Crystal Structure and Magnetic Properties of Two Two-dimensional Sheet-like Polynuclear Copper Complexes with Bridging *trans*-Oxamidate and 4,4′-Bipyridine or Pyrimidine†

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Two two-dimensional complex polymers $[Cu_2L(4,4'\text{-bipy})_2]_n[ClO_4]_{2n}$ **1** and $[Cu_2L'(pym)_2]_n[ClO_4]_{2n}$ **2**, where H_2L = *N,N′*-bis(2-aminoethyl)oxamide, H_2L' = *N,N′*-bis(2-aminopropyl)oxamide, 4,4′-bipy = 4,4′-bipyridine and pym = pyrimidine, have been synthesised, and characterized by crystallographic, spectroscopic and magnetic methods. Both compounds crystallize in the monoclinic system, space group $P2_1/c$ and $Z = 4$, with $a = 6.859(1)$, $b = 20.085(4)$, $c = 11.860(4)$ Å and $\beta = 93.56(2)°$ for **1**, and $a = 8.721(2)$, $b = 8.679(2)$, $c = 16.741(2)$ Å and $\beta = 98.59(1)°$ for **2**. The structures of the two compounds consist of layers of two-dimensional networks along the *a*-axis. Within each layer, *trans*-oxamidato-bridged copper(II) dimers asymmetrically connected by 4,4′-bipyridine or pyrimidine extend along *bc* plane to form an infinite network. The copper(II) has a square-pyramidal coordination geometry with N_3O atoms forming the basal plane and a nitrogen atom from 4,4′-bipyridine or pyrimidine occupying the apical position. Both compounds exhibit strong antiferromagnetic coupling with $J = -335$ for **1** and -560 cm^{-1} for **2**, owing to the efficiency of the oxamidato bridges in facilitating such coupling between copper(II) ions which are separated by more than 5.2 Å.

The magnetic properties of transition-metal polynuclear complexes have been investigated by a number of groups,[1–4] particular attention being devoted to two- and three-dimensional network complex polymers, as it is believed that increasing dimensionality enhances bulk magnetic properties.[5–10]

Bridging oxamidates have played a key role in the design of polymetallic systems owing to their ability to facilitate strong exchange interactions.[11] One of the most important properties of these ligands is their easy *cis–trans* conformational change affording symmetric and asymmetric oxamidato bridges. The bis(tridentate) character of these ligands in *trans* conformation allows the formation of *trans*-oxamidato-bridged dinuclear copper(II) units which can be linked by bridging ligands such as acetate, azide or cyanate to form one-dimensional chains.[12–14] However, until now no *trans*-oxamidato-bridged dinuclear copper(II) units bridged by second ligands to form two-dimensional sheet-like or three-dimensional network polymers have been reported. Our work is aimed at obtaining complex polymers of higher dimensionality by linking the dinuclear copper(II) units by bis(monodentate) bridging ligands such as 4,4′-bipyridine or pyrimidine. We report here the syntheses, crystal structures and magnetic properties of two two-dimensional infinite-layer copper(II) complex polymers bridged antisymmetrically by *trans*-oxamidate and 4,4′-bipyridine (4,4′-bipy) (**1**) or pyrimidine (pym) (**2**).

Experimental

Syntheses.—The ligands H_2L [*N,N′*-bis(2-aminoethyl)oxamide] and H_2L' [*N,N′*-bis(2-aminopropyl)oxamide] and their mononuclear complexes, $[CuL]\cdot 2H_2O$ and CuL' were obtained by literature methods.[15]

$[Cu_2L(4,4'\text{-bipy})_2]_n[ClO_4]_{2n}$ **1**. To an 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. Then a warm aqueous solution of 4,4′-bipyridine (2 mmol, 20 cm^3) was added dropwise to the above blue solution, affording a blue-green precipitate that was filtered, washed with water, and dried in a desiccator containing silica gel (Found: C, 38.40; H, 3.45; N, 13.80; Cu, 15.90. Calc. for $C_{26}H_{28}Cl_2Cu_2N_8O_{10}$: C, 38.15; H, 3.40; N, 13.70; Cu, 15.65%). Well-shaped single crystals were obtained by the slow-diffusion method using an H-tube, where the starting materials were aqueous solutions of 4,4′-bipyridine, and $[CuL]\cdot 2H_2O$ and copper perchlorate in a 1 : 1 molar ratio.

