A Mixed-bridged Cu_3 Cluster with an Isosceles-triangular Array of Copper(II) Ions: Synthesis, Crystal Structure and Magnetic Properties†

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The reaction of H_2L [H_2L = *N,N'*-bis(1,3-dimethyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dion-6-yl)propylenediamine] with an excess of $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol gave the dinuclear complex $[Cu(\mu\text{-}HL)Cu(H_2O)_2(EtOH)][ClO_4]_3$ **1**, magnetic studies of which revealed that the antiferromagnetic exchange interaction mediated by the oximate groups is so strong that it causes a complete spin coupling at room temperature. This compound reacted with NaCl in ethanol–water (5:1) to afford the mixed-bridged trinuclear copper(II) complex $[\{Cu(\mu\text{-}HL)Cu(H_2O)Cu(\mu\text{-}L)\}(\mu\text{-}Cl)][ClO_4]_2 \cdot 4.88H_2O$ **2** the crystal structure of which was solved by single-crystal X-ray diffraction. Compound **2** consists of discrete trinuclear cations $[\{Cu(\mu\text{-}HL)Cu(H_2O)Cu(\mu\text{-}L)\}(\mu\text{-}Cl)]^{2+}$, non-co-ordinated perchlorate anions and lattice water molecules. Within the trinuclear cation, which has C_{2v} symmetry the three copper ions are arranged at the corners of an isosceles triangle. Each terminal copper atom Cu(2) and the central copper atom Cu(1) are bibridged by *syn,syn* oximate groups with a Cu(1)$\cdots$Cu(2) distance of 3.373(4) Å, whereas a chloride anion bridges the two terminal copper atoms with a Cu(2)$\cdots$Cu(2) distance of 4.770(4) Å. The angles Cu(2)–Cu(1)–Cu(2) and Cu(2)–Cl(1)–Cu(2) are 90.0(1) and 144.4(4)°, respectively. The central Cu(1) exhibits a square pyramidal CuO_5 co-ordination environment with four oxygen atoms of oximate groups in the basal plane and the water oxygen at the apical site. The terminal Cu(2) atoms occupy the N_4 inner site of the ligand with the chloride bridging anion occupying the axial position of the square pyramidal CuN_4Cl co-ordination environment. From magnetic susceptibility measurements, complex **2** was found to exhibit a very strong antiferromagnetic exchange interaction through the oximate bridges ($J = -189$ cm^{-1}), leading to complete spin coupling at 120 K. Magnetic parameters are discussed on the basis of the structural results and compared with those of other related complexes.

Magnetic-exchange interactions in polynuclear metal complexes are of continuing interest for inorganic chemists seeking to design new molecular materials exhibiting unusual magnetic, optical and electrical properties, and for bioinorganic chemists investigating the structure and magnetic properties of polynuclear active sites in metalloproteins.[1–3] Among polynuclear systems, trinuclear complexes are of increasing interest in connection with the binding and multielectron reduction of dioxygen to water in multicopper oxidases, such as ascorbate oxidase and laccase. Magnetic circular dichroism studies of laccase have confirmed a trinuclear copper(II) active site, which consists of a mononuclear type 2 and dinuclear type 3 copper(II) centres.[4] In the type 3 centres, copper(II) ions are strongly antiferromagnetically coupled so that, at room temperature, the dinuclear site is diamagnetic and ESR undetectable.[5] For the oxidized ascorbate oxidase, a crystal structure (resolution 2.5 Å) revealed the existence of an angled trinuclear copper centre with approximate C_2 symmetry and copper–copper distances of 3.4, 3.9 and 4.0 Å.[6]

On the other hand, it is known that the oximato group can bridge two metal ions to afford bi-, tri-nuclear and chain complexes,[7,8] in which the oximate group generally mediates a very strong antiferromagnetic exchange interaction, so that, in some cases,[7] a nearly complete spin coupling is observed at room temperature. Previously[9] we reported the first examples of structurally and magnetically characterized oximate-bridged heterodinuclear Cu^{II}/Ni^{II} complexes with the ligand *N,N'*-bis(1,3-dimethyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dion-6-yl)propylenediamine, H_2L (see Scheme 1).

We report here some magnetochemical studies of the dinuclear complex $[Cu(\mu\text{-}HL)Cu(H_2O)_2(EtOH)][ClO_4]_3$ **1** and the structure and magnetic properties of $[\{Cu(\mu\text{-}HL)Cu(H_2O)Cu(\mu\text{-}L)\}(\mu\text{-}Cl)][ClO_4]_2 \cdot 4.88H_2O$ **2**, which was obtained from the reaction of **1** with NaCl. Complex **2** is a mixed-bridged trinuclear copper(II) cluster with an isosceles array of copper(II) ions, potentially relevant to the multicopper oxidases.

