An Alternating Copper(II) Chain with Bridging Azide and Oxamidate Ligands: Crystal Structure and Magnetic Properties of $[Cu_2(dmaeoxd)(N_3)_2(H_2O)_2]$ and $[\{Cu_2(dmaeoxd)(N_3)_2\}_n]$ $\{H_2dmaeoxd = N,N'$-bis[2-(dimethylamino)ethyl]oxamide$\}$†

José Antonio Real,[a] Rafael Ruiz,[a] Juan Faus,[a] Francesc Lloret,*,[a] Miguel Julve,[a] Yves Journaux,[b] Michèle Philoche-Levisalles[c] and Claudette Bois[c]

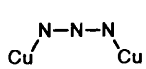
[a] *Departament de Química Inorgànica, Facultat de Química de la Universitat de València, Dr. Moliner 50, 46100, Burjassot, València, Spain*

[b] *Laboratoire de Chimie Inorganique, URA CNRS 420, Université de Paris Sud, 91405 Orsay, France*

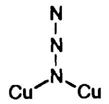
[c] *Laboratoire de Chimie des Métaux de Transition, URA CNRS 419, Université Pierre et Marie Curie, 75252 Paris, France*

Two new azide-containing complexes $[Cu_2(dmaeoxd)(N_3)_2(H_2O)_2]$ **1** and $[\{Cu_2(dmaeoxd)(N_3)_2\}_n]$ **2** $\{H_2dmaeoxd = N,N'$-bis[2-(dimethylamino)ethyl]oxamide$\}$ have been synthesized and characterized by single-crystal X-ray diffraction methods: **1**, triclinic, space group $P\bar{1}$, $a = 8.620(3)$, $b = 9.824(3)$, $c = 11.216(3)$ Å, $\alpha = 85.56(3)$, $\beta = 86.90(3)$, $\gamma = 89.98(3)°$ and $Z = 2$; **2**, monoclinic, space group $P2_1/n$, $a = 9.185(1)$, $b = 11.477(4)$, $c = 7.917(3)$ Å, $\beta = 100.88(3)°$ and $Z = 2$. The structure of **1** is made up of two neutral centrosymmetric *trans* oxamidate-bridged copper(II) dinuclear units with unidentate azide ligands and weakly co-ordinated water molecules. Each copper atom has a distorted square-pyramidal geometry with an oxygen and two nitrogen atoms from the oxamidate group and one nitrogen atom from the azide group forming the equatorial plane and one oxygen atom from water at the axial position. The structure of **2** consists of neutral chains of copper(II) with an alternating azide–oxamidate bridging arrangement. The oxamidate group acts as a bis(terdentate) ligand as in **1** and the azide bridges the metal atoms in an asymmetrical end-on fashion. Each copper atom has a distorted square-pyramidal geometry with one oxygen and two nitrogen atoms from the oxamidate ligand and one nitrogen atom from the azide group in the equatorial plane, whereas the axial position is occupied by a nitrogen atom of another azide group. The metal–metal separation through the oxamidate in each compound is very similar [5.202(1) and 5.232(1) in **1** and 5.286(1) Å in **2**] and much larger than that through azide in **2** [3.395(1) Å]. An investigation of the magnetic properties of **1** and **2** in the temperature range 80–300 K revealed the occurrence of strong antiferromagnetic interactions through oxamidate in both compounds and a weaker ferromagnetic coupling through the end-on azide bridge in **2**.

Azido-bridged copper(II) dinuclear complexes have been of great interest from both structural and magnetic viewpoints in the last decade.[1–3] The azide group is very versatile, and can adopt either end-to-end (μ-1,3) (**I**) and end-on (μ-1,1) (**II**) co-ordination modes when acting as a bridging ligand between copper(II) ions, the magnetic coupling being antiferromagnetic in the former situation[4] and ferromagnetic in the latter.[5] An orbital model based on the concept of spin polarization[6] was proposed to explain this striking ability of azide to stabilize either the singlet or the triplet ground state in azide-bridged copper(II) dinuclear complexes.