$[Cu_2L'(pym)_2]_n[ClO_4]_{2n}$ **2**. To a heated aqueous solution of $[CuL']$ (1 mmol, 40 cm^3) was added an aqueous solution of copper perchlorate (1 mmol, 5 cm^3) with stirring. Then an aqueous solution of pyrimidine (1 mmol, 20 cm^3) was added to the blue solution and after standing at room temperature for several days, well-shaped black-green prismatic single crystals were obtained by slow evaporation (Found: C, 27.90; H, 3.35; N, 16.10; Cu, 18.35. Calc. for $C_{16}H_{24}Cl_2Cu_2N_8O_{10}$: C, 27.95; H, 3.50; N, 16.30; Cu, 18.50%).

Physical Measurements.—Magnetic measurements on powder samples were carried out with a CF-1 type extracting-sample magnetometer in the temperature range 4–300 K for complex **1**, and with a CAHN-2000 Faraday-type magnetometer in the temperature range 70–300 K for **2**. Corrections for the diamagnetism of the complexes were estimated from Pascal's constants to be -462×10^{-6} and -219×10^{-6} cm^3 mol^{-1} for complexes **1** and **2**, respectively. 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 run on a Shimadzu UV-240 spectrophotometer.

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

Crystal Structure Determinations.—The intensity data were collected at room temperature on a R3M/E four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using the θ–2θ scan technique. Details of the crystal data, collection and refinement are listed in Table 1. Lattice parameters were obtained by a least-squares fit of 25 reflections in the range 6–24°. Intensity data were collected in the 2θ range 2–48° for **1** and of 2–50° for **2**, respectively, with a scan speed of 8° min^{-1}. The intensity was corrected for Lorentz-polarization and absorption effects. Of the 2905 (for **1**) and 2557 (for **2**) measured independent reflections, 2218 and 1869 were observed with $I \geqslant 3\sigma(I)$ for **1** and **2**, respectively, and used for the structure refinements.

Refinements were carried out by full-matrix least-square techniques, starting with the positions of the heavy atoms determined from the experimental Patterson function, and using Fourier and Fourier-difference syntheses to locate the lighter atoms. All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms from the ΔF map were refined with a common thermal parameter. Calculations were performed using SHELX 76 programs.[16] Throughout the refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The final least-squares refinement converged at R (R') 0.057 (0.056) for **1** and 0.059 (0.055) for **2**. The atomic coordinates for the non-hydrogen atoms are listed in Tables 2 and 3 and selected bond distances and angles are presented in Tables 4 and 5 for compounds **1** and **2** 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

Crystal Structure of $[Cu_2L(4,4'\text{-bipy})_2]_n[ClO_4]_{2n}$ **1**.—The structure of **1** consists of a two-dimensional array of copper(II) ions bridged by the bis(tridentate) ligand L in a *trans*-conformation and a bis(monodentate) 4,4'-bipyridine in an asymmetric bonding mode. A perspective view of the asymmetric units together with the atom-labelling scheme and of three symmetry-related units is depicted in Fig. 1. There is an inversion centre at the middle of C(1)–C(1a) bond.

The copper atoms have a distorted square-based pyramidal geometry with a CuN_4O chromophore. The equatorial plane is defined by the carbonyl O(1), amide N(1) and amine N(2) of L in a *trans*-conformation, and the N(3) atom of a 4,4'-bipyridine ligand bonded axially to another neighbouring copper centre through its N(4) atom. The axial site is occupied by N(4b) from another 4,4'-bipyridine ligand bound equatorially to the next Cu(b) centre by its N(3b) atom. 4,4'-Bipyridine bridges copper centres in an asymmetric fashion with the axial bond distance of Cu–N(4b) [2.308(4) Å] being longer than the equatorial Cu(b)–N(3b) distance [1.996(4) Å]. The largest deviation from the least-squares plane through N(1)N(2)N(3)O(1) is 0.0209 Å at N(1), and the copper centre lies 0.2260 Å out of this plane. The Cu–N(1) bond distance [1.925(4) Å], which is shorter than that for Cu–O(1) and Cu–N(2) [2.031(3) and 2.041(5) Å, respectively], is in accord with those found in other oxamidato-bridged copper(II) complexes.[13,14,17] The significant shortening of Cu–N(1) is consistent with the strong basicity of the deprotonated amide nitrogen atom.

