# Crystal Structure and Magnetic Properties of a Two-dimensional Sheet-like Copper(II) Complex with Bridging *trans*-Oxamidate and Azide†

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A novel sheet-like complex polymer $[Cu_4L_2(N_3)_3]_n[ClO_4]_n\cdot 2nH_2O$, where $H_2L$ is *N,N'*-bis(2-aminoethyl)oxamide, has been prepared and characterized by X-ray crystallography, and magnetic and spectroscopic measurements. It crystallizes in the triclinic system, space group $P\bar{1}$, with $a$ = 11.486(2), $b$ = 11.706(3), $c$ = 12.291(3) Å, $\alpha$ = 77.42(2), $\beta$ = 67.59(2), $\gamma$ = 77.96(2)° and $Z$ = 2. The structure consists of a two-dimensional network of copper(II) ions bridged by L in a *trans* conformation, and by azido ligands in three different bonding modes, *i.e.* asymmetric end-to-end, asymmetric end-on and symmetric end-on. The repeating asymmetric unit comprises a tetranuclear copper(II) fragment with two of the copper atoms in approximately square-planar environments, and two with distorted-pyramidal geometries. Magnetic susceptibility data have been measured in the temperature range 4–300 K indicating an antiferromagnetic exchange interaction between copper(II) ions bridged alternately by L and azido ligands. This results from the efficiency of the *trans*-oxamidato and symmetric end-on azido bridges in facilitating an antiferromagnetic exchange interaction ($J = -516.8$ cm$^{-1}$) between copper(II) ions which are separated by about 5.2 and 3.3 Å, respectively. The best fit of the magnetic data is obtained by considering the system to comprise CuLCu dimers linked by end-on azido bridges which create a molecular field, with negligible exchange through the asymmetric end-to-end azido groups.

The magnetic properties of low-dimensional compounds have been investigated by a number of groups,[1–5] particular attention being devoted to two- and(or) three-dimensional network complex polymers as it is believed that increasing dimensionality enhances bulk magnetic properties.[6–10] A number of strategies may be employed in synthesizing such polymeric complexes with potentially good magnetic properties. One is to allow metal ions to react with two different potentially bridging ligands such as oxamidate and azide to give infinite networks.

The azido group is a versatile bridging ligand which can co-ordinate two copper ions in either an end-on[11–14] or end-to-end fashion;[15–19] probably the most fascinating aspect of μ-azido copper(II) dinuclear complexes is their versatile magnetic properties. Although both kinds of complexes are structurally and magnetically well characterized, few compounds reported to date are two-dimensional complexes with both end-to-end and end-on bridging modes.[20]

Bridging oxamidates have played a key role in the design of polymetallic systems owing to their ability to facilitate strong exchange interactions.[21] One of the properties of these ligands is their easy *cis-trans* conformational change affording symmetric or antisymmetric oxamidato bridges. The bis(tridentate) character of these ligands in *trans* conformation allows the formation of *trans*-oxamidato-bridged copper(II) dimers which can be linked by bridging ligands such as acetate,[22] cyanate[23] or azide[24] to form one-dimensional chains. In order to extend this study, our work is aimed at obtaining complex polymers of higher dimensionality by linking the copper(II) dimers with bis(monodentate) bridging ligands such as azide or carboxylate. In this paper we present the synthesis, X-ray structure and magnetic behaviour of the first two-dimensional sheet-like copper(II) complex with mixed *trans*-oxamidato and azido bridges in both end-on and end-to-end bonding modes.

## Experimental

*Synthesis.*—The ligand $H_2L$ and its mononuclear complex $[CuL]\cdot 2H_2O$ were obtained by literature methods.[25]

$[CuL_2(N_3)_3]_n[ClO_4]_n\cdot 2nH_2O$ **1**. To a heated aqueous solution of $[CuL]\cdot 2H_2O$ (1 mmol, 40 cm$^3$) was added an aqueous solution of copper perchlorate (1 mmol, 5 cm$^3$) with stirring. The resulting blue solution was then adjusted to pH 5.1 by adding 0.70 mol dm$^{-3}$ perchloric acid. After standing at room temperature for 12 h, an aqueous solution of sodium azide (1 mmol, 30 cm$^3$) was added dropwise to the solution followed by sodium perchlorate (0.5 g). After standing in a refrigerator at 4 °C for several days, black-green crystals were collected (Found: C, 16.50; H, 3.20; N, 27.65; Cu, 29.15. Calc. for $C_{12}H_{28}ClCu_4N_{17}O_{10}$: C, 16.75; H, 3.25; N, 27.70; Cu, 29.55%).