I



II

In recent work on the solution and solid-state co-ordination chemistry of N,N'-disubstituted oxamides we investigated the complex formation between copper(II) and $dmaeoxd^{2-}$ (L^{2-}) $\{H_2dmaeoxd = N,N'$-bis[2-(dimethylamino)ethyl]oxamide$\}$.[7] The dinuclear complex $[Cu_2L]^{2+}$, which was shown to be the main species over a wide pH range, was isolated and structurally characterized as the cyanato complex of formula $[Cu_2L(NCO)_2(H_2O)_2]$. In this compound dmaeoxd acts as bis(terdentate) ligand and a strong intramolecular antiferromagnetic coupling [J (singlet–triplet energy gap) $= -560$ cm^{-1}] occurs as usual for this class of dimers.[8] The strong coupling is due to the large σ in-plane overlap between the two d_{xy} magnetic orbitals centred on each copper(II) ion through the oxamidate bridge.[8d] Such a remarkable ability of the *trans*-oxamidate group to transmit the exchange interaction between two copper(II) ions and the great stability in solution of the dinuclear species $[Cu_2L]^{2+}$ makes it a suitable precursor to alternating chains of type –L′–M–L–M–L′–M–L–M– (**III**) where L′ is a potentially bridging ligand. An appropriate choice of L′ (*e.g.* azide anion) could lead to alternating antiferro- and ferro-magnetic interactions within the chain. Such chains are of particular interest because only a few examples are known[9–13] and the study of their magnetic properties has been hampered by the lack of published theoretical models to analyse them.

Our first attempts along these lines gave the dinuclear

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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

precursor [Cu_2(dmaeoxd)$(N_3)_2(H_2O)_2$] **1** and its related chain compound [{Cu_2(dmaeoxd)$(N_3)_2$}$_n$] **2** which exhibits alternating oxamidato and azido bridges. We report here the synthesis and structural characterization of **1** and **2** together with a comparative description of their magnetic properties.

Experimental

Materials.—Copper(II) nitrate trihydrate, sodium azide and lithium hydroxide were obtained from commercial sources and used as received. *N,N'*-Bis[2-(dimethylamino)ethyl]oxamide (H_2dmaeoxd) was prepared by literature methods.[7] Elemental analyses (C, H, N) were performed by the Servicio de Análisis Elemental de la Universidad Autónoma de Madrid.

Preparations.—[Cu_2(dmaeoxd)$(N_3)_2(H_2O)_2$] **1**. Large dark green prismatic crystals of complex **1** suitable for X-ray diffraction were obtained by slow diffusion of aqueous solutions of $[Cu_2L]^{2+}$ (10 cm^3) [prepared by mixing stoichiometric amounts of copper(II) nitrate trihydrate (1 mmol), H_2L (0.5 mmol) and lithium hydroxide (1 mmol)] and azide in an H-shaped tube. They were collected, washed with cold water and air-dried (Found: C, 25.20; H, 5.10; N, 29.30. Calc. for $C_{10}H_{24}Cu_2N_{10}O_4$: C, 25.25; H, 5.10; N, 29.45%).

[{Cu_2(dmaeoxd)$(N_3)_2$}$_n$] **2**. This compound was isolated as a light green crystalline powder by slow addition of an aqueous solution of sodium azide (2 mmol, 10 cm^3) to an aqueous solution (150 cm^3) containing stoichiometric amounts of copper(II) nitrate trihydrate (2 mmol) and L^{2-} (1 mmol). The solid was filtered off, washed with water and dried in a desiccator over silica gel. The yield is almost quantitative (Found: C, 27.40; H, 4.70; N, 31.50. Calc. for $C_{10}H_{20}Cu_2N_{10}O_2$: C, 27.35; H, 4.60; N, 31.90%). A small amount of cubic green single crystals of **2** was obtained by slow evaporation of the filtrate at room temperature.

Physical Techniques.—Magnetic susceptibility measurements were carried out on polycrystalline samples in the temperature range 80–300 K with a fully automatized AZTEC DSM8 pendulum-type susceptometer[14] equipped with a TBT continuous-flow cryostat and a Brüker BE15 electromagnet, operating at 1.8 T. The apparatus was calibrated with mercury tetrakis(thiocyanato)cobaltate(II). Diamagnetic corrections to the susceptibility of the complexes were calculated from Pascal's constants.[15] Magnetic susceptibility data were also corrected for the magnetization of the sample holder. Room-temperature X-band EPR spectra were recorded on polycrystalline samples with a Brüker ER 200D spectrometer equipped with a nitrogen cryostat.