The deprotonated ligand L adopts a *trans* conformation forming two five-membered chelate rings with each metal ion. The three atoms [Cu, C(2) and C(1a)] around N(1) lie in a plane with bond angles of 118.3(3), 116.5(3) and 125.1(4)° for

Table 1 Summary of crystal data, data collection and structure refinement for complexes **1** and **2**[a]

Compound	**1**	**2**
Formula	$C_{26}H_{28}Cl_2Cu_2N_8O_{10}$	$C_{16}H_{24}Cl_2Cu_2N_8O_{10}$
M	812.15	686.70
Crystal size/mm	0.32 × 0.40 × 0.60	0.24 × 0.28 × 0.50
a/Å	6.859(1)	8.721(2)
b/Å	20.085(4)	8.679(2)
c/Å	11.860(4)	16.741(2)
β/°	93.56(2)	98.59(1)
U/Å^3	1630.6(7)	1252.8(4)
D_c/g cm^{-3}	1.65	1.82
μ(Mo-Kα)/cm^{-1}	15.37	19.83
F(000)	824	696
2θ Range/°	2–48	2–50
No. of unique reflections	2905	2557
No. of observed reflections [$I \geqslant 3\sigma(I)$]	2218	1869
R[b]	0.057	0.059
R'[c]	0.056	0.055
No. of variables	326	196

[a] Details in common: monoclinic, space group $P2_1/c$, Z = 4, λ(Mo-Kα) = 0.710 73 Å. [b] $R = ||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = \Sigma(||F_o| - |F_c||w^{\frac{1}{2}})/\Sigma|F_o|w^{\frac{1}{2}}$.

Table 2 Atomic positional parameters for complex **1**

Atom	x	y	z
Cu	0.0622(1)	0.5715(1)	0.3194(1)
Cl	0.8768(3)	0.3875(1)	0.1145(1)
N(1)	0.1760(5)	0.4972(2)	0.4024(3)
N(2)	0.2499(7)	0.4507(2)	0.2030(4)
N(3)	−0.0987(6)	0.6342(2)	0.2217(3)
N(4)	−0.7422(6)	0.8485(2)	−0.0913(3)
O(1)	−0.1344(4)	0.5684(2)	0.4405(3)
O(2)	0.8305(14)	0.3542(5)	0.0068(7)
O(3)	0.8931(27)	0.4483(5)	0.0785(11)
O(4)	0.7289(30)	0.3724(8)	0.1796(11)
O(5)	1.0448(23)	0.3636(10)	0.1487(10)
C(1)	−0.0901(6)	0.5212(2)	0.5099(4)
C(2)	0.3439(8)	0.4637(3)	0.3573(5)
C(3)	0.4190(10)	0.5104(3)	0.2681(6)
C(4)	−0.1067(8)	0.6990(3)	0.2450(4)
C(5)	−0.2247(8)	0.7425(2)	0.1820(4)
C(6)	−0.3471(7)	0.7183(2)	0.0937(4)
C(7)	−0.3361(8)	0.6514(3)	0.0694(4)
C(8)	−0.2119(8)	0.6112(3)	0.1340(5)
C(9)	−0.4847(7)	0.7640(2)	0.0294(4)
C(10)	−0.6024(8)	0.8073(2)	0.0840(4)
C(11)	−0.7308(8)	0.8476(3)	0.0216(4)
C(12)	−0.6273(8)	0.8070(3)	−0.1439(5)
C(13)	−0.4987(8)	0.7634(3)	−0.0872(4)

Table 3 Atomic positional parameters for complex **2**

Atom	x	y	z
Cu	0.1353(1)	0.5638(1)	0.6478(1)
Cl	0.3349(2)	0.1472(2)	0.6444(1)
N(1)	0.1730(5)	0.5869(6)	0.5380(2)
N(2)	0.3588(5)	0.6344(7)	0.6727(3)
N(3)	0.1030(5)	0.4956(6)	0.7589(2)
N(4)	−0.0169(5)	0.3135(6)	0.8351(3)
O(1)	0.0669(4)	0.5268(5)	0.4065(2)
O(2)	0.3580(11)	0.0216(9)	0.6986(4)
O(3)	0.4548(12)	0.2484(13)	0.6599(7)
O(4)	0.3032(30)	0.0963(17)	0.5718(5)
O(5)	0.2189(19)	0.2321(22)	0.6515(17)
C(1)	0.0688(5)	0.5318(6)	0.4827(3)
C(2)	0.3235(6)	0.6461(10)	0.5269(3)
C(3)	0.4270(8)	0.6364(17)	0.5993(4)
C(4)	0.5833(7)	0.7080(11)	0.6040(4)
C(5)	0.0086(7)	0.3795(7)	0.7665(3)
C(6)	0.0580(7)	0.3781(8)	0.9027(3)
C(7)	0.1555(8)	0.5004(8)	0.9010(3)
C(8)	0.1769(7)	0.5565(7)	0.8275(3)