*Physical Measurements.*—Magnetic measurements on powder samples were carried out with a VSM-type magnetometer in the temperature range 4–300 K. Correction for diamagnetism was estimated from Pascal's constants to be $-320 \times 10^{-6}$ cm$^3$ mol$^{-1}$. The powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer, and IR spectra on a Nicolet FT-IR 170SX spectrophotometer as KBr pellets. Reflectance spectra were obtained using a Shimadzu UV-240 spectrophotometer.

*Crystal Structure Determination.*—The intensity data were collected at room temperature on an R3M/E four-circle

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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:* $\mu_B \approx 9.274\,02 \times 10^{-24}$ J T$^{-1}$.

**Table 1** Summary of crystal data, data collection and structure refinement for $[Cu_4L_2(N_3)_3]_n[ClO_4]_n \cdot 2nH_2O$

| | |
|---|---|
| Formula | $C_{12}H_{28}ClCu_4N_{17}O_{10}$ |
| $M$ | 860.1 |
| Crystal size/mm | 0.4 × 0.4 × 0.4 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$/Å | 11.486(2) |
| $b$/Å | 11.706(3) |
| $c$/Å | 12.291(3) |
| $\alpha$/° | 77.42(2) |
| $\beta$/° | 67.59(2) |
| $\gamma$/° | 77.96(2) |
| $U$/Å$^3$ | 1476.5(6) |
| $Z$ | 2 |
| $D_c$/g cm$^{-3}$ | 1.93 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 30.17 |
| $F$(000) | 864 |
| $\lambda$(Mo-K$\alpha$)/Å | 0.710 73 |
| Scan type | $\theta$–2$\theta$, |
| 2$\theta$ range/° | 1–45 |
| Check reflections | −3 2 0, 0 0 4 |
| No. of unique reflections | 4224 |
| No. of observed reflections | 3416 |
| Selection criterion | $I \geqslant 1.5\sigma(I)$ |
| $R^a$ | 0.0470 |
| $R'^b$ | 0.0465 |
| Goodness of fit | 1.422 |
| Largest shift/e.s.d. | −0.045 |
| $R$(int) | 0.0162 |
| Residual extrema/e Å$^{-3}$ | 1.921 |

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

**Table 2** Atomic positional parameters for $[Cu_4L_2(N_3)_3]_n$-$[ClO_4]_n \cdot 2nH_2O$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu(1) | 0.5530(1) | 0.1580(1) | 0.3058(1) |
| Cu(2) | 0.4798(1) | 0.4420(1) | 0.2255(1) |
| Cu(3) | 1.0719(1) | 0.3194(1) | 0.1409(1) |
| Cu(4) | 1.0295(1) | 0.0485(1) | 0.2730(1) |
| Cl | 0.2834(2) | 0.7546(2) | 0.1898(2) |
| N(1) | 0.5271(5) | 0.1416(4) | 0.1571(4) |
| N(2) | 0.4705(4) | 0.0183(4) | 0.3690(4) |
| N(3) | 0.3915(5) | 0.3257(4) | 0.3538(4) |
| N(4) | 0.3401(5) | 0.3440(5) | 0.4553(5) |
| N(5) | 0.2888(9) | 0.3565(8) | 0.5524(6) |
| N(6) | 0.5623(5) | 0.5180(4) | 0.3041(4) |
| N(7) | 0.5689(4) | 0.5413(4) | 0.0852(4) |
| N(8) | 1.1288(5) | 0.3398(4) | 0.2710(4) |
| N(9) | 1.0258(4) | 0.4879(4) | 0.1321(4) |
| N(10) | 1.1374(4) | 0.1494(4) | 0.1342(4) |
| N(11) | 1.1950(5) | 0.1133(4) | 0.0397(4) |
| N(12) | 1.2533(7) | 0.0791(6) | −0.0475(5) |
| N(13) | 0.9405(5) | −0.0215(4) | 0.1967(4) |
| N(14) | 0.9373(4) | −0.0486(4) | 0.4144(4) |
| N(15) | 0.6854(6) | 0.2626(4) | 0.2259(4) |
| N(16) | 0.7777(5) | 0.2570(4) | 0.2501(4) |
| N(17) | 0.8695(5) | 0.2551(5) | 0.2706(5) |
| O(1) | 0.5742(4) | 0.1276(3) | 0.4653(3) |
| O(2) | 0.4119(4) | 0.3957(3) | 0.1129(3) |
| O(3) | 1.0342(4) | 0.3473(3) | −0.0106(3) |
| O(4) | 1.0924(4) | 0.0990(3) | 0.3850(3) |
| O(5) | 0.1849(12) | 0.8320(15) | 0.2255(11) |
| O(6) | 0.3981(10) | 0.7975(14) | 0.1594(18) |
| O(7) | 0.2928(5) | 0.7126(5) | 0.0865(5) |
| O(8) | 0.3043(12) | 0.6600(12) | 0.2693(8) |
| O(w1) | 0.0884(4) | 0.8362(4) | 0.0058(4) |
| O(w2) | 0.4225(5) | 0.3389(4) | 0.5075(4) |
| C(1) | 0.4215(7) | 0.0720(6) | 0.1929(6) |
| C(2) | 0.4287(6) | −0.0270(5) | 0.2909(5) |
| C(3) | 0.4704(5) | −0.0330(5) | 0.4727(5) |
| C(4) | 0.6734(7) | 0.5658(7) | 0.2110(6) |
| C(5) | 0.6476(6) | 0.6164(6) | 0.0979(5) |
| C(6) | 0.4536(5) | 0.4566(4) | 0.0102(5) |
| C(7) | 1.0484(8) | 0.4434(6) | 0.3207(6) |
| C(8) | 1.0347(7) | 0.5426(5) | 0.2235(5) |
| C(9) | 0.9970(5) | 0.5420(4) | 0.0406(4) |
| C(10) | 0.8301(6) | −0.0699(6) | 0.2901(5) |
| C(11) | 0.8614(6) | −0.1266(5) | 0.4012(5) |
| C(12) | 1.0449(5) | 0.0434(4) | 0.4900(4) |