X-Ray Data Collection and Structure Refinement.—Crystals of dimensions 0.55 × 0.55 × 0.20 (**1**) and 0.40 × 0.25 × 0.20 mm (**2**) were mounted on a Philips PW1100 four-circle diffractometer and used for data collection. Intensity data were collected at 18 °C by using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) with the θ–2θ scan technique where the scan width was $(1.2 + 0.34 \tan\theta)°$ for **1** and $(1.1 + \tan\theta)°$ for **2**. The unit-cell parameters were determined from least-squares refinements of 25 reflections in the ranges θ 12–14 (**1**) and 17–18° (**2**). A summary of pertinent crystal parameters and refinement results is given in Table 1. The intensities of two standard reflections measured every 2 h showed no significant variations. Intensity data were corrected for Lorentz-polarization and absorption effects (an absorption correction was performed by use of DIFABS[16]). Of the 2976 (**1**) and 1274 (**2**) measured independent reflections, 2533 and 932 were unique with $I \geqslant 3\sigma(I)$ and used for the structure refinements.

The structures were solved by Patterson methods with the program CRYSTALS[17] followed by successive Fourier syntheses and least-squares refinements in six (**1**) and three (**2**) blocks (310 and 157 parameters respectively) with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were located from a ΔF map, and were refined with an overall isotropic thermal parameter. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme for complex **1** was $w = w'[1 - (\Delta F/6\sigma|F_o|^2)^2]$ where $w' = 1/\Sigma A_r T_r(X)$ with three coefficients (2.93, 1.61 and 2.18) for a Chebyshev polynomial $T(X)$ in which $X = F_o/F_c$ (maximum).[17] A secondary extinction coefficient was introduced in the final stage of the refinement for **1**. Each reflection was assigned a unit weight for **2**. The scattering factors for all atoms and the anomalous dispersion correction term for Cu were taken from ref. 17. The refinement converged at R (R') of 0.043 (0.057) for **1** and 0.029 (0.032) for **2**. The final Fourier-difference maps showed residual maxima and minima of 1.1 and −1.0 (**1**) and 0.3 and −0.3 e Å^{-3} (**2**). All crystallographic calculations were performed on a VAX725 computer using CRYSTALS.[17] Final fractional coordinates for non-hydrogen atoms are listed in Tables 2 (**1**) and 3 (**2**) and main interatomic bond distances and angles in Tables 4 and 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Structures.—[Cu_2(dmaeoxd)$(N_3)_2(H_2O)_2$] **1**. The structure of complex **1** consists of two kinds of neutral centrosymmetric, crystallographically independent but almost identical copper(II) dinuclear units in which dmaeoxd and azide groups act as bis(terdentate) and monodentate ligands, respectively. A perspective view of one of the dimers is depicted in Fig. 1 and a stereoview of the cell is given in the Supplementary Material.

The environment of each copper(II) ion is distorted square pyramidal, CuN_3O_2. The basal plane comprises the carbonyl oxygen O(1), amide N(1) and amine N(3) nitrogen atoms of the oxamidate ligand and the azide N(3) atom whereas the apical position is occupied by atom O(2) of a water molecule. The three copper–oxamidate bond distances [2.050(3), 1.926(3) and 2.077(4) Å for Cu–O(amide), Cu–N(amide) and Cu–N(amine), respectively] are very close to those found in the parent [Cu_2(dmaeoxd)$(NCO)_2(H_2O)_2$][7] and [Cu_2(dmaeoxd)$(NCS)_2$(dmf)$_2$] (dmf = dimethylformamide).[18] The Cu–N(azide) bond distances [1.948(4) and 1.940(4) Å for Cu(1)–N(3) and Cu(2)–N(8), respectively] are similar to those observed in other copper(II) complexes containing terminally bonded azide.[19] The axial Cu–O(water) bond length is somewhat longer [2.232(3) and 2.241(3) Å for Cu(1)–O(2) and Cu(2)–O(4), respectively]. The four equatorial atoms around each copper atom are practically coplanar, Cu(1) and Cu(2) being pulled out of this plane towards the apical water molecule by 0.188 and 0.186 Å, respectively.