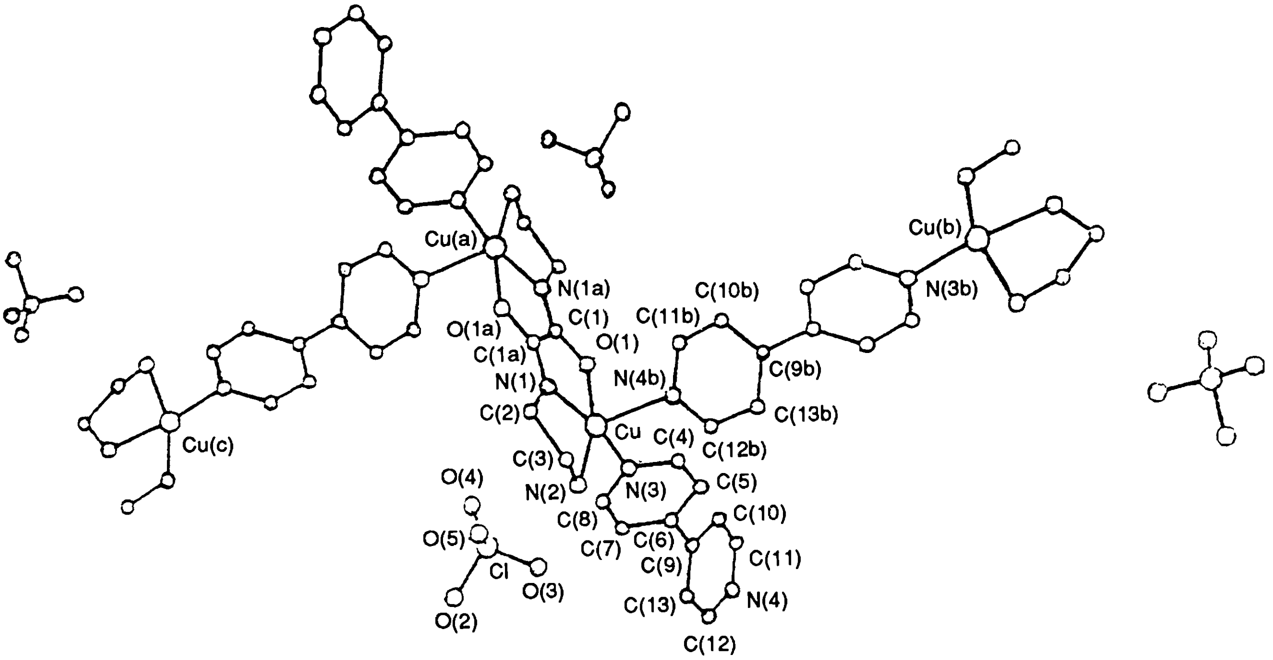

Fig. 1 View of complex **1** with the atom numbering scheme

Table 4 Selected bond distances (Å) and angles (°) for complex **1**

Cu–N(1)	1.925(4)	O(1)–C(1)	1.281(5)
Cu–O(1)	2.031(3)	C(2)–C(3)	1.527(9)
N(1)–C(2)	1.463(7)	C(6)–C(7)	1.378(7)
N(3)–C(4)	1.332(6)	C(9)–C(10)	1.375(7)
N(4)–C(12)	1.329(7)	Cu–N(3)	1.996(4)
C(1)–C(1a)	1.530(9)	C(12)–C(13)	1.387(7)
C(5)–C(6)	1.388(7)	N(2)–C(3)	1.484(8)
C(7)–C(8)	1.372(7)	N(4)–C(11)	1.336(7)
C(10)–C(11)	1.377(7)	C(1)–N(1a)	1.281(6)
Cu–N(2)	2.041(5)	C(4)–C(5)	1.379(7)
Cu–N(4b)	2.308(4)	C(6)–C(9)	1.492(6)
N(1)–C(1a)	1.281(6)	C(9)–C(13)	1.379(7)
N(3)–C(8)	1.341(6)		
N(1)–Cu–N(2)	81.8(2)	N(1)–Cu–N(3)	167.1(2)
N(2)–Cu–N(3)	98.5(2)	N(1)–Cu–O(1)	83.1(1)
N(2)–Cu–O(1)	160.6(2)	N(3)–Cu–O(1)	93.6(1)
N(1)–Cu–N(4b)	95.7(1)	N(2)–Cu–N(4b)	98.5(2)
N(3)–Cu–N(4b)	96.4(1)	O(1)–Cu–O(4b)	95.2(1)
Cu–N(1)–C(2)	118.3(3)	Cu–N(1)–C(1a)	116.5(3)
C(2)–N(1)–C(1a)	125.1(4)	Cu–N(2)–C(3)	106.2(4)
Cu–N(3)–C(4)	121.6(3)	Cu–N(3)–C(8)	120.4(3)
C(11b)–N(4b)–Cu	117.7(3)	C(12b)–N(4b)–Cu	124.4(3)
Cu–O(1)–C(1)	109.6(3)	O(1)–C(1)–N(1a)	129.3(4)
O(1)–C(1)–C(1a)	118.3(5)	N(1)–C(2)–C(3)	106.1(4)
N(2)–C(3)–C(2)	109.0(5)	N(3)–C(4)–C(5)	122.5(5)

Table 5 Selected bond lengths (Å) and angles (°) for complex **2**

Cu–N(1)	1.925(4)	N(3)–C(8)	1.339(6)