diffractometer with graphite-monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) by using the $\theta$–2$\theta$ scan technique. Details of crystal data, collection and refinement are listed in Table 1. Lattice parameters were obtained by a least-squares fit of 23 reflections in the range 7–23°. Intensity data were collected in the 2$\theta$ range 1–45° with scan rate of 8° min$^{-1}$. The intensities were corrected for Lorentz-polarization and absorption effects. Of the 4224 measured independent reflections, 3416 were observed with $I \geqslant 1.5\sigma(I)$ and used for the structure refinement.

The structure was solved using standard Patterson methods and subsequently by Fourier difference maps. Full-matrix least-squares refinement was carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms, from the $\Delta F$ map, were included with a common thermal parameter. The calculations were performed using the SHELX 76 program.[26] The final least-squares refinement converged at $R$ ($R'$) 0.0470 (0.0465). The atomic coordinates for the non-hydrogen atoms are listed in Table 2, and selected bond distances and angles are presented in Tables 3 and 4, respectively.

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 Crystal Structure of* $[Cu_4L_2(N_3)_3]_n$-$[ClO_4]_n \cdot 2nH_2O$.—This complex consists of a two-dimensional array of copper(II) ions bridged by both L and azide, the former behaving as a bis(terdentate) ligand in a *trans* conformation whereas the latter bridges copper(II) centres in both end-to-end and end-on fashions extending out to form an infinite network as shown in Fig. 1. Inversion centres are at the middle of C–C bonds of the amides in the oxamidato groups.

The repeating asymmetric unit is a tetranuclear fragment in which the geometries of the four copper centres are not identical. The Cu(2) and Cu(4) atoms are in approximately square-planar environments, whereas Cu(1) and Cu(3) have distorted square-based pyramidal geometries. The co-ordination plane for Cu(2) is defined by the O(2), N(7) and N(6) atoms of a *trans*-oxamidato group and an N(3) atom from an azido [N(3)N(4)N(5)] group in an asymmetric end-on fashion which is also axially bound to the neighbouring Cu(1) centre. The largest deviation from the least-squares plane through O(2)N(7)N(6)N(3) is 0.0589 Å at N(7), and Cu(2) lies 0.0166 Å out of this plane. The Cu(4) centre is bonded to the O(4), N(14) and N(13) atoms of a *trans*-oxamidato group and an N(10) atom from a symmetric end-on azido group [N(10)N(11)N(12)] which is equatorially bound to the neighbouring Cu(3) atom. The largest deviation from the least-squares plane through O(4)N(14)N(13)N(10) is 0.0302 Å at N(14), and the Cu(4) atom is pulled out of this plane by 0.0019 Å. The basal plane for the Cu(1) is defined by the N(1), N(2) and O(1) atoms of a *trans*-oxamidato group and an N(15) atom from an asymmetric end-to-end azido group [N(15)N(16)N(17)] which is axially bound to the neighbouring Cu(3) atom, the axial co-ordination site of Cu(1) being occupied by the N(3) atom from an asymmetric end-on azido group which is equatorially bound to Cu(2). The largest deviation from the least-squares plane through