Experimental

Preparation of Compounds.—The ligand H_2L was prepared as described previously.[10]

$[Cu(\mu\text{-}HL)Cu(H_2O)_2(EtOH)][ClO_4]_3$ **1**. Copper(II) perchlorate hexahydrate (1.48 g, 4 mmol) was added to a stirred suspension of H_2L (0.4 g, 1 mmol) in ethanol (50 cm^3). After 10 min, all the ligand dissolved and a green powder precipitated,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

which was filtered off, washed with ethanol and air dried; yield, 90% (Found: C, 21.95; H, 3.00; Cl, 11.20; Cu, 14.0; N, 12.80. Calc. for $C_{17}H_{29}Cl_3Cu_2N_8O_{21}$: C, 22.30; H, 3.15; Cl, 11.65; Cu, 13.90; N, 12.25%). Water plus ethanol content was determined thermogravimetrically. (Found, 9.29; calc., 9.00%). IR cm^{-1}: ν(OH) 3550, 3428, ν(C^2=O) 1731, δ(OH) 1670, ν(C^4=O) 1623, ν(Cl–O) 1087 cm^{-1}.

$[\{Cu(\mu\text{-}HL)Cu(H_2O)(\mu\text{-}L)Cu\}](\mu\text{-}Cl)[ClO_4]_2\cdot 4.88H_2O$. The successive addition of NaCl (0.03 g, 0.5 mmol) and water (10 cm^3) to a suspension of **1** (1 g, 1.1 mmol) in ethanol (50 cm^3) at 60 °C gave, after a few minutes, a black homogeneous solution. This solution, kept at room temperature for 1 d, yielded black crystals suitable for X-ray analysis; yield, 72%. A subsequent synthesis using the same conditions yielded crystals of $[\{Cu(\mu\text{-}HL)Cu(H_2O)Cu(\mu\text{-}L)\}(\mu\text{-}Cl)][ClO_4]_2\cdot 4H_2O$ **2a.**

Found: C, 26.95; H, 3.40; Cl, 8.05; Cu, 14.35; N, 16.85. Calc for $C_{30}H_{48.76}Cl_3Cu_3N_{16}O_{25.88}$ **2**: C, 26.80; H, 3.65; Cl, 7.90; Cu, 14.20; N, 16.65%. IR: ν(OH) 3554, 3466, ν(C^2=O) 1724, δ(OH) 1675, ν(C^4=O) 1607, ν(Cl–O) 1069 and 1096 cm^{-1}. (Found: C, 27.1; H, 3.70; Cl, 7.80; Cu, 14.50; N, 16.25. Calc. for $C_{30}H_{47}Cl_3Cu_3N_{16}O_{25}$ **2a**: C, 27.10, H, 3.55; Cl, 8.00; Cu, 14.35; N, 16.85%).

Physical Measurements.—Microanalysis, ESR spectra and magnetic susceptibility data were obtained as described previously.[11]

X-Ray Data Collection and Structure Determination of **2** *and* **2a**.—Two types of crystals were isolated by the same method of preparation. Since they exhibited significantly different IR spectra in the 3400–3600 cm^{-1} region, we decided to determine the structure of both types of crystals, **2** and **2a**.

Single crystal data collections were performed at 296 K with a Nicolet P3F diffractometer using graphite-monochromatized Mo-Kα (λ = 0.710 69 Å) radiation.

A black crystal of $[\{Cu(\mu\text{-}HL)Cu(H_2O)(\mu\text{-}L)Cu\}(\mu\text{-}Cl)][ClO_4]_2\cdot 4H_2O$ **2a** with dimensions 0.35 × 0.32 × 0.12 mm was used. The unit cell parameters were obtained by least-squares refinement of 25 carefully centred reflections ($12 < 2\theta < 24°$). The compound crystallizes in the tetragonal system and systematic absences indicated two possibles space groups, $I4_1md$ (no. 109) and $I\bar{4}2d$ (no. 122). Structure analysis confirmed the space group $I4_1md$, with $a = 22.61(1)$, $c = 9.867(6)$ Å, $U = 5044(5)$ Å^3, $Z = 4$, $D_c = 1.764$ g cm^{-3}, μ(Mo-Kα) = 1.50 mm^{-1}. A total of 5846 reflections were collected ($2\theta_{max} = 53°$, $h = 0$–28, $k = 0$–28, $l = 0$–12), giving 1463 unique reflections of which 1026 were considered as observed with $|F| > 4\sigma(F)$. Intensities of three check reflections measured after every 200 reflections showed only statistical fluctuations during the course of the data collection. The data were corrected for Lorentz-polarization effects and for dispersion, but not for absorption or extinction.

The structure was solved by direct methods by using the SHELXS 86 program,[12] and consists of the trinuclear complex unit with *mm* symmetry, two perchlorate ions at *m* and four crystallisation water molecules in general positions. The bridging Cl(1) atom is disordered occupying two positions. The copper atoms and the chlorine atom of ClO_4^- anions were refined anisotropically and the other non-hydrogen atoms isotropically. Hydrogen atoms bonded to carbons were placed at their calculated positions (C–H 0.96 Å). The hydrogen atoms of the co-ordinated water molecule O(9) were located on the Fourier map and not refined whereas those of O(13) could not be positioned. The final refinement gave $R = 0.076$ ($R' = 0.060$) for 110 parameters.

