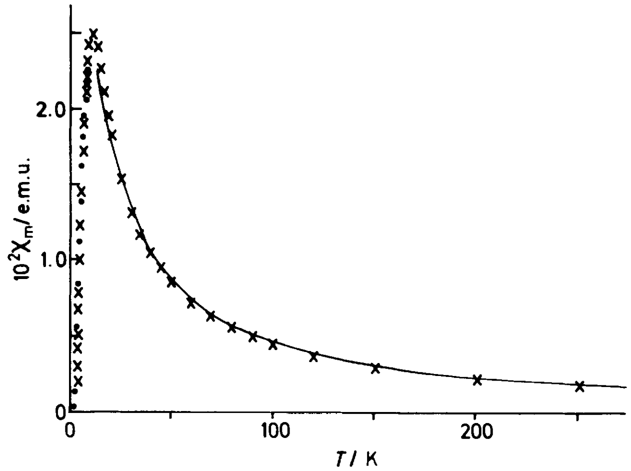

Figure 4. Variation with temperature of the molar susceptibility of $[\{Cu(bipyam)(sal)\}_2][ClO_4]_2$. (×) Experimental points, (●) calculated points from Bleaney–Bowers equation

Magnetic Properties.—The susceptibility per mol of copper ions is plotted as a function of temperature in Figures 2—4 for each complex. All three complexes obey the Curie–Weiss law at high temperatures, with normal magnetic moments for $50 \leqslant T \leqslant 298$ K. Plots of χ_M^{-1} *vs.* T for the bipy and phen mixed-ligand complexes are shown in Figure 2 and 3. The regression analysis of χ_M using the Bleaney–Bowers equation gives $2J = -2.08$ and -1.58 cm^{-1} respectively. The g values used in the fit were 2.14 and 2.06. The best fit of the experimental data permits calculation of $T_{max.} = 1.85$ and 1.45 K respectively, thus demonstrating very weak intramolecular antiferromagnetic interactions for both complexes.

The experimental data for the bipyam complex were plotted as χ_M *vs.* T in order to show the dominant features of these data: a maximum near 10 K and a rapid decrease to zero at lower temperatures, indicating antiferromagnetism with an isolated dimeric compound. The g value used in the fit of the experimental data was 2.28, and $2J = -11.70$ cm^{-1} was obtained (Figure 4).

Table 1. Bond lengths (Å) and angles (°) for the complexes

	[{Cu(bipyam)(sal)}$_2$][ClO$_4$]$_2$	[{Cu(bipy)(sal)}$_2$][ClO$_4$]$_2$	[{Cu(phen)(sal)}$_2$][ClO$_4$]$_2$
Cu(1)–O(5)	2.642(3)	2.555(4)	2.496(3)
Cu(1)–O(1)	1.932(3)	1.897(2)	1.900(2)
Cu(2)–O(1)	2.436(2)	2.690(3)	2.622(2)
Cu(1)–O(2)	1.974(2)	1.948(3)	1.941(2)
Cu(1)–N(1)	2.005(3)	1.981(3)	1.995(3)
Cu(1)–N(2)	2.007(2)	1.983(3)	1.993(3)
Cu(1)–Cu(2)	3.343(0)	3.452(0)	3.369(1)
O(1)–Cu(1)–N(1)	172.86(9)	174.1(1)	173.1(1)
O(1)–Cu(1)–N(2)	90.63(9)	93.5(1)	92.3(1)
O(1)–Cu(1)–O(2)	87.97(8)	93.6(6)	93.5(1)
O(2)–Cu(1)–N(1)	90.65(9)	91.2(1)	92.1(1)
O(2)–Cu(1)–N(2)	170.24(9)	172.7(1)	173.9(1)
N(2)–Cu(1)–N(1)	91.9(1)	82.3(1)	81.8(1)
Cu(1)–O(1)–Cu(2)	99.2(1)	96.1(1)	95.0(1)

Table 2. Magnetic and structural data

Complex	[{Cu(bipyam)(sal)}$_2$][ClO$_4$]$_2$	[{Cu(bipy)(sal)}$_2$][ClO$_4$]$_2$	[{Cu(phen)(sal)}$_2$][ClO$_4$]$_2$
$\mu_{eff.}$ (298 K)	1.93	1.85	1.84
$-2J$/cm^{-1}	11.70	2.08	1.58
g	2.28	2.14	2.06
$T_{max.}$/K	10.50	1.85	1.45
Cu(1)–O(1)–Cu(2)(°)	99.2	96.1	95.0

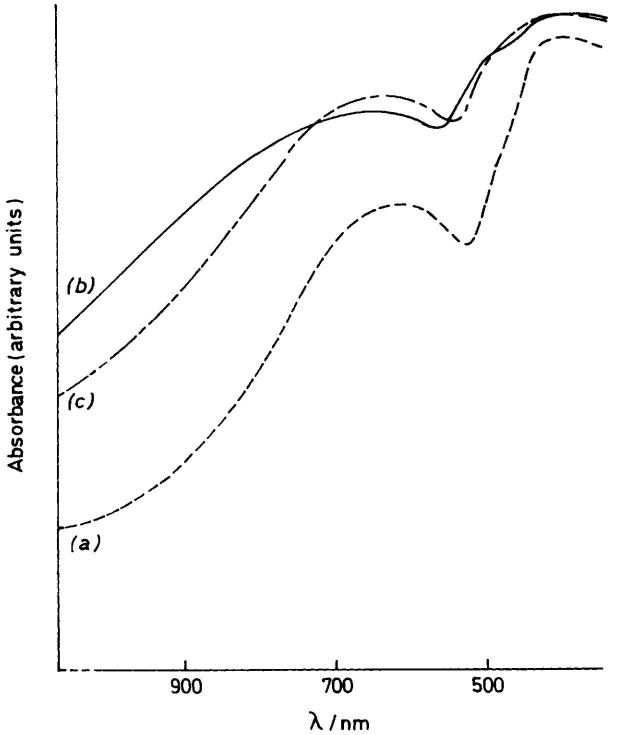

Figure 5. Visible reflectance spectra of (*a*) [{Cu(bipyam)(sal)}$_2$][ClO$_4$]$_2$, (*b*) [{Cu(bipy)(sal)}$_2$][ClO$_4$]$_2$, and (*c*) [{Cu(phen)(sal)}$_2$][ClO$_4$]$_2$