The deprotonated dmaeoxd^{2-} ligand exhibits a *trans* conformation with an inversion centre at the middle of the carbon–carbon(amide) bond. It forms two five-membered chelate rings around each metal ion with somewhat depressed values for the two copper–oxamidate angles [averages 82.3 and 82.8° for O(carbonyl)–Cu–N(amide) and N(amide)–Cu–N(amine), respectively]. The oxamidato bridge is planar

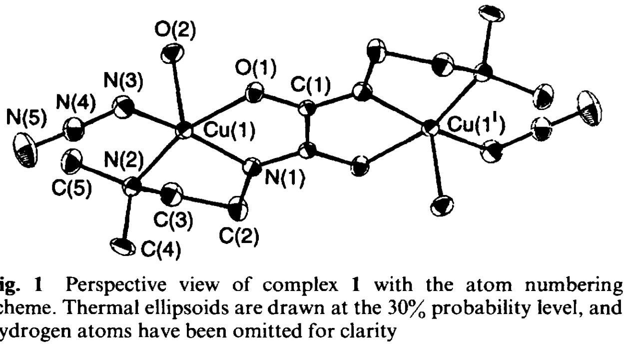

Fig. 1 Perspective view of complex **1** with the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted for clarity

Table 1 Summary of crystal data for [Cu_2(dmaeoxd)$(N_3)_2(H_2O)_2$] **1** and [{Cu_2(dmaeoxd)$(N_3)_2$}$_n$] **2**

Compound	**1**	2
Formula	$C_{10}H_{24}Cu_2N_{10}O_4$	$C_{10}H_{20}Cu_2N_{10}O_2$
M	475.4	439.4
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	8.620(3)	9.185(1)
b/Å	9.824(3)	11.477(4)
c/Å	11.216(3)	7.917(3)
α/°	85.56(3)	90
β/°	86.90(3)	100.88(3)
γ/°	89.98(3)	90
U/Å^3	946(1)	819.6(6)
Z	2	2
D_c/g cm^{-3}	1.669	1.780
F(000)	484	424
μ(Mo-Kα)/cm^{-1}	22.9	26.3
θ range/°	1–25	2–25
R^a	0.043	0.029
R'^b	0.057	0.032

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 2 Final atomic coordinates for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.137 63(5)	0.165 07(5)	0.138 20(4)
O(1)	0.195 1(3)	0.058 2(3)	−0.007 7(3)
O(2)	0.074 1(4)	0.359 3(4)	0.036 1(3)
N(1)	−0.060 5(4)	0.077 7(4)	0.126 8(3)
N(2)	0.030 5(4)	0.232 4(4)	0.293 2(3)
N(3)	0.355 6(4)	0.203 2(5)	0.159 7(4)
N(4)	0.413 8(4)	0.229 5(4)	0.249 3(4)
N(5)	0.474 2(6)	0.255 2(7)	0.334 0(5)
C(1)	0.074 6(4)	−0.005 2(4)	−0.037 1(4)
C(2)	−0.184 1(5)	0.105 0(6)	0.215 1(5)
C(3)	−0.138 4(6)	0.234 5(5)	0.268 9(5)
C(4)	0.061 3(8)	0.128 5(6)	0.393 9(5)
C(5)	0.077 8(7)	0.368 2(5)	0.323 5(6)
Cu(2)	0.341 44(5)	0.663 29(5)	0.139 49(4)
O(3)	0.309 1(3)	0.563 9(3)	−0.011 6(3)
O(4)	0.428 2(4)	0.858 5(4)	0.041 9(3)
N(6)	0.538 0(4)	0.570 6(4)	0.131 7(3)
N(7)	0.420 4(4)	0.723 2(4)	0.299 1(3)
N(8)	0.122 0(4)	0.706 1(4)	0.155 9(4)
N(9)	0.046 4(4)	0.735 4(4)	0.242 0(4)
N(10)	−0.029 9(6)	0.763 0(8)	0.322 5(5)
C(6)	0.432 6(4)	0.499 3(4)	−0.040 9(4)
C(7)	0.644 6(5)	0.591 5(5)	0.224 2(4)
C(8)	0.593 8(5)	0.722 0(5)	0.279 9(5)
C(9)	0.366 8(7)	0.624 5(6)	0.399 9(5)
C(10)	0.372 6(7)	0.861 7(6)	0.330 1(7)