Cu–N(4c)	2.435(5)	O(1)–C(1)	1.273(5)
N(1)–C(1)	1.290(6)	C(3)–C(4)	1.490(11)
N(3)–C(5)	1.319(8)	Cu–N(3)	2.012(4)
N(4)–C(6)	1.342(7)	C(7)–C(8)	1.362(8)
C(2)–C(3)	1.401(8)	N(2)–C(3)	1.443(8)
Cu–N(2)	2.026(5)	N(4)–C(5)	1.331(7)
Cu–O(1a)	2.019(3)	C(1)–C(1a)	1.512(10)
N(1)–C(2)	1.477(7)	C(6)–C(7)	1.363(10)
N(1)–Cu–N(2)	82.5(2)	N(1)–Cu–N(3)	168.7(2)
N(2)–Cu–N(3)	99.3(2)	N(1)–Cu–N(4c)	98.9(2)
N(2)–Cu–N(4c)	96.8(2)	N(3)–Cu–N(4c)	91.9(2)
N(1)–Cu–O(1a)	82.7(2)	N(2)–Cu–O(1a)	163.6(2)
N(3)–Cu–O(1a)	93.9(2)	O(4)–Cu–O(5)	103.1(16)
Cu–N(1)–C(1)	116.4(4)	Cu–N(3)–C(5)	119.3(3)
Cu–N(1)–C(2)	116.6(3)	C(1)–N(1)–C(2)	126.5(4)
Cu–N(2)–C(3)	109.5(4)	Cu–N(3)–C(8)	124.1(4)
C(5)–N(4)–C(6)	115.1(5)	C(5)–N(4)–Cu(b)	127.8(4)
C(6)–N(4)–Cu(b)	115.8(4)	C(1)–O(1)–Cu(a)	110.1(3)
N(1)–C(1)–O(1)	129.4(5)	N(1)–C(1)–C(1a)	112.0(5)
O(1)–C(1)–C(1a)	118.6(5)	N(1)–C(2)–C(3)	110.3(6)
N(2)–C(3)–C(2)	116.3(6)	N(2)–C(3)–C(4)	116.8(6)
C(2)–C(3)–C(4)	119.1(7)	N(3)–C(5)–N(4)	126.8(5)
N(4)–C(6)–C(7)	122.3(5)	C(6)–C(7)–C(8)	117.8(5)
N(3)–C(8)–C(7)	121.4(6)		

Cu–N(1)–C(2), Cu–N(1)–C(1a) and C(2)–N(1)–C(1a), respectively. This, together with the bond distances and planarity of the oxamidato bridge reveals that N(1) and its symmetry-related N(1a) are sp^2-hybridized and that the π electrons of C(1)–O(1) and C(1a)–O(1a) are delocalized to form a conjugated system.

