Crystal Structure and Electronic Properties of Dibromo- and Dichlorotetrakis[μ_3-bis(2-pyridyl)amido]tricopper(II) Hydrate†

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The crystal structures of $[Cu_3(bipyam\text{–}H)_4Cl_2]\cdot H_2O$ (**1**) and $[Cu_3(bipyam\text{–}H)_4Br_2]\cdot H_2O$ (**2**) where bipyam–H = bis(2-pyridyl)amide, have been determined by *X*-ray analysis, in the orthorhrombic space group *Pnn*2: (**1**), a = 14.092(3), b = 12.895(3), (c) = 11.190(2) Å, Z = 2, and R = 0.032 for 2 453 observed and 2 029 unique reflections; (**2**), a = 14.186(3), b = 13.040(3), c = 11.313(2) Å, Z = 2, and R = 0.043 for 1 574 observed and 1 465 unique reflections. The two structures are isomorphous with near isostructural $[Cu_3(bipyam\text{–}H)_4X_2]$ units in special positions of two-fold symmetry and a non-co-ordinated water molecule. The $Cu_3N_{12}X_2$ chromophores involve nearly linear Cu_3 units, Cu–Cu–Cu 178.4° (mean), terminated by the two halide anions. The four separate bipyam–H ligands act as tridentate ligands, involving co-ordination to the three separate copper(II) ions, with Cu–Cu distances of 2.471(1) and 2.468(1) Å, for (**1**) and (**2**), respectively. If the Cu–Cu separations are ignored, the central Cu atom in both structures involves a four-co-ordinate rhombic coplanar CuN_4 chromophore generated by the central amido nitrogens of the four bipyam–H ligands. The two terminal Cu atoms involve a square-based pyramidal CuN_4X chromophore, generated by the terminal pyridine nitrogens of the four bipyam–H ligands and an axial halide anion. An average dihedral angle of 48° is involved between the planes of the pyridine rings of the individual bipyam–H ligands, which results in a spiral configuration of the $[Cu_3(bipyam\text{–}H)_4X_2]$ units. The spin-only magnetic moment of complex (**1**) is *ca.* 1.40 B.M. per Cu atom, consistent with antiferromagnetic coupling between the copper(II) atoms of the trimer. Both complexes are e.s.r. silent, again consistent with strong antiferromagnetic coupling. The electronic spectra of (**1**) and (**2**) have a band maximum at 15 500 cm^{-1}, with a high-energy shoulder at 19 230 cm^{-1}, consistent with the two different stereochemistries present.

The reduction of $[Cu(bipyam)_2X]X$ complexes [bipyam = bis(2-pyridyl)amine, X = Cl or Br] by refluxing with copper metal in acetonitrile solution under methane gas yields a yellow solution of a copper(I) species, from which yellow-orange crystals of the corresponding $[Cu^I (bipyam)_2]X\cdot H_2O$ complex can be isolated.[1] If the reduction is carried out in air, in the presence of excess of bipyam, dark purple crystals of the complexes $[Cu_3(bipyam\text{–}H)_4Cl_2]\cdot H_2O$ (**1**) and $[Cu_3(bipyam\text{–}H)_4Br_2]\cdot H_2O$ (**2**) can be isolated. In view of the novel stoicheiometry and the presence of the uncommon bis(2-pyridyl)amide anion[2,3] as a ligand in the product, the crystal structures of (**1**) and (**2**) have been determined and their electronic properties studied.

Experimental

Preparation.—The preparation of complexes (**1**) and (**2**) was carried out by dissolving $[Cu(bipyam)_2Cl]Cl$[4] (0.75 g, 1.57 mmol) in acetonitrile (50 cm^3), plus excess of bipyam (0.20 g, 1.17 mmol), and refluxing the solution in air for 10 h with copper metal sheet (0.3 g). The initial blue-green solution turned yellow, and on standing overnight in air the solution turned dark purple and deposited purple crystals of complex (**1**), which adhered to the surface of the glass. A small amount of an amorphous blue-green powder was also formed; this was suspended in solution and removed by successive decantation. The purple crystals were removed from the glass surface, rapidly filtered off, and dried under vacuum [Found: for (**1**): C, 50.15; H, 3.15; Cl, 8.15; Cu, 18.85; N, 17.95. Calc. for $C_{40}H_{34}Cl_2Cu_3N_{12}O$: C, 50.00; H, 3.55; Cl, 7.40; Cu, 19.85; N, 17.50%]. A corresponding method of preparation was used for (**2**), involving $[Cu(bipyam)_2Br_2]$ (0.89 g), and yielded dark purple crystals [Found for (**2**): C, 46.00; H, 3.50; Br, 15.75; Cu, 17.90; N, 16.35. Calc. for $C_{40}H_{34}Br_2Cu_3N_{12}O$: C, 45.80; H, 3.25; Br, 15.25; Cu, 18.15; N, 16.05%].