Table 3 Final atomic coordinates for compound **2** with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.007 83(6)	0.075 07(5)	0.317 20(7)
O(1)	−0.127 2(4)	−0.023 3(3)	0.138 9(4)
N(1)	0.127 2(4)	0.081 7(4)	0.141 3(5)
N(2)	0.140 8(4)	0.216 9(3)	0.410 0(5)
N(3)	−0.126 8(4)	0.076 7(4)	0.481 6(5)
N(4)	−0.260 0(4)	0.072 0(4)	0.431 1(5)
N(5)	−0.386 4(5)	0.068 9(5)	0.388 6(7)
C(1)	−0.073 3(5)	−0.029 8(4)	0.002 8(6)
C(2)	0.259 4(5)	0.154 8(4)	0.165 9(7)
C(3)	0.284 9(5)	0.195 1(5)	0.353 1(6)
C(4)	0.168 1(6)	0.230 1(5)	0.599 4(7)
C(5)	0.070 8(6)	0.324 2(5)	0.327 9(8)

as observed in other oxamidate-bridged copper(II) complexes.[7,8,18,20] The mean plane through the four basal atoms around Cu(1) and the oxamidato plane form a dihedral angle of 4.3° [4.4° for Cu(2)].

The azide anion is practically linear, whereas the Cu(1)–N(3)–N(4) and Cu(2)–N(8)–N(9) linkages are bent with angles of 127.8 and 129.3°, respectively. The two bond lengths involving the azide group are significantly different, the longer bond involving the nitrogen atom linked to the metal (averages 1.192 *versus* 1.146 Å), as observed in other copper(II) complexes with terminally bound azide.[4d,h,19]

The intramolecular metal–metal separation [5.202(1) and 5.232(1) Å for Cu(1)···Cu(1^I) and Cu(2)···Cu(2^{II}) (symmetry codes: I $-x$, $-y$, $-z$; II $1 - x$, $1 - y$, $-z$)] and the shorter intermolecular metal–metal distance [5.202 and 5.322 Å for Cu(1)···Cu(2) and Cu(1)···Cu(2^{III}) (symmetry code: III x, $y - 1$, z)] are very similar. This is due to the occurrence of hydrogen bonds involving the co-ordinated O(2) and O(4) water molecules, O(1) and O(3) amide oxygens and the N(3) and N(8) azide nitrogen atoms (see end of Table 4).

[{Cu_2(dmaeoxd)$(N_3)_2$}$_n$] **2**. The structure of complex **2** is made up of neutral zigzag chains of copper(II) ions alternately bridged by dmaeoxd and azide groups as illustrated in Fig. 2. The former acts as bis(terdentate) ligand whereas the latter bridges copper atoms in an asymmetrical end-on fashion, in contrast to compound **1**. Inversion centres occur at the middle of the Cu(1)···Cu(1^I) distance and C(1)–C(1^{II}) amide bond (symmetry codes: I $-x$, $-y$, $1 - z$; II $-x$, $-y$, $-z$). The packing of the chains running parallel to the c axis is illustrated in the Supplementary Material.

The co-ordination geometry around each copper atom is a distorted square-based pyramid, CuN_4O. The equatorial plane is defined by the carbonyl oxygen O(1), the amide N(1) and amine N(2) nitrogen atoms of the oxamidate ligand and the azide N(3) atom as in **1**, whereas the axial co-ordination site is occupied by another azide nitrogen N(3^I) of a symmetry-related unit. The equatorial copper–oxamidate bond lengths [2.036(3), 1.929(4) and 2.084(4) Å for Cu(1)–O(1), Cu(1)–N(1) and Cu(1)–N(2), respectively] compare well with those observed in **1**. The two copper to azide nitrogen bonds are markedly different from each other, the equatorial one [1.957(4) Å for Cu(1)–N(3)] being shorter than the axial [2.472 Å for Cu(1)–N(3^I)] due to the Jahn–Teller effect. The largest deviation from the mean equatorial plane is 0.133 Å at N(1) and the metal atom is pulled out from this mean plane towards the apical site by 0.202 Å.