The two aromatic rings in the 4,4′-bipyridine ligand are not coplanar, with a dihedral angle of 48.1° to each other, thus differing from other cases where the rings are co-planar.[3] The mean planes of N(3)C(4)C(5)C(6)C(7)C(8) and N(4b)C(11b)-C(10b)C(9b)C(13b)C(12b), the former equatorially bound to Cu by its N(3) atom and the latter axially by its N(4b) atom, have dihedral angles of 73.1 and 26.5°, respectively, with the mean plane of CuO(1)N(1)N(2)N(3) defined by Cu and its four equatorially bound atoms. The Cu ··· Cu separations through L and 4,4′-bipyridine bridges are 5.271 and 11.339 Å. The shortest interlayer Cu ··· Cu distance is 6.859 and 7.712 Å for Cu(a)–Cu(a′) and Cu–Cu(a′), respectively, where a′ and a denote the symmetry operations 1 − *x*, 1 − *y*, 1 − *z* and −*x*, 1 − *y*, 1 − *z*.

Crystal Structure of $[Cu_2L'(pym)_2]_n[ClO_4]_{2n}$ **2**.—The structure of **2** shows a pronounced two-dimensional character developing along the *a*-axis similarly to complex **1**. Within the layer, the copper(II) ions are bridged by both L′ and pyrimidine, the former behaving as a bis(tridentate) ligand in a *trans*

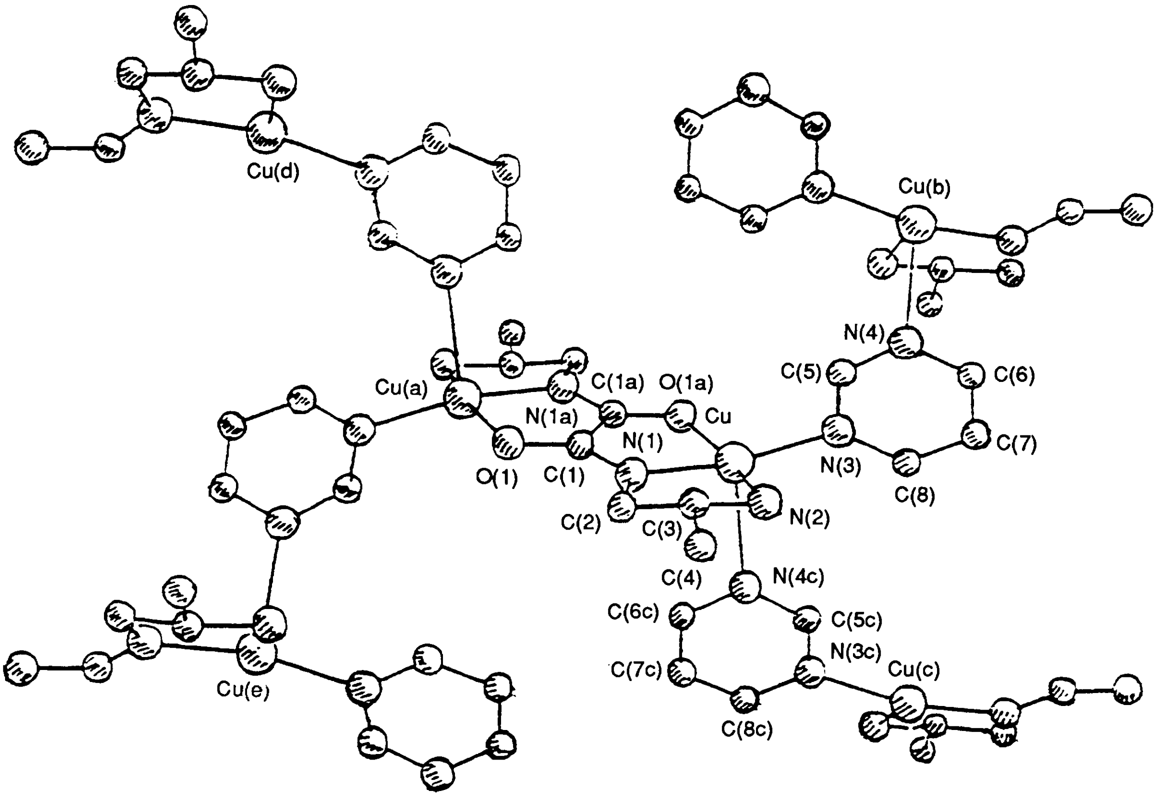

Fig. 2 View of complex **2** with the atom numbering scheme

conformation whereas the latter bridges the copper centres in an asymmetric fashion extending along the *bc* plane to form an infinite network as shown in Fig. 2.