**Table 3** Selected bond distances (Å) for $[Cu_4L_2(N_3)_3]_n[ClO_4]_n\cdot 2nH_2O$

| | | | |
|---|---|---|---|
| Cu(1)–N(1) | 2.014(6) | Cu(1)–N(2) | 1.925(5) |
| Cu(1)–N(3) | 2.407(4) | Cu(1)–N(15) | 1.973(5) |
| Cu(1)–O(1) | 2.014(5) | Cu(2)–N(3) | 1.946(4) |
| Cu(2)–N(6) | 2.012(6) | Cu(2)–N(7) | 1.910(4) |
| Cu(2)–O(2) | 2.036(5) | Cu(3)–N(8) | 2.018(6) |
| Cu(3)–N(9) | 1.923(4) | Cu(3)–N(10) | 1.978(4) |
| Cu(3)–N(17) | 2.427(5) | Cu(3)–O(3) | 2.012(5) |
| Cu(4)–N(10) | 1.977(4) | Cu(4)–N(13) | 2.003(6) |
| Cu(4)–N(14) | 1.916(4) | Cu(4)–N(4) | 2.013(5) |
| N(1)–C(1) | 1.475(10) | N(2)–C(2) | 1.454(10) |
| N(2)–C(3) | 1.284(7) | N(3)–N(4) | 1.205(7) |
| N(4)–N(5) | 1.139(9) | N(6)–C(4) | 1.468(8) |
| N(7)–C(5) | 1.455(10) | N(7)–C(6c) | 1.288(8) |
| N(8)–C(7) | 1.457(8) | N(9)–C(8) | 1.452(10) |
| N(9)–C(9) | 1.289(8) | N(10)–N(11) | 1.219(7) |
| N(11)–N(12) | 1.134(8) | N(13)–C(10) | 1.468(7) |
| N(14)–C(11) | 1.458(10) | N(14)–C(12c) | 1.283(8) |
| N(15)–N(16) | 1.190(9) | N(16)–N(17) | 1.170(9) |
| O(1)–C(3c) | 1.281(6) | O(2)–C(6) | 1.272(6) |
| O(3)–C(9c) | 1.281(6) | O(4)–C(12) | 1.277(5) |
| C(1)–C(2) | 1.493(9) | C(3)–O(1c) | 1.281(6) |
| C(3)–C(3c) | 1.518(14) | C(4)–C(5) | 1.500(10) |
| C(6)–N(7c) | 1.288(8) | C(6)–C(6c) | 1.539(12) |
| C(7)–C(8) | 1.505(9) | C(9)–O(3c) | 1.281(6) |
| C(9)–C(9c) | 1.522(12) | C(10)–C(11) | 1.521(10) |
| C(12)–N(14c) | 1.283(8) | C(12)–C(12c) | 1.515(12) |