Crystallography.—The crystal and refinement data for complexes (**1**) and (**2**) are shown in Table 1. The unit-cell data (25 reflections, θ 3—25°) and intensities for (**1**) were collected on a Philips PW 1100 diffractometer and those for (**2**) on an Enraf-Nonius CAD4 diffractometer, both with graphite-monochromatised Mo-K_α radiation. Reflections with $3.0 < \theta < 25°$ in one octant were examined in the ω—2θ scan mode, with a constant scan speed of 0.05 s^{-1} and a variable scan width of $(0.7 + 0.1 \tan \theta)°$. With an acceptance criterion of $I > 2.5\sigma(I)$, 2 453 observed reflections were retained for (**1**) and 1 574 for (**2**). Lorentz and polarisation corrections were applied for (**1**) and (**2**), and correction was made for absorption in (**2**) but not in (**1**). Both

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. units employed: B.M. ≈ 9.27×10^{-24} J T^{-1}.

Table 1. Crystal and refinement data *

Complex	**(1)**	**(2)**
M	960.31	1 049.22
Stoicheiometry	$C_{40}H_{34}Cl_2Cu_3N_{12}O$	$C_{40}H_{34}Br_2Cu_3N_{12}O$
a/Å	14.092(3)	14.186(3)
b/Å	12.895(3)	13.040(3)
c/Å	11.190(2)	11.313(2)
U/Å^3	2 033.41	2 092.74
D_m(float)/g cm^{-3}	1.56(3)	1.72(3)
D_c/g cm^{-3}	1.57	1.660
F(000)	947	1 046
μ/cm^{-1}	16.78	33.85
Data collected h	0—18	0—16
k	0—16	0—15
l	0—13	0—13
No. of reflections collected	2 453	1 574
No. of reflections used (N_o)	2 029	1 465
No. of parameters varied (N_v)	262	262
N_o/N_v	7.74	5.59
$R = (\Sigma\Delta/\Sigma\lvert F_o\rvert)$	0.0321	0.0432
$R' = (\Sigma\Delta w^{\frac{1}{2}}/\Sigma\lvert F_o\rvert w^{\frac{1}{2}})$	0.0370	0.0473
k	1.0000	0.8031
g	0.002 05	0.001 63
Maximum final shift/error ratio	0.001	0.007
Maximum and minimum residual electron density (e Å^{-3})	0.58, −0.37	0.42, −0.92

* Details in common orthorhombic; space group $Pnn2$; $Z = 2$; anisotropic atoms, 29.

Table 2. Fractional atomic co-ordinates with estimated standard deviations in parentheses

$[Cu_3(bipyam{-}H)_4Cl_2]\cdot H_2O$ (**1**)