A black crystal of $[\{Cu(\mu\text{-}HL)Cu(H_2O)(\mu\text{-}L)Cu\}(\mu\text{-}Cl)][ClO_4]_2\cdot 4.88H_2O$ **2** with dimensions 0.35 × 0.20 × 0.15 mm was used for X-ray analysis. The unit cell parameters were determined by least-squares refinement of 25 carefully centred reflections ($6 < 2\theta < 12°$). The compound crystallizes in the tetragonal system, space group $I4_1md$ (no. 109) with $a = 22.737(7)$, $c = 9.466(5)$ Å, $U = 4894(4)$ Å^3, $D_c = 1.825$ g cm^{-3}, μ(Mo-Kα) = 1.56 mm^{-1}.

A total of 5651 reflections were collected ($2\theta_{max} = 53°$, $h = 0$–28, $k = 0$–28, $l = 0$–11) giving 1412 unique reflections of which 907 were considered as observed according to the criterion $|F| > 4\sigma(F)$. The data were corrected as for **2a**.

Structure analysis was begun using the solution for **2a**, which confirmed the trinuclear complex unit with *mm* symmetry and two perchlorate anions at *m*. Moreover the structure contains several disordered water molecules of crystallisation. Refinement of the non-hydrogen atoms, with the copper and chlorine atoms anisotropic, resulted in somewhat high thermal parameters for the atoms of the perchlorate anions. The hydrogen atoms bonded to carbons were placed at their calculated positions (C–H 0.96 Å), those of the water molecules of crystallisation could not be positioned. This model converged to $R = 0.078$ ($R' = 0.050$) for 119 parameters.

All refinements were performed using the XTAL program system,[13] which minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma F^2$. All calculations were carried out on a CONVEX C3840 computer. Neutral atomic scattering factors were those included in the programs.

Comparison of distances and angles within the trinuclear unit for **2** with those for **2a** reveals no significant differences, with the exception of the variations in Cu(1)···Cu(2) and Cu(2)–Cl(1) distances (0.076 and 0.080 Å, respectively) and O(5)–Cu(1)–O(5^I) (I: $1 - x$, $1 - y$, z), Cu(2)–Cl(1)–Cu(2^I) and Cu(1)–O(5)–N(5) angles (*ca.* 6.7, 4.3 and 3.8°, respectively). The most important differences between the two structures are the number of lattice water molecules and the disorder affecting the bridging chlorine anion in **2a** and water molecules of crystallization in **2** which results in different hydrogen-bond networks. Thus, in **2**, perchlorate anions, water molecules, O(5) oxime and O(4) carbonyl oxygen atoms are involved in hydrogen bonding while in **2a**, perchlorate and O(5) oxygen atoms do not participate in such bonding. Moreover, there is a noticeable shortening (*ca.* 0.34 Å) of the shortest intermolecular Cu···Cu distance on going from **2a** to **2**.

Since both types of crystals exhibit essentially the same structure, for the sake of clarity further discussion will concern the $4.88H_2O$ adduct **2**. Atomic coordinates for the non-hydrogen atoms of **2** are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles for complex **2** and atomic coordinates, thermal parameters and bond lengths and angles for **2a**.

Results and Discussion

The preparation of the complex $[\{Cu(\mu\text{-}HL)Cu(H_2O)(\mu\text{-}L)Cu\}(\mu\text{-}Cl)][ClO_4]_2\cdot 4.88H_2O$ **2** is achieved in two steps. First, the complex formulated as $[Cu(\mu\text{-}HL)Cu(H_2O)_2(EtOH)][ClO_4]_3$ **1** is obtained by the reaction of H_2L with an excess of $Cu(ClO_4)_2\cdot 6H_2O$ in absolute ethanol. Secondly, this presumably dinuclear complex reacts with Cl^- in ethanol–water (5:1) to afford **2**.

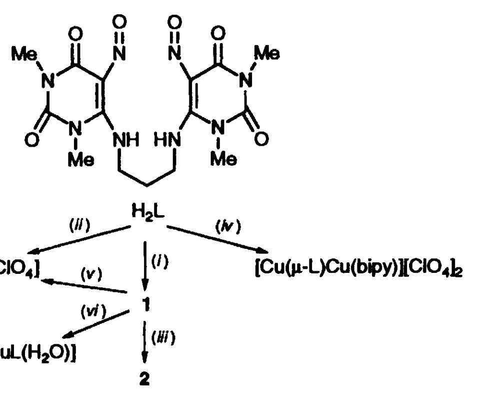
The formation of **1**, in which H_2L is monodeprotonated, is not unexpected in view of the following (see Scheme 1): (*i*) H_2L reacts with $Cu(ClO_4)_2\cdot 6H_2O$ in a 1:1 mol ratio in absolute ethanol to afford the complex $[Cu(HL)][ClO_4]$, (*ii*) the ability of the NO groups to co-ordinate a second metal ion, giving rise to dinuclear species. Furthermore, the fact that **1** reacts with 2,2′-bipyridyl (bipy) to give $[Cu(\mu\text{-}L)Cu(bipy)][ClO_4]_2$[14] may support the dinuclear structure of **1**.