**Table 4** Bond angles (°) for $[Cu_4L_2(N_3)_3]_n[ClO_4]_n\cdot 2nH_2O$

| | | | |
|---|---|---|---|
| N(1)–Cu(1)–N(2) | 82.5(2) | N(1)–Cu(1)–N(3) | 96.3(2) |
| N(2)–Cu(1)–N(3) | 107.5(2) | N(1)–Cu(1)–N(15) | 96.2(2) |
| N(2)–Cu(1)–N(15) | 161.6(2) | N(3)–Cu(1)–N(15) | 90.9(2) |
| N(1)–Cu(1)–O(1) | 164.5(2) | N(2)–Cu(1)–O(1) | 83.1(2) |
| N(3)–Cu(1)–O(1) | 93.5(2) | N(15)–Cu(1)–O(1) | 95.7(2) |
| N(3)–Cu(2)–N(6) | 103.2(2) | N(3)–Cu(2)–N(7) | 172.1(2) |
| N(6)–Cu(2)–N(7) | 83.7(2) | N(3)–Cu(2)–O(2) | 90.4(2) |
| N(6)–Cu(2)–O(2) | 166.3(2) | N(7)–Cu(2)–O(2) | 82.9(2) |
| N(8)–Cu(3)–N(9) | 82.2(2) | N(8)–Cu(3)–N(10) | 99.3(2) |
| N(9)–Cu(3)–N(10) | 174.0(2) | N(8)–Cu(3)–N(17) | 96.6(2) |
| N(9)–Cu(3)–N(17) | 100.0(2) | N(10)–Cu(3)–N(17) | 85.5(2) |
| N(8)–Cu(3)–O(3) | 162.4(2) | N(9)–Cu(3)–O(3) | 83.4(2) |
| N(10)–Cu(3)–O(3) | 94.1(2) | N(17)–Cu(3)–O(3) | 95.8(2) |
| N(10)–Cu(4)–N(13) | 101.2(2) | N(10)–Cu(4)–N(14) | 175.0(2) |
| N(13)–Cu(4)–N(14) | 83.6(2) | N(10)–Cu(4)–O(4) | 92.2(2) |
| N(13)–Cu(4)–O(4) | 166.6(2) | N(14)–Cu(4)–O(4) | 83.1(2) |
| Cu(1)–N(1)–C(1) | 107.9(4) | Cu(1)–N(2)–C(2) | 117.7(3) |
| Cu(1)–N(2)–C(3) | 115.8(5) | C(2)–N(2)–C(3) | 126.0(5) |
| Cu(1)–N(3)–Cu(2) | 97.3(2) | Cu(1)–N(3)–N(4) | 120.5(4) |
| Cu(2)–N(3)–N(4) | 122.6(5) | N(3)–N(4)–N(5) | 176.7(8) |
| Cu(2)–N(6)–C(4) | 107.8(4) | Cu(2)–N(7)–C(5) | 117.0(4) |
| Cu(2)–N(7)–C(6c) | 117.5(4) | C(5)–N(7)–C(6c) | 125.2(4) |
| Cu(3)–N(8)–C(7) | 106.3(5) | Cu(3)–N(9)–C(8) | 117.6(4) |
| Cu(3)–N(9)–C(9) | 115.9(4) | C(8)–N(9)–C(9) | 126.4(5) |
| Cu(3)–N(10)–Cu(4) | 111.8(2) | Cu(3)–N(10)–N(11) | 121.3(3) |
| Cu(4)–N(10)–N(11) | 121.4(4) | N(10)–N(11)–N(12) | 178.6(8) |
| Cu(4)–N(13)–C(10) | 108.6(4) | Cu(4)–N(14)–C(11) | 117.1(4) |
| Cu(4)–N(14)–C(12c) | 116.3(4) | C(11)–N(14)–C(12c) | 126.5(4) |
| Cu(1)–N(15)–N(16) | 125.3(4) | N(15)–N(16)–N(17) | 177.4(5) |
| Cu(3)–N(17)–N(16) | 129.9(4) | Cu(1)–O(1)–C(3c) | 110.4(4) |
| Cu(2)–O(2)–C(6) | 109.7(4) | Cu(3)–O(3)–C(9c) | 110.2(4) |
| Cu(4)–O(4)–C(12) | 109.9(4) | | |

N(1)N(2)O(1)N(15) is 0.096 Å at N(2), and Cu(1) is pulled out of this plane toward the apical site by 0.2263 Å. The equatorial plane for Cu(3) comprises the O(3), N(9) and N(8) atoms of a *trans*-oxamidato group, and an N(10) atom from a symmetric end-on azido group [N(10)N(11)N(12)] which is equatorially bound to the next Cu(4) centre, the apical position being occupied by the N(17) atom from an asymmetric end-to-end azido group which equatorially co-ordinates Cu(1), and Cu(3) is displaced out of the equatorial plane toward the axial N(17) atom by 0.1423 Å. Although Cu(1) and Cu(3) both have square-based pyramidal geometries, the former is more distorted than the latter.

The azides bridge the copper centres in different fashions, connecting the *trans*-oxamidato-bridged copper(II) dimers to give an infinite two-dimensional network structure that can be regarded to consist of two kinds of non-equivalent alternating chains [··· Cu(2c) ··· Cu(1c) ··· Cu(1) ··· Cu(2) ··· Cu(2a) ··· Cu(1a) ··· and ··· Cu(3b) ··· Cu(4b) ··· Cu(4) ··· Cu(3) ··· Cu(3d) ··· Cu(4d) ··· as shown in Fig. 1] which are connected by asymmetric end-to-end azido bridges. In the asymmetric unit, both Cu(1) ··· Cu(2) and Cu(3) ··· Cu(4) are bridged separately by end-on azido ligands with the former in an asymmetric end-on mode [Cu(1)–N(3) 2.407(4), Cu(2)–N(3) 1.946(4) Å] and the latter in a symmetric mode [Cu(3)–N(10) 1.978(4), Cu(4)–N(10) 1.977(4) Å]. The Cu(1)–N(3)–Cu(2) and Cu(3)–N(10)–Cu(4) angles are 97.3(2) and 111.8(2)°, respectively, the former being close to the values reported previously,[11–14] while the latter is much greater. The Cu(1) and Cu(3) atoms are linked by an azido group in an asymmetric end-to-end fashion, with Cu(1)–N(15) 1.973(5) and Cu(3)–N(17) 2.427(15) Å and the azido groups are quasi-linear with N(3)–N(4)–N(5), N(10)–N(11)–N(12) and N(15)–N(16)–N(17) angles of 176.7(8), 178.6(8) and 177.4(5)°, respectively. Moreover, the differences in bond lengths (Δ) between the neighbouring N–N bonds for the end-on azido groups [0.066 and 0.085 Å for N(3)N(4)N(5) and N(10)N(11)N(12), respectively] are larger than that for the end-to-end one (0.020 Å). This agrees with the general trend for co-ordinated azide.[27]