Atom	X/a	Y/b	z/c
Cu(1)	0.000 0	0.000 0	0.752 0(2)
Cu(2)	0.908 1(3)	0.163 2(3)	0.748 3(3)
Cl	0.812 5(8)	0.323 2(8)	0.747 4(8)
N(1)	0.877 4(2)	0.107 1(3)	0.581 3(4)
C(1)	0.850 7(4)	0.177 8(4)	0.500 0(5)
C(2)	0.824 5(5)	0.153 0(5)	0.385 1(6)
C(3)	0.828 4(5)	0.050 0(5)	0.351 2(5)
C(4)	0.858 1(4)	−0.022 6(4)	0.429 9(5)
C(5)	0.882 0(3)	0.004 7(3)	0.547 5(4)
N(2)	0.917 4(3)	0.938 3(3)	0.631 3(4)
C(6)	0.902 0(3)	0.835 3(3)	0.631 7(4)
C(7)	0.818 7(4)	0.786 2(4)	0.588 2(6)
C(8)	0.807 7(4)	0.681 7(4)	0.600 1(6)
C(9)	0.875 4(4)	0.622 9(4)	0.656 8(6)
C(10)	0.954 1(3)	0.673 0(3)	0.698 6(5)
N(3)	0.968 9(3)	0.776 1(3)	0.686 3(4)
N(4)	0.804 4(2)	0.066 1(3)	0.816 6(4)
C(11)	0.713 3(3)	0.094 7(4)	0.794 8(5)
C(12)	0.636 7(4)	0.039 1(4)	0.838 6(6)
C(13)	0.654 9(4)	−0.048 0(4)	0.906 6(6)
C(14)	0.746 2(3)	−0.079 3(4)	0.926 4(6)
C(15)	0.822 7(3)	−0.021 4(3)	0.877 6(4)
N(5)	0.915 4(3)	−0.052 0(3)	0.879 7(4)
C(16)	0.953 3(3)	−0.121 0(3)	0.960 9(4)
C(17)	0.920 4(4)	−0.131 5(5)	1.080 2(5)
C(18)	0.966 3(4)	−0.199 9(5)	1.155 2(5)
C(19)	1.045 8(4)	−0.254 0(5)	1.114 9(5)
C(20)	1.075 5(3)	−0.238 0(4)	1.000 0(5)
N(6)	1.031 2(3)	−0.174 8(3)	0.923 5(3)
O	−0.567 3(10)	0.024 1(15)	1.486 9(17)

$[Cu_3(bipyam{-}H)_4Br_2]\cdot H_2O$ (**2**)

Atom	X/a	Y/b	Z/c
Cu(1)	0.000 0	0.000 0	0.753 5(5)
Cu(2)	0.910 8(6)	0.162 5(7)	0.750 7(6)
Br	0.811 7(6)	0.333 8(6)	0.747 2(7)
N(1)	0.879 9(5)	0.108 7(5)	0.581 1(7)
C(1)	0.858 2(7)	0.180 5(7)	0.500 1(9)
C(2)	0.834 0(9)	0.157 3(8)	0.384 6(9)
C(3)	0.836 3(9)	0.055 1(8)	0.347 4(9)
C(4)	0.862 2(8)	0.981 1(8)	0.430 4(9)
C(5)	0.883 0(6)	0.008 2(7)	0.547 8(8)
N(2)	0.915 5(6)	0.941 0(7)	0.629 7(8)
C(6)	0.901 4(6)	0.838 1(7)	0.628 9(8)
C(7)	0.817 2(6)	0.792 5(7)	0.582 9(10)
C(8)	0.802 9(7)	0.689 6(7)	0.596 0(11)
C(9)	0.869 0(7)	0.629 6(7)	0.653 6(10)
C(10)	0.947 0(7)	0.678 1(7)	0.698 3(9)
N(3)	0.964 7(5)	0.779 8(6)	0.685 0(7)
N(4)	0.807 1(5)	0.068 3(6)	0.813 6(7)
C(11)	0.716 1(7)	0.094 7(8)	0.789 6(9)
C(12)	0.639 1(7)	0.043 1(8)	0.834 1(11)
C(13)	0.657 2(7)	0.954 2(8)	0.903 7(11)
C(14)	0.744 9(6)	0.923 6(7)	0.920 6(10)
C(15)	0.823 1(6)	0.978 9(6)	0.872 4(8)
N(5)	0.916 1(7)	0.949 0(6)	0.875 0(7)
C(16)	0.954 1(6)	0.880 2(6)	0.958 4(8)
C(17)	0.920 4(8)	0.871 2(8)	0.072 6(9)
C(18)	0.964 0(8)	0.804 5(8)	0.150 4(9)
C(19)	0.043 8(8)	0.749 9(8)	0.111 6(10)
C(20)	0.073 7(7)	0.762 9(7)	0.997 8(8)
N(6)	0.030 2(5)	0.827 8(5)	0.919 1(7)
O	0.434 6(12)	0.982 7(14)	0.502 6(15)