On the other hand, when **1** and $[Cu(HL)][ClO_4]$ are dissolved in water they lose the NOH proton to give the complex $[CuL(H_2O)]\cdot 3H_2O$. It seems that depending on the water–ethanol ratio, complexes with deprotonated or partly

Table 1 Non-hydrogen positional parameters for **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	$\frac{1}{2}$	$\frac{1}{2}$	0.500 00
Cu(2)	0.3 951(1)	$\frac{1}{2}$	0.752 0(6)
Cl(1)	$\frac{1}{2}$	$\frac{1}{2}$	0.833(1)
N(1)	0.334 1(5)	0.333 6(5)	0.844(1)
C(1)	0.281(1)	0.336(2)	0.936(5)
O(2)	0.323 9(5)	0.234 2(5)	0.833(1)
C(2)	0.346 3(6)	0.280 3(6)	0.787(1)
N(3)	0.383 9(5)	0.278 2(5)	0.670(1)
C(3)	0.397(2)	0.221(1)	0.623(5)
O(4)	0.425 9(4)	0.319 6(4)	0.478(1)
C(4)	0.402 6(6)	0.325 4(7)	0.593(2)
O(5)	0.441 7(4)	0.436 5(4)	0.506(1)
N(5)	0.411 3(5)	0.434 6(5)	0.621(1)
C(5)	0.391 1(6)	0.381 8(6)	0.660(2)
N(6)	0.361 6(5)	0.435 1(5)	0.865(1)
C(6)	0.360 2(6)	0.385 1(6)	0.798(2)
C(7)	0.342 5(6)	0.445 4(6)	1.014(2)
C(8)	0.369 6(8)	$\frac{1}{2}$	1.068(2)
O(9)[a]	$\frac{1}{2}$	0.472(1)	0.272(3)
Cl(2)	$\frac{1}{2}$	0.285 2(3)	0.957(1)
O(10)	$\frac{1}{2}$	0.331(1)	0.853(3)
O(11)	$\frac{1}{2}$	0.232(1)	0.883(3)
O(12)	0.448 9(9)	0.288 8(8)	1.024(3)
O(13[a]	$\frac{1}{2}$	0.423(1)	0.148(4)
O(14)[b]	$\frac{1}{2}$	0.365 4(8)	0.347(2)
O(15)[c]	0.421 7(7)	0.376 7(8)	0.227(2)

[a] Site occupancy 0.50. [b] Site occupancy 0.56(2). [c] Site occupancy 0.44(2).



Scheme 1 (*i*) $Cu(ClO_4)_2 \cdot 6H_2O$ (excess) in EtOH, (*ii*) $Cu(ClO_4)_2$ in EtOH; (*iii*) NaCl; (*iv*) bipy in EtOH–water; (*v*) acetonitrile; (*vi*) water

deprotonated NOH groups can be obtained, which may serve to explain the presence of both types of these groups in **2**, which was prepared in a water–ethanol medium.

Crystal Structure of **2**.—The crystal structure of **2** consists of discrete trinuclear cations $[\{Cu(\mu\text{-}HL)Cu(H_2O)(\mu\text{-}L)Cu\}(\mu\text{-}Cl)]^{2+}$, non-co-ordinated perchlorate anions and lattice water molecules. A perspective view of the cation with atom labelling is shown in Fig. 1. Selected bond lengths and angles are given in Table 2.

Within the trinuclear cation with C_{2v} symmetry, the three copper ions are arranged at the corners of an isosceles triangle. The Cu(2) ··· Cu(1) and Cu(2) ··· Cu(2^{I}) distances are 3.373(4) and 4.770(4) Å, respectively, and the Cu(2)–Cu(1)–Cu(2^{I}) angle is 90.0(1)°. On the two sides that are of the same length, copper(II) ions are bibridged by *syn,syn* oximato groups whereas a chloride anion bridges the copper(II) ions on the other side, with a Cu(2)–Cl(1)–Cu(2^{I}) angle of 144.4(4)°. As far as we know, this complex represents one of the few examples of mixed-bridged trinuclear complexes with a triangular Cu_3 unit.[15]