The deprotonated ligand L adopts a *trans* conformation forming two five-membered chelate rings with each copper ion. The Cu(1)–N(2) bond distance [1.925(5) Å] is shorter than those for Cu(1)–O(1) and Cu(1)–N(1) [2.014(5) and 2.014(6) Å], which is in accord with distances in other oxamidato-bridged copper(II) complexes.[28–30] The significant shortening of Cu(1)–N(2) is consistent with the strong basicity of the deprotonated amide nitrogen atom. The three atoms [Cu(1), C(2) and C(3)] around N(2) lie in a plane with bond angles of 117.7(3), 115.8(5) and 126.0(5)° for Cu(1)–N(2)–C(2), Cu(1)–N(2)–C(3) and C(2)–N(2)–C(3), respectively. This, together with the bond distances and planarity of the oxamidato bridges reveals that N(2) and its symmetry-related N(2c) are $sp^2$-hybridized and the π electrons of C(3)–O(1c) and C(3c)–O(1) are delocalized to form a conjugated system.

The Cu(1) ··· Cu(2), Cu(3) ··· Cu(4) and Cu(1) ··· Cu(3) distances, bridged by asymmetric end-on, symmetric end-on and asymmetric end-to-end azido groups are 3.370, 3.275 and 6.084 Å, respectively. The Cu ··· Cu separations through the *trans*-oxamidato groups are 5.264, 5.273, 5.260 and 5.250 Å for Cu(1) ··· Cu(1c), Cu(2) ··· Cu(2a), Cu(3) ··· Cu(3d) and Cu(4) ··· Cu(4b), respectively.

*EPR Spectra and Magnetic Data.*—The EPR spectra recorded at room temperature show an asymmetric feature at $g = 2.10$ and no signal at half-field. The spectra do not change on lowering the temperature, they simply decrease in intensity and show no hyperfine splitting.

The temperature dependence of the magnetic moment per copper atom of $[Cu_4L_2(N_3)_3]_n[ClO_4]_n\cdot 2nH_2O$ in the form of $\mu_{eff}$ *vs.* $T$ is shown in Fig. 2. The $\mu_{eff}$ for each copper atom at 300 K is only 0.986 $\mu_B$, much less than expected for a paramagnetic system with $S = \frac{1}{2}$. This value, together with the smooth decrease of $\mu_{eff}$ with $T$ in the range 300–4 K indicates there is an antiferromagnetic exchange between the copper atoms at temperatures higher than 300 K. Two different exchange pathways are possible, one through the L and the other through the azido ligands. Oxamidato bridges are known to be very effective in facilitating an exchange interaction between copper ions when both the sets of oxygen and nitrogen donors occupy equatorial co-ordination sites in the metal environment, with