The deprotonated dmaeoxd^{2-} ligand adopts the *trans* conformation forming two five-membered chelate rings at each metal ion as in complex **1**. The mean basal plane around Cu(1) and the oxamidato plane form a dihedral angle of 10.9°, somewhat greater than that observed in **1** and reflecting the differences in the crystal-packing requirements for the two compounds. As far as the di-μ-azido bridge is concerned, the Cu(1)–N(3)–Cu(1^I) bridging angle 99.4(2)° and the dihedral angle between the Cu(1)N(3)Cu(1^I)N(3^I) and O(1)N(1)N(2)-N(3) mean planes is 88.9°. The distance between the two parallel mean basal planes around Cu(1) and Cu(1^I) is 2.51 Å.

The azide anion is quasi-linear, whereas the Cu(1)–N(3)–N(4) linkage is bent [120.3(3)°]. The nitrogen–nitrogen bond lengths within the azide ligand [1.214(5) and 1.147(5) Å for N(3)–N(4) and N(4)–N(5), respectively] show a larger difference than that observed in complex **1** because of the different co-ordination modes (monodentate in **1** and asymmetric end-on bridge in **2**).

The intrachain copper–copper distances through the dmaeoxd and azido bridges are 5.286(1) and 3.395(1) Å, respectively. The shortest interchain metal–metal separation is 6.784(1) Å for Cu(1)···Cu(1^{III}) and Cu(1)···Cu(1^{IV}) (symmetry codes: III $x - \frac{1}{2}$, $\frac{1}{2} - y$, $z - \frac{1}{2}$; IV $x + \frac{1}{2}$, $\frac{1}{2} - y$, $z + \frac{1}{2}$).

Table 4 Selected bond lengths (Å) and interbond angles (°) for compound **1** with e.s.d.s in parentheses

Copper environment

Cu(1)–O(1)	2.050(3)	Cu(2)–O(3)	2.052(3)
Cu(1)–O(2)	2.232(3)	Cu(2)–O(4)	2.241(3)
Cu(1)–N(1)	1.926(3)	Cu(2)–N(6)	1.924(3)
Cu(1)–N(2)	2.077(4)	Cu(2)–N(7)	2.076(4)
Cu(1)–N(3)	1.948(4)	Cu(2)–N(8)	1.940(4)
O(1)–Cu(1)–N(1)	82.3(1)	O(3)–Cu(2)–N(6)	82.2(1)
O(1)–Cu(1)–N(2)	163.9(1)	O(3)–Cu(2)–N(7)	164.3(1)
O(1)–Cu(1)–N(3)	91.2(1)	O(3)–Cu(2)–N(8)	91.3(1)
N(1)–Cu(1)–N(2)	82.7(1)	N(6)–Cu(2)–N(7)	82.9(1)
N(1)–Cu(1)–N(3)	164.6(2)	N(6)–Cu(2)–N(8)	164.3(2)
N(2)–Cu(1)–N(3)	102.0(2)	N(7)–Cu(2)–N(8)	101.8(2)
O(2)–Cu(1)–O(1)	96.7(1)	O(4)–Cu(2)–O(3)	95.6(1)
O(2)–Cu(1)–N(1)	95.2(1)	O(4)–Cu(2)–N(6)	95.6(1)
O(2)–Cu(1)–N(2)	90.2(1)	O(4)–Cu(2)–N(7)	90.9(1)
O(2)–Cu(1)–N(3)	99.4(2)	O(4)–Cu(2)–N(8)	99.3(2)

Hydrogen bonds*

A	D	H	A···D	A···H–D
O(1)	$O(4^{III})$	$H(4^{III})$	2.854(5)	168(6)
O(3)	O(2)	H(1)	2.854(5)	161(6)
N(3)	$O(4^{II})$	$H(3^{II})$	2.951(5)	166(9)
N(8)	$O(2^{IV})$	$H(2^{IV})$	2.919(5)	165(8)

* Symmetry codes: II 1 − *x*, 1 − *y*, −*z*; III *x*, *y* − 1, *z*; IV −*x*, 1 − *y*, −*z*.