Even though the charge balance indicates that one of the four protons from the two H_2L ligands remains in the complex, this cannot be located in the structure. The isosceles triangular Cu_3 cation has two crystallographic mirror planes which are perpendicular to each other, one including the three coppers and the bridging chloride, the other containing the central copper atom, the bridging chloride and the disordered oxygen atom O(9) of the co-ordinated water molecule. As Cu(1) is located on both planes, four equivalent short bonds of 1.960(9) Å are formed with the strictly coplanar oxygen atoms of the oximate groups. The water oxygen atom O(9) is co-ordinated at a longer distance of 2.25(3) Å, giving rise to a CuO_5 square-pyramidal co-ordination polyhedron. The Cu(1) atom lies 0.054 Å above the square basal plane toward the axially bound water molecule. Owing to the 'bite' of the CuL and Cu(HL) moieties in forming six-membered chelate rings, bond angles in the basal plane deviate from the ideal value of 90°. Thus, the internal O(5)–Cu(1)–O(5^{II}) angle opens to 94.9(4)° whereas the external O(5)–Cu–O(5^{III}) is 85.0(4)°.

The chloride bridging anion, which also lies on both mirror planes, occupies the apical position of the square pyramidal co-ordination geometries of the terminal Cu(2) and Cu(2^{I}) centres at a distance of 2.505(4) Å. The basal plane is formed by the N(5), N(5^{II}), N(6) and N(6^{II}) nitrogen atoms from the inner site of the ligand, with Cu(2)–N(5) and Cu(2)–N(6) distances of 1.97(1) and 1.98(1) Å, respectively, which do not differ significantly from those observed in the complex $[CuL(H_2O)] \cdot 3H_2O$.[9] The four equatorial nitrogen atoms are coplanar while the Cu(2) and Cu(2^{I}) atoms are lifted 0.215(5) Å from the N_4 basal plane toward the axial donor Cl(1). The dihedral angle between the N_4 basal plane and the aromatic uracil rings is 9.3(4)°, indicating that the CuL and CuHL entities are almost planar. The dihedral angle between the basal planes of Cu(1) and Cu(2) atoms is 64.0(4)°.

Hydrogen bonding involving the disordered water molecules,

Table 2 Selected bond distances (Å) and angles (°) for complex **2**

Cu(1)–O(5)	1.960(9)	Cu(2)–N(5)	1.97(1)
Cu(1)–O(9)	2.25(3)	Cu(2)–N(6)	1.98(1)
N(5)–O(5)	1.29(2)	Cu(2)–Cl(1)	2.505(4)
N(5)–C(5)	1.34(2)	C(6)–N(6)	1.30(2)
C(5)–C(6)	1.49(2)		
N(5)–Cu(2)–N(6)	81.4(5)	Cu(2)–Cl(1)–Cu(2^{I})	144.4(4)
N(5)–Cu(2)–N(5^{II})	97.8(5)	O(5)–Cu(1)–O(5^{I})	176.8(6)
N(5)–Cu(2)–N(6^{II})	167.5(5)	O(5)–Cu(1)–O(5^{II})	94.9(4)
N(6)–Cu(2)–N(6^{II})	96.7(5)	O(5)–Cu(1)–O(5^{III})	85.0(4)
O(5)–Cu(1)–O(9)	79.7(6)	Cl(1)–Cu(2)–N(5)	90.9(3)
Cl(1)–Cu(2)–N(6)	101.6(4)		

Symmetry relations: I $1 - x$, $1 - y$, z; II x, $y - 1$, z; III $1 - x$, y, z.

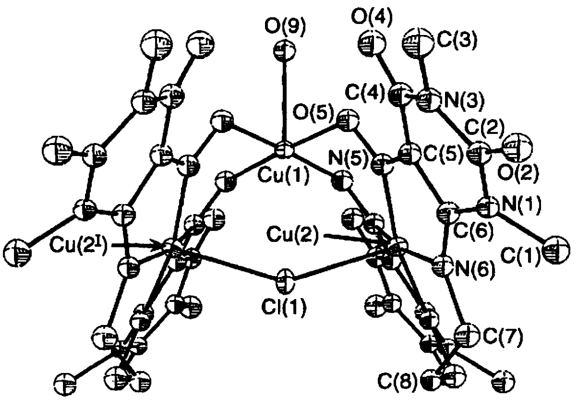


Fig. 1 Perspective view of the trinuclear cation $[\{Cu(\mu\text{-}HL)Cu(H_2O)(\mu\text{-}L)Cu\}(\mu\text{-}Cl)]^{2+}$ along the Cl(1)–Cu(1)–O(9) axis. Perchlorate anions and water molecules are omitted for clarity

O(5) oxime and O(4) carbonyl oxygen atoms is evident, and relevant oxygen–oxygen distances are summarized in the supplementary material. The perchlorates are associated with the trinuclear cation both through long-range Cu···O interactions, Cu(2)–O(11^{IV}) 3.10(3) Å (IV: $\frac{1}{2} - y, 1 - x, -\frac{1}{4} + z$), and through hydrogen bonds, O(15)···O(12^{V}) 2.84(3) Å (V: $x, y, z - 1$). A perspective view of the molecular packing is shown in Fig. 2. The shortest intermolecular Cu···Cu distance is 7.47(3) Å, the next closest 9.47(3) Å.