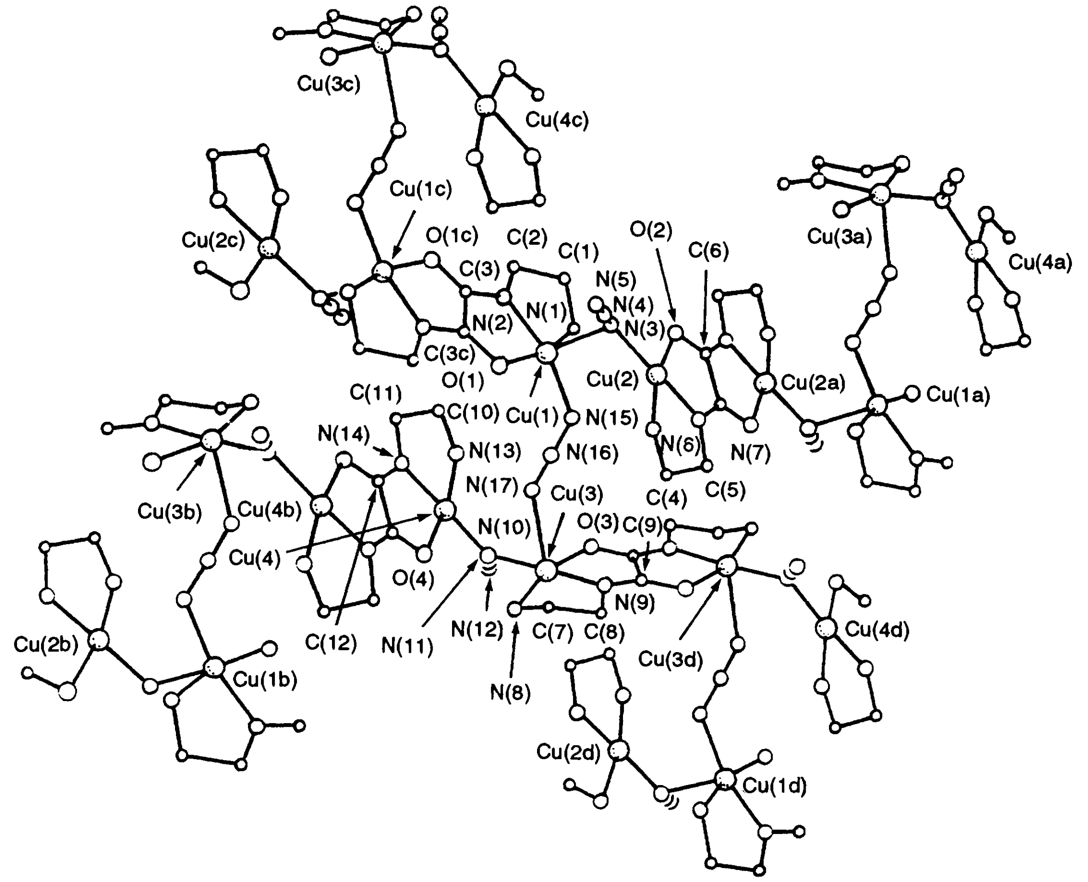
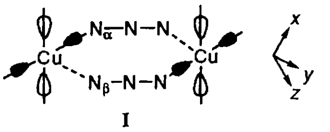


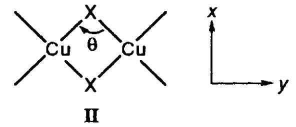
Fig. 1 A perspective view of the five symmetry-related asymmetric units for $[Cu_4L_2(N_3)_3]_n[ClO_4]_n{\cdot}2nH_2O$

$|J| > 300$ cm$^{-1}$.[31] The versatile magnetic properties of the azido ligands provide the most fascinating aspect of the chemistry of μ-azido copper(II) dinuclear complexes.[32] In complexes with asymmetric end-to-end bridges with short equatorial Cu–N bonds and a long axial Cu–N bond, the exchange interaction is negligible for square pyramidal geometry at the copper,[11,19,23] because the relative orientations of the two magnetic orbitals are particularly unfavourable for transmitting electronic effects between two Cu$^{II}$ ions of the same molecular entity. In this case, the magnetic orbitals on the two neighbouring copper ions are parallel to each other as shown in I and do not interact.[32] However, when $N_3^-$ ligands bridge the copper ions in an end-on fashion as shown in $[Cu_4L_2(N_3)_3]_n[ClO_4]_n{\cdot}2nH_2O$, the situation is apparently very complicated, and the extent of interaction depends on the nature of the whole bridging network.



I

As has been shown experimentally and discussed theoretically, a planar network such as in II allows the magnetic orbitals to lie orthogonal to each other.[11] For azido-bridged copper(II) dimers, the θ value is *ca.* 103°; for θ < 103°, the $J_F$ contribution is predominant and the observed coupling is ferromagnetic, however, for θ > 103°, $J_{AF}$ is the dominant contribution and the observed coupling is antiferromagnetic. In $[Cu_4L_2(N_3)_3]_n[ClO_4]_n{\cdot}2nH_2O$, θ for the asymmetric end-on azido bridges is 97.3(2)°, so a ferromagnetic coupling is expected; however, for the symmetric end-on azido bridges θ is 111.8(2)°, so the observed coupling is antiferromagnetic. Since the difference between 103° and 111.8° is larger than that between 103° and 97.3°, the total coupling transmitted by the end-on azido groups should be antiferromagnetic.