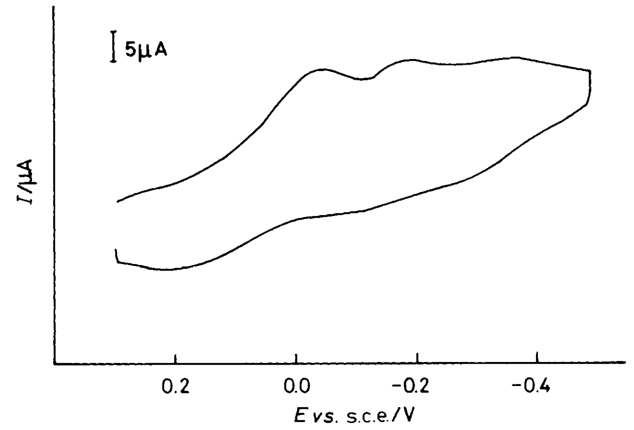

Figure 6. Electrochemical behaviour of the mixed copper(II) complex [Cu(bipyam)(sal)][ClO$_4$] in acetonitrile solution

The orientation of the copper co-ordination polyhedron with respect to the Cu$_2$O$_2$ bridging system is important in relation to the magnitude of the magnetic interaction in binuclear copper(II) complexes.[5] The orthogonality of the copper–oxygen–copper angle usually leads to a low degree of magnetic interaction due to unfavourable orientation of the metal orbitals with respect to the oxygen *p* orbitals.[10,11] The *p* orbitals of the bridging phenoxide oxygen, in an axial position relative to Cu(1) and equatorial relative to Cu(2), have bonding interactions with the d_{z^2} and $d_{x^2-y^2}$ orbitals of Cu(1) and Cu(2) respectively. Since both copper ions can be considered to be in an octahedral geometry with high tetragonal distortion, they will have $d_{x^2-y^2}$ ground states. Thus the oxygen atom does not mediate a real interaction between the ground states. Therefore, it is not surprising that the $2J$ values are small and increase as the Cu–O–Cu angle increases (Table 2).

Absorption Spectra.—All three complexes absorb in the u.v. region; the bands correspond to ligand absorptions. The visible reflectance spectra of the solid complexes are shown in Figure 5. The absorption band in the range 430—470 nm is assigned to a phenoxide to copper(II) charge transfer since bands at 410—450 nm have previously been assigned to charge transfer in mononuclear and dimeric copper(II) compounds.[18–23] The absorption band at *ca.* 650 nm is assigned to a *d–d* transition. The absorption spectrum in acetonitrile solution presents the same features, indicating that the octahedral geometry is maintained ($\varepsilon = 90$ dm^3 mol^{-1} cm^{-1}). Probably, the sixth position of the octahedron is occupied by a solvent molecule, which replaces the perchlorate anion.

Electrochemistry.—The electrochemical behaviour of the copper(II) complexes was studied by cyclic voltammetry. Each compound undergoes irreversible reduction in the range 0.0 to -1.1 V *vs.* saturated calomel electrode (s.c.e.). Two peaks were observed in acetonitrile solution, as expected for two consecutive one-electron processes, reduction from a Cu^{II}–Cu^{II} species to Cu^{II}–Cu^{I} and from Cu^{II}–Cu^{I} to the Cu^{I}–Cu^{I} species.[24] As the potential is increased to -1.1 V reduction to metallic copper is observed at -0.8 V. The reduction peak obtained is identical to that produced by $[Cu(CH_3CN)_4][ClO_4]$. The oxidation peak at -0.2 V is also identical to that obtained for the solvated copper(I) ion. This indicates that the copper(I) species is not stable but decomposes to the solvated copper(I) ion (Figure 6).

Small shifts, to more positive potentials, are observed when 1,10-phenanthroline is replaced by 2,2′-bipyridine and by bis(2-pyridyl)amine. Presumably this is due to the greater flexibility of the bis(2-pyridyl)amine molecule which better accommodates the copper(I) ion, in a pseudo-tetrahedral environment, in the Cu^{II}–Cu^{I} species.[25,26]

Electrochemical studies have shown that, in general, negative reduction potentials (*vs.* s.c.e.) prevail in binuclear copper(II) complexes involving oxygen-atom bridges,[26–32] even though strong antiferromagnetic exchange is observed in many cases. Reversible and quasi-reversible redox processes are observed for many of these systems. However, the mixed complexes studied show a lack of reversibility in the redox process.

The compounds studied here have weak Cu^{II}–Cu^{II} interactions, as can be seen by the calculated $2J$ values. As a result, a small separation between the two reduction potentials was expected ($E_1 - E_2 < 35.6$ mV).[33] A large separation has been observed in macrocyclic binuclear copper(II) complexes containing bridging phenoxide-type oxygen and moderately strong antiferromagnetic exchange.[34,35] Therefore the results obtained were in accordance with the trend observed by other researchers.

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