It must be noted that with H_2L and related ligands, the copper(II) ion shows a great tendency to form square-pyramidal CuN_4Cl co-ordination environments, in which the chloride occupies the axial position. Thus, for instance, compound **1** and [Cu(HL)X] (where X = NO_3^- or ClO_4^-) react with Cl^- in a 1 : 1 mol ratio in ethanol–water (5 : 1 v/v) to afford the complex [Cu(HL)Cl]. Furthermore, an analogous complex [Cu(HL')Cl] (where H_2L' is *N,N'*-bis(1,3-dimethyl-5-nitrosopyrimidine-2,4(1*H*,3*H*)-dion-6-yl)butanediamine) reacts with $[Cu(bipy)_2][ClO_4]_2$ giving rise to the oximato–chloride mixed-bridged dinuclear complex $[Cu(\mu\text{-}L')(\mu\text{-}Cl)Cu(bipy)][ClO_4]$.[14] In view of this and the crystal structure of **2**, we tentatively suggest that the formation of this complex from two molecules of **1** might take place through a chloride-bridged intermediate, which subsequently or simultaneously yields **2** by elimination of copper(II) perchlorate.

Magnetic Properties.—At room temperature, complex **1** is diamagnetic, thus indicating that the antiferromagnetic exchange interaction is strong enough to attain complete spin coupling, and a value of the exchange parameter J (with $H = JS_1S_2$) larger than 1000 cm^{-1} can be estimated. The antiferromagnetic coupling between the copper(II) ions is also supported by the polycrystalline ESR spectra of **1**. The X-band spectrum at 308 K exhibits a symmetric splitting pattern centred at $g = 2.12$. No half-field transition or hyperfine structure is observed. The signal intensity decreases on lowering the temperature, and no signal is observed at 77 K, in accordance with only the diamagnetic singlet state being populated at this temperature.

It is well known that the oximato group generally mediates a strong antiferromagnetic exchange interaction, which gives rise to a perfect spin coupling at room temperature in some dinuclear and trinuclear oximato-bridged copper(II) complexes.[7,8] The majority of these complexes exhibit a coplanar structure, suggesting that a coplanar structure is essential for attaining a complete spin coupling at room temperature, since generally the exchange coupling decreases as the structure is bent at the bridging oximato oxygen atoms. However, this assumption must be used with caution, since an oximato-bridged trinuclear copper(II) complex with non-planar structure has recently been reported to exhibit essentially complete spin coupling at room temperature.[7f]

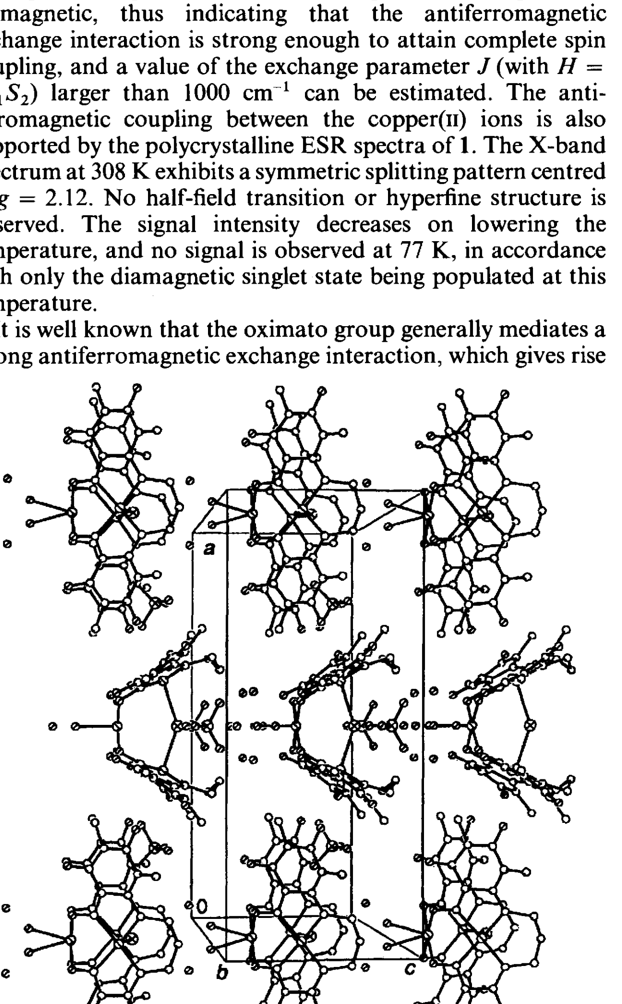


Fig. 2 View of the molecular packing of **2** down the *b* axis, with the hydrogen atoms omitted for clarity. The molecules of water are represented by circles