II

Since asymmetric end-to-end azido groups do not transmit magnetic interactions, it should be possible to treat the magnetic data for the two unequivalent alternating bimetallic chains separately, because the sheet-like structure can be regarded as consisting of two kinds of non-equivalent alternating chains which are connected by asymmetric end-to-end azido bridges. We attempted to fit the magnetic data for these different alternating chains, one being bridged by *trans*-oxamidate and symmetric end-on azide (both of which transmit strong antiferromagnetic exchange) the other being alternately bridged by *trans*-oxamidato ligands (transmitting strong antiferromagnetic coupling) and asymmetric end-on azide ligands (mediating ferromagnetic exchange). We attempted to fit the magnetic data by the empirical relation [equation (1)] proposed by Hatfield,[34] where α is the exchange alternating parameter. However the curve calculated by this model did not fit the experimental points satisfactorily.

$$\mathscr{H} = -J \sum_{i=1}^{n/2} (S_{2i}S_{2i+1} + \alpha S_{2i}S_{2i+1}) \qquad (1)$$

Therefore, since this magnetic system is too complex to be fitted for two different alternating chains, we attempted to simplify the magnetic system into chains of interacting dimers, CuLCu, with exchange through the end-on azide bridges

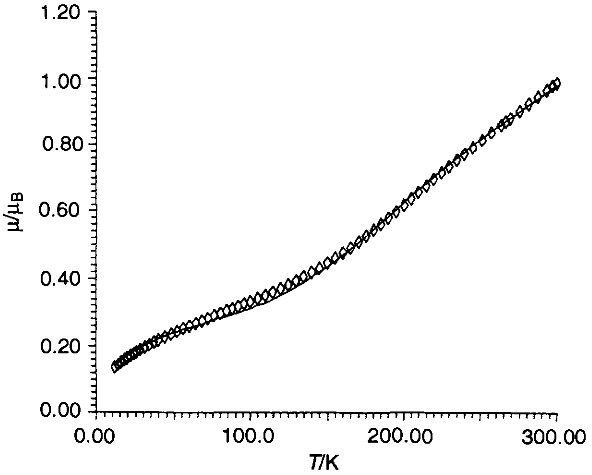


**Fig. 2** Experimental (◇) and calculated (—) temperature dependence of $\mu_{eff}$ for $[Cu_4L_2(N_3)_3]_n[ClO_4]_n{\cdot}2nH_2O$

creating an interdimeric molecular field, thus allowing interpretation of the data with the modified Bleaney–Bower equation (2), where ρ represents the percentage of

$$\chi_M = (2N\beta^2g^2)/K(T - \theta)\,[3 + \exp(-J/KT)]^{-1}(1 - \rho) + [Ng^2\beta^2/2k(T - \theta)]\rho + 2N\alpha \quad (2)$$

paramagnetic impurities which exhibit a Weiss constant θ. The least-squares fit of the magnetic data by equation (2) gave $g = 2.10$, $J = -516.8$ cm$^{-1}$, $\rho = 0.0187$ and $\theta = -42.3$ K with $R = 3.6 \times 10^{-4}$ $[R = \Sigma(\mu_{obs} - \mu_{calc})^2/\Sigma(\mu_{obs})^2]$. The calculated curve fits the experimental points satisfactorily as shown in Fig. 2. The negative θ value shows an antiferromagnetic contribution from the symmetric end-on azido ligands, which is not totally compensated by the ferromagnetic contribution from the asymmetric end-on azido bridges.[35] However, the magnitude of the resulting antiferromagnetic interaction is less pronounced than in similar complexes with $N_3^-$ bridges allowing antiferromagnetic exchange.

*IR and Electronic Spectra.*—The IR spectrum for $[Cu_4L_2(N_3)_3]_n[ClO_4]_n{\cdot}2nH_2O$ shows the band due to perchlorate at 1090 cm$^{-1}$. The ν(C=O) stretching frequency of the oxamidato group at 1661 cm$^{-1}$ is shifted to a higher wavenumber compared with that of the mononuclear compound $[CuL]{\cdot}2H_2O$ (1615 cm$^{-1}$) owing to the higher bond order of C=O in the polynuclear compound. The two strong bands at 2097 and 2060 cm$^{-1}$ are assigned to $\nu_{asym}(N_3^-)$ which splits into two bands for the different co-ordination modes of the azido groups. The $\nu_{sym}(N_3^-)$ band is observed at 1374 cm$^{-1}$.

The powder reflectance spectrum of the complex consists of a broad band at 15 900 cm$^{-1}$ ascribed to a d–d transition with square-planar geometry. Compared with the mononuclear compound $[CuL]{\cdot}2H_2O$ which has a *cis* conformation with a $CuN_4$ chromophone, this polynuclear complex has a *trans* conformation with a $CuN_3O$ chromophone and exhibits a red shift. This can be attributed to (*i*) the weaker ligand field associated with an oxygen donor compared with nitrogen-donor ligand, and (*ii*) the reduced co-planarity relative to mononuclear $[CuL]{\cdot}2H_2O$.

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