Table 5 Selected bond lengths (Å) and interbond angles (°) for compound **2** with e.s.d.s in parentheses*

Copper environment

Cu(1)–O(1)	2.036(3)	Cu(1)–N(3)	1.957(4)
Cu(1)–N(1)	1.929(4)	$Cu(1)–N(3^{I})$	2.472(4)
Cu(1)–N(2)	2.084(4)		
O(1)–Cu(1)–N(1)	82.9(1)	$N(3^{I})–Cu(1)–O(1)$	101.2(1)
O(1)–Cu(1)–N(2)	156.6(1)	$N(3^{I})–Cu(1)–N(1)$	104.5(2)
O(1)–Cu(1)–N(3)	95.0(2)	$N(3^{I})–Cu(1)–N(2)$	99.5(1)
N(1)–Cu(1)–N(2)	81.3(2)	$N(3^{I})–Cu(1)–N(3)$	80.6(2)
N(1)–Cu(1)–N(3)	174.8(2)	$Cu(1)–N(3)–Cu(1^{I})$	99.4(2)
N(2)–Cu(1)–N(3)	99.2(2)		

* Symmetry translation: I −*x*, −*y*, 1 − *z*.

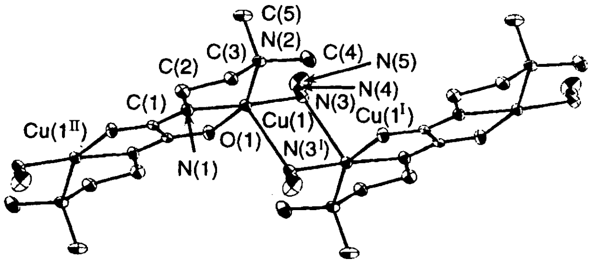

Fig. 2 Perspective view of the asymmetric unit and of three symmetry-related units of complex **2** with the atom numbering scheme. Other details as in Fig. 1

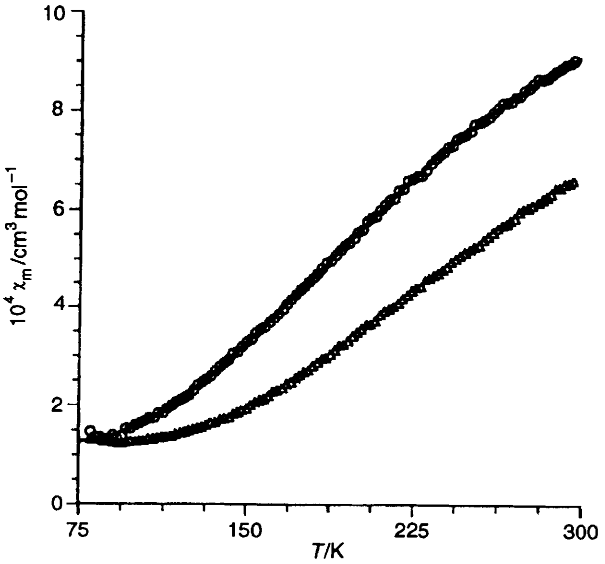

Fig. 3 Thermal dependence of the magnetic susceptibility per two copper(II) ions for complexes **1** (△) and **2** (○). The solid lines correspond to the best theoretical fits (see text)

Magnetic Properties and EPR Data.—The thermal variation of the magnetic susceptibility per two copper(II) ions of complexes **1** and **2** is shown in Fig. 3. Both curves exhibit a behaviour characteristic of strong antiferromagnetic coupling. The magnetic data for **1** were fitted by a simple Bleaney–Bowers equation[21] for a dinuclear copper(II) complex with the interaction Hamiltonian defined as $\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$. Least-squares fitting of the experimental data led to $J = -591$ cm^{-1}, $g = 2.10$ and $R = 3.9 \times 10^{-5}$ where R is the agreement factor defined as $\Sigma_i[(\chi_m)_{obs}(i) - (\chi_m)_{calc}(i)]^2/\Sigma_i[(\chi_m)_{obs}(i)]^2$. The magnitude of the antiferromagnetic coupling agrees well with those reported for the parent dinuclear complexes $[Cu_2(dmaeoxd)(NCO)_2(H_2O)_2]$ **3** and $[Cu_2(dmaeoxd)(NCS)_2(dmf)_2]$ **4** (see Table 6) and demonstrates the remarkable ability of the oxamidato bridge to transmit the exchange interaction between two copper(II) ions when the magnetic orbitals are in the plane of the oxamidate ligand.[22] The same treatment applied to the magnetic data for **2** led to values of J, g and R of -480 cm^{-1}, 2.01 and 1.8×10^{-4}, respectively. The reduction of the coupling in **2** respect to that in **1** cannot be explained only on the basis of pertinent structural differences such as the larger dihedral angle between the mean basal plane around the copper atom and the oxamidate plane (10.9° in **2** *versus* 4.3° in **1**).[23]