Accordingly it is reasonable to assume a coplanar or nearly coplanar dimeric structure for **1** given also that the complex $[Cu(\mu\text{-}L)Cu(bipy)][ClO_4]_2$, which is obtained by treating **1** with bipy in ethanol–water, has a coplanar structure and is diamagnetic at room temperature.[14]

The temperature dependence of χ_MT for complex **2** is given in Fig. 3. At room temperature χ_MT is very low (0.63 cm^3 mol^{-1} K) with respect to the value expected for three independent copper(II) ions. As the temperature is lowered χ_MT decreases and reaches a plateau (0.44 cm^3 mol^{-1} K) between 120 and 10 K, this value corresponding well to the spin-only value of 0.437 cm^3 mol^{-1} K for one unpaired electron with $g = 2.17$. This behaviour clearly indicates that a very strong antiferromagnetic spin-exchange interaction between the copper(II) ions operates in **2**, so that only the spin-doublet state is populated below *ca.* 120 K. Below 10 K, χ_MT decreases, reaching a value of 0.40 cm^3 mol^{-1} K at 5 K, which may be the result of weak antiferromagnetic interactions between neighbouring trinuclear units.

From the known structure of **2**, the data may be analysed using the isotropic spin Hamiltonian (1) for three interacting

$$\mathcal{H} = -2J(S_1S_2 + S_1S_2') - 2J'(S_2S_2') \qquad (1)$$

paramagnetic centres in C_{2v} symmetry[16] where J and J' describe the exchange interactions between adjacent and terminal copper ions, respectively. Defining the spin operators $S = S_1 + S^*$ and $S^* = S_2 + S_2'$ for three interacting $S_i = \frac{1}{2}$ centres, the following spin levels S,S^* and energies are obtained: one quartet, $\frac{3}{2}$, 1, at $-J - (J'/2)$ and two doublets $\frac{1}{2}$, 0 and $\frac{1}{2}$, 1 at $\frac{3}{2}J'$ and $2J - (J'/2)$, respectively. In the case of antiferromagnetic coupling the doublet $\frac{1}{2}$, 1 is the ground state. Variable-temperature magnetic susceptibility data for **2** were fitted by the theoretical expression, which results from the spin Hamiltonian (1). To take into account the intercluster exchange interactions a molecular-field correction was inserted into this expression giving equation (2), where $\chi_C = f(J, J', g, T)$ is as

$$\chi_M = \frac{\chi_C}{1 - (2zjNg^2\beta^2)\chi_C} \qquad (2)$$

given in the literature;[17] j is the intercluster-exchange constant and z is the number of interacting nearest neighbours.

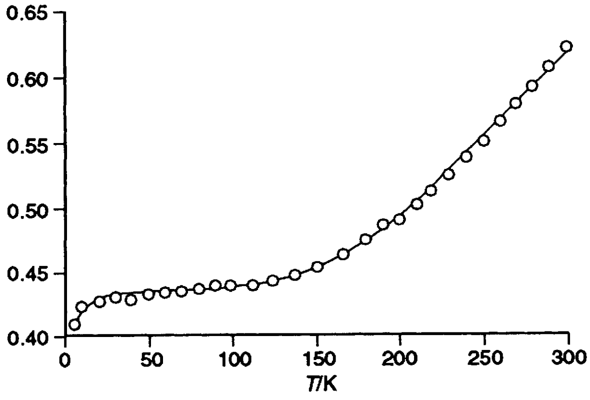


Fig. 3 Temperature dependence of χ_MT for **2** (o). The solid line is generated from the best-fit magnetic parameters

Since the only effect of J' is to vary the energy of the excited doublet, its influence on the magnetic properties is negligible. In fact, the quality of the fit does not depend on J', so that J can be obtained with a reasonable accuracy from susceptibility data while J' is determined with a high degree of uncertainty. In view of this, the experimental data were fitted to equation (2) by holding $J' = 0$ and allowing J, g and j to vary. Assuming that the g values for all three copper atoms are equal, the parameters resulting from the best fit of the magnetic data in the temperature range 300–5 K are $J = -189$ cm^{-1}, $g = 2.16$ and $j = -0.6$ cm^{-1} and R, defined as $\Sigma_i[(\chi_i^{obs} - \chi_i^{calc})^2/(\chi_i^{obs})^2]$, $= 5 \times 10^{-4}$.

The polycrystalline X-band EPR spectrum of **2** at 4.2 K exhibits a quasi-isotropic resonance at $g = 2.07$. The spectrum is devoid of any half-field ($\Delta M_s = 2$) transition or fine structure so that it resembles that of an axial doublet associated with a mononuclear $s = \frac{1}{2}$ system with a $d_{x^2-y^2}$ ground state.