The copper atoms are surrounded by four nitrogen atoms and one oxygen atom forming a distorted square-based pyramid. The basal plane is defined by the carbonyl O(1a), amide N(1) and amine N(2) atoms of the oxamidato ligand in a *trans* conformation, and the N(3) atom of an asymmetric pyrimidine bridge bonded axially to the neighbouring Cu(b) atom through its N(4) atom. The axial site is occupied by N(4c) atom from another bridged pyrimidine which has been equatorially bound to the next Cu(c) centre by its N(3c) atom. The largest deviation from the least-squares plane through N(1)N(2)N(3)O(1a) is 0.0264 Å at N(1), and the copper centre lies 0.1682 Å out of this plane. The mean planes of the two pyrimidines, one axially and the other equatorially bound to a copper centre, which form a dihedral angle of 78.4° to each other, have dihedral angles of 27.7 and 74.2°, respectively, with the mean plane defined by the copper centre and its four equatorially bound atoms. The Cu $\cdots$ Cu separations through the L′ and pyrimidine bridges are 5.272 and 6.210 Å, respectively.

Both the L′ and pyrimidine ligands are planar, with atom–mean plane distances no larger than 0.05 and 0.02 Å, respectively. From one layer to another, both the ligands L′ and pyrimidine are symmetry related, so their mean planes are strictly parallel. They overlap only partially with a distance of 3.66 and 6.57 Å between mean planes of L′ and pyrimidine ligands, respectively. The shortest interlayer Cu $\cdots$ Cu distances are 8.694 and 8.721 Å for Cu $\cdots$ Cu(a′) and Cu(a) $\cdots$ Cu(a′) where a′ and a denote the symmetry operations $1 - x$, $1 - y$, $1 - z$ and $-x$, $1 - y$, $1 - z$, respectively.

Spectroscopic Data.—*Infrared spectra.* The powder reflectance spectra show two bands near 16 100 and 17 000 cm^{-1} for both compounds **1** and **2**. Comparing the mononuclear complexes [CuL]·2H$_2$O and [CuL′] with compounds **1** and **2**, the copper(II) ion exhibits different chromophores and consequently different ligand fields. A CuN$_4$ chromophore with two amine and two amide nitrogen donors is present in [CuL]·2H$_2$O and [CuL′] with the ligands L and L′ adopting the *cis* conformation. The ν_{d-d} for the mononuclear compounds appears at higher wavenumbers (19 100 for [CuL]·2H$_2$O and 19 300 cm^{-1} for [CuL′]) than those of the corresponding amine complexes, revealing that a square-planar environment and a strong ligand field are achieved with L and L′ in a *cis* conformation. In the polymeric species **1** and **2**, the oxamidato ligands exhibit a *trans* conformation, which leads to a CuN$_3$O chromophore in the equatorial plane, so a red shift is observed owing to (*i*) the weaker ligand field associated with oxygen- compared with nitrogen-donor ligands, and (*ii*) the reduced coplanarity relative to the mononuclear ligands.

The IR spectra show bands at 1085 cm^{-1} due to perchlorate for both compounds. The ν_{asym}(C=O) and ν_{sym}(C=O) stretching frequencies of the oxamidato groups at 1650, 1614, 1590, and 1320 cm^{-1} in **1**, and 1659, 1594, 1335 cm^{-1} in **2**, are diagnostic of bis(tridentate) behaviour.[18] The amide ν(C=O) bands of the two complexes shift considerably toward higher wavenumber (20–40 cm^{-1}) compared with those of [CuL]·2H$_2$O (1615 cm^{-1}) and [CuL′] (1640 cm^{-1}) owing to the higher C=O bond order in the polynuclear compounds.[11] The ν(NH$_2$) bands are in the expected region between 3200 and 3320 cm^{-1} in the polymers.

EPR spectra and magnetic properties. The polycrystalline room-temperature powder EPR spectra of complexes **1** and **2** consist of single quasi-symmetric signals centred at $g = 2.10$ whose intensities decrease with lowering temperature. No half-field transition due to a weak zero-field splitting is observed.