The structure of complex **2** reveals that two exchange pathways are possible, one through the oxamidate and the other through the azide. The magnitude of the latter coupling is expected to be much weaker and most likely ferromagnetic [the magnetic orbitals of neighbouring atoms Cu(1) and $Cu(1^{I})$ are parallel to each other in two different planes and separated by 2.51 Å]. Consequently, magnetically, **2** should behave as a chain of weakly interacting dimers. As its magnetic susceptibility data closely adhere to those of a dinuclear copper(II) unit, we used the EPR technique in order to check whether the interdimer interactions allow one to differentiate **2** from **1**. The room-temperature EPR spectrum of **2** exhibits an slightly asymmetric feature at $g = 2.11$ and no signal at half-field. This was checked by measuring the spectra at the maximum receiver-gain setting of our instrument. The EPR spectrum of **1** shows a symmetric feature at the same g value as that of **2** and a weak $\Delta M_S = \pm 2$ forbidden transition at 1650 G. The central feature for **2** exhibits exchange narrowing with respect to that of **1** (peak-to-peak widths 230 and 175 G for **1** and **2**, respectively). Both spectra do not change on lowering the temperature: they simply decrease in intensity and never show any fine splitting. They completely vanish at 80 K revealing that no paramagnetic impurities are present. The narrowing effect in **2** as well as the lack of any resolved fine splitting and $\Delta M_S = \pm 2$ transition are indicative of the existence of an interdimer exchange interaction in this compound,[20d] suggesting that its magnetic behaviour corresponds to that of an alternating chain. Accordingly, we attempted to fit the data of **2** by use of such a hypothesis using the Hamiltonian $\hat{H} = -J\Sigma(\hat{S}_{2i}\cdot\hat{S}_{2i-1} - \alpha\hat{S}_{2i}\cdot\hat{S}_{2i+1})$, where α is the alternation parameter defined as $J'/|J|$.[12,24] The best fit led to $J = -500$ cm^{-1}, $\alpha = 0.1$ and $g = 2.10$ ($R = 3.8 \times 10^{-5}$) (solid line in Fig. 3). It is clear that the value of the coupling

Table 6 Relevant structural and magnetic data for *trans* dmaeoxd bridged copper(II) complexes

Compound	Nuclearity	Donor set[a]	h_M[b]/Å	γ[c]/°	Cu···Cu/Å	$-J$[d]/cm^{-1}	Ref.
1	Dimer	ON_3O	0.19	4.3	5.20	591	This work
			0.19	4.4	5.23		
2	Chain	ON_3N	0.20	10.9	5.29	480	This work
3	Dimer	ON_3O	0.19	4.0	5.31	560	7
4	Dimer	ON_3O	0.22	10.2	5.15	580	4*a*, 18

[a] The first four atoms comprise the basal plane and the fifth occupies the apical position. [b] The height of the metal atom above the basal plane towards the apical ligand. [c] Dihedral angle between the mean basal plane around the metal atom and the oxamidato plane. [d] Singlet–triplet energy gap evaluated through a simple Bleaney–Bowers analysis.

through the oxamidate is still too low. Moreover, although the coupling through the azide is found to be ferromagnetic ($J' = 50$ cm^{-1}) as expected, it could be overestimated in the light of previously reported values for the exchange coupling in asymmetric end-on azide-bridged copper(II) complexes.[25] When a more reasonable value of J such as -560 cm^{-1} is kept constant in the fitting procedure, a large value of $\alpha = 0.8$ is obtained which leads to an unreal value of $J' \approx +400$ cm^{-1}. In summary, the magnetostructural data of **1** and **2** are consistent with the occurrence of alternating antiferro- and ferro-magnetic interactions in **2**, the value of the ferromagnetic coupling being undetermined because of the large antiferromagnetic interaction through the oxamidate (maximum susceptibility of **2** is at $T > 290$ K).

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