The strong antiferromagnetic interaction in **2** is consistent with the nature of the magnetic orbitals on Cu(1) and Cu(2) and bridging groups. The atoms Cu(1) and Cu(2) have square-pyramidal environments, in which the unpaired electron is adequately described by a $d_{x^2-y^2}$ type orbital. In the former, the magnetic orbital points from the metal toward the four oxygen atoms of the four NO bridging groups, whereas, in the latter, it points along the Cu–N directions in the basal plane. Thus, both magnetic orbitals on Cu(1) and Cu(2) are delocalized toward the 2p oxygen and nitrogen orbitals of the NO bridges, and are favourably oriented to give a strong overlap and hence a strong antiferromagnetic interaction. In addition, there is the possibility of a Cu(2)–Cu(2^{I}) exchange interaction along atoms Cu(2)–Cl(1)–Cu(2^{I}); this pathway *via* the chloride atom may yield either ferro- or antiferro-magnetic interactions depending on the Cu(2)–Cl–Cu(2^{I}) angle. Using a molecular-orbital argument it was shown that, for single chloride-bridged planar copper(II) dimers, a ferromagnetic coupling would be expected for angles close to 90°;[18] for angles above 90° antiferromagnetic interactions occur, which become greater as the bridging angle increases further. For **2**, the Cu(2)–Cl–Cu(2^{I}) angle is 144.4(4)°, so a significant antiferromagnetic exchange interaction is expected. However, because the chloride bridges the two terminal Cu(2) ions in an axial position where the spin density of the unpaired electron must be very low, there may only be a weak exchange interaction *via* the chloride. In support of this, the single chloride-bridged copper(II) chain complex $[Cu(dmso)Cl_2]$ (dmso = dimethyl sulfoxide), in which copper atoms with approximately square-pyramidal geometry are bridged sequentially by chloride anions from an equatorial to an axial position with a Cu–Cl–Cu angle of 146.6(1)°, exhibits an antiferromagnetic interaction with $J = -6.1$ cm^{-1}.[19] Thus, we suggest that J is largely determined by the exchange pathway involving the oximate groups.

The decrease in the exchange coupling for **2**, with respect to those observed in **1** and the coplanar dinuclear copper(II) complex $[Cu(\mu\text{-}L)Cu(bipy)][ClO_4]_2$, is consistent with the observation that in copper(II) complexes with double oximato bridges the magnitude of the exchange coupling is dependent on the angles between the basal planes in which the unpaired electrons are located, so that the antiferromagnetic interaction decreases as the structure is distorted from coplanarity. Thus, nearly coplanar trinuclear complexes, such as $[Cu_3(dmg)_2(bipy)_2(MeOH)_2][NO_3]_2$ and $[Cu_3(dpg)_2(bipy)_2(MeOH)_2][NO_3]_2$[7e] ($H_2dmg$ = dimethylglyoxime, H_2dpg = diphenylglyoxime) have been shown to be almost spin-coupled at room temperature with an estimated exchange integral $J > 300$ cm^{-1}, whereas for the trinuclear copper(II) complex $[Cu(CuL)_2][ClO_4]_2$ [H_2L = 3,3′-(trimethylenedinitrilo)bis(butan-2-one oxime)], with a dihedral angle between the basal planes of 55.88(9)° and a pseudo-tetrahedral geometry around the central copper, a much weaker antiferromagnetic interaction ($J = -146$ cm^{-1}) has been observed by Luneau *et al.*[8] In **2**, with copper atoms in square-pyramidal environments and a dihedral angle between basal planes of 64.0(4)°, the J value of -189 cm^{-1} is not unexpected. It should be noted that despite the significant distortion from coplanarity in **2**, the antiferromagnetic interaction is quite strong, which is in accord with the suggestion made by Chaudhuri *et al.*[7f] that the σ pathway, which is not dependent on the angles between copper basal planes, provides the dominant antiferromagnetic interaction in oximato-bridged copper(II) complexes.

Finally, it should be noted that the ensemble of copper–copper distances within the trinuclear unit of **2** as well as its symmetry are close to those found in the active site of ascorbate oxidase. Thus, the Cu(2)•••Cu(1) distance of 3.373(4) Å is similar to the copper-copper separation of 3.4 Å within the type 3 centre whereas the Cu(2)•••Cu(2^{I}) distance of 4.770(4) Å is not far from those observed between type 2 and type 3 centres of *ca.* 4 Å. Furthermore, the nature and magnitude of the exchange coupling of **2** are similar to those observed in T1Hg laccase in which the type 1 Cu^{2+} has been selectively replaced by Hg^{2+}, leaving type 2 and type 3 sites intact.[20] In this sense compound **2** and related trinuclear copper(II) complexes may provide useful information for understanding some properties of multicopper oxidases.

Work is in progress to obtain Cu_3 complexes analogous to **2** containing bridging anions other than chloride.

Acknowledgements

E. C., J. M. D.-V. and A. R. are grateful to the Dirección General de Investigación Científica y Técnica for the project of investigation PB91-0725 and to the Junta de Andalucía for financial support. R. K. thanks Suomen Kulttuurirahasto for a grant.

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Received 20*th June* 1994; *Paper* 4/03742A