It is known that the bis(bidentate) ligands *cis*- or *trans*-$C_2X_2Y_2^{2-}$ (X, Y = O, NR or S) may be remarkably efficient in propagating antiferromagnetic interactions between two relatively distant metal centres with $|J| > 300$ cm^{-1} ($\mathcal{H} = -JS_1S_2$),[19] *e.g.* where a $C_2X_2Y_2^{2-}$ bis(bidentate) ligand bridges two copper(II) ions in elongated tetragonal surroundings with a co-planar or almost co-planar basal plane.[19] The dinuclear copper units (4,4′-bipy)CuLCu(4,4′-

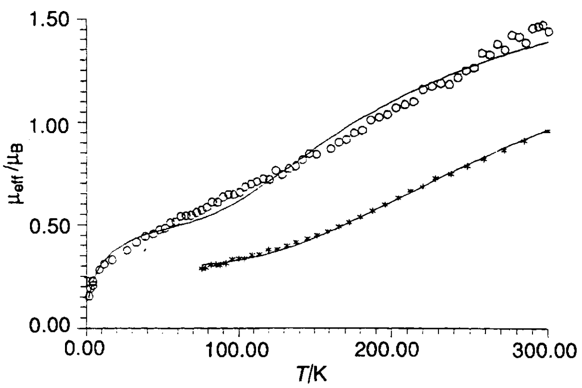

Fig. 3 Experimental (○, ✱) and calculated (–) temperature dependence of μ_{eff} for complexes **1** (○) and **2** (✱)

bipy) for **1** or (pym)CuL′Cu(pym) for **2**, bridged by *N*,*N*′-disubstituted oxamides, are linked by 4,4′-bipyridine or pyrimidine ligands to form an infinite two-dimensional network. It is known that bridging ligands such as 4,4′-bipyridine, pyrazine, and pyrimidine are unable to facilitate efficient magnetic coupling as shown in $[Cu_2(dien)_2(4,4'\text{-bipy})(ClO_4)_2][ClO_4]_2$,[3] $[Cu_2(dien)_2(pyz)(ClO_4)_2][ClO_4]_2$,[3] and $[Cu_2(dien)_2(pym)(ClO_4)_2][ClO_4]_2$ (dien = diethylenetriamine, pyz = pyrazine),[20] with $|J| < 5$ cm^{-1}. Therefore, although polymers **1** and **2** are two-dimensional infinite network structures, compared with the strong magnetic coupling transmitted by L or L′, the exchange by 4,4′-bipyridine or pyrimidine is negligible, and the complex magnetic system for polymers **1** and **2** can be simplified into the magnetic exchange within the dinuclear units.

The μ_{eff} value for each copper in compound **1** at 300 K is 1.39 μ_B, lower than that expected for a system with $S = \frac{1}{2}$; also, the value decreases with decreasing temperature, revealing a strong antiferromagnetic interaction between two copper centres in a dinuclear unit. Therefore, it should be possible to interpret the data using a modification of the Bleaney–Bowers equation (1), taking into account a small amount of paramagnetic impurity ρ which exhibits a Weiss constant θ, where $|J|$ is the single–triplet

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

$$\mu_{eff}(Cu) = 2.828\sqrt{\chi_M T/2} \quad (2)$$

energy gap and the other symbols have their usual meaning. Using $g = 2.10$, the average value measured from EPR spectra on a powder sample, and varying the other parameters, a least-squares fit of all experimental data over the range 4–300 K gave $J = -335$ cm^{-1}, $\rho = 0.084$ and $\theta = -19.8$ K, with an agreement factor $R = \Sigma(\mu_{obs} - \mu_{calc})^2/\Sigma(\mu_{obs})^2$ of 2×10^{-3}. The curve of the calculated μ_{eff} values [equation (2)] at different temperatures fits the experimental points satisfactorily as shown in Fig. 3.

Compound **2** exhibits a magnetic behaviour similar to **1**, μ_{eff} decreasing with decreasing temperature. Nevertheless, the much smaller μ_{eff} value of each copper for **2** (0.96 μ_B) than that for **1** (1.36 μ_B) at 300 K shows a stronger antiferromagnetic interaction within the dinuclear unit for compound **2**, and so a much larger value of $|J|$ is expected. Since the molar susceptibility at low temperature is close to Pascal's constant used for diamagnetic correction, the susceptibility was only measured down to 70 K. Fitting the experimental data for compound **2** to equation (1) (where $\theta = 0$), yields a best fit with the parameters $J = -560$ cm^{-1}, $\rho = 0.017$ and $R = 3 \times 10^{-4}$ for $g = 2.10$.

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