structures was solved by the SHELX 76[5] direct methods and Fourier difference techniques and refined by full-matrix least-squares analysis, $\Sigma w|F_o - F_c|^2$, with the initial weighting $w = 1/\sigma^2(F_o)$, and with anisotropic thermal parameters for all the non-hydrogen atoms. A refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$, was finally used and the results for both complexes are given in Table 1. The positions of the H atoms were calculated geometrically and 'floated' on the adjacent carbon or oxygen atoms, assuming C–H and O–H distances of 1.08 Å and a fixed thermal parameter of 0.07 Å^2. Complex neutral atom scattering factors were employed and those for Cu were taken from ref. 6. All calculations were carried out with the SHELX 76,[5] XANADU,[7] CHEM-X,[8] and PUBTAB[9] programs, on the mainframe IBM 4341 and VAX 11/780 computers

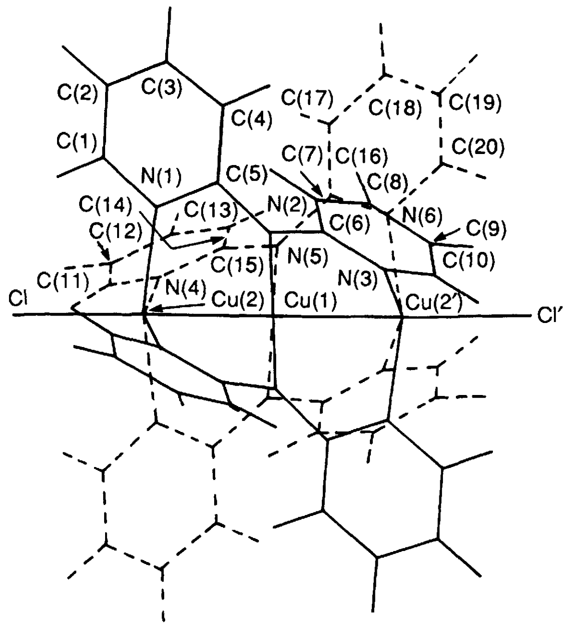


Figure 1. The molecular structure of [Cu_3(bipyam–H)$_4$$X_2$] and the atom numbering scheme used

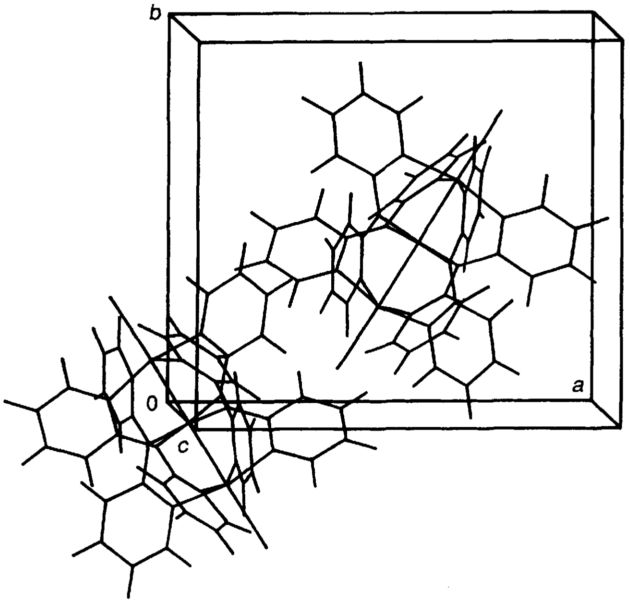


Figure 2. The unit-cell packing diagrams of complexes (**1**) and (**2**)

University College, Cork. The final atomic co-ordinates are given in Table 2, selected bond lengths and angles in Table 3, and some relevant mean planes in Table 4. Figure 1 illustrates the local molecular structures of both complexes and the atomic numbering scheme used. The molecular arrangement within the unit cell, for both (**1**) and (**2**), is shown in Figure 2.

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

Spectroscopic Measurements.—The i.r. spectra were recorded on a Matteson Polaris Fourier-transform IR10410 Spectrometer in the range 4 000—500 cm^{-1}, using the KBr disc technique. E.s.r. spectra were obtained on a Decca XI spectrometer as polycrystalline samples, diffuse reflectance spectra in the range 4 000—25 000 cm^{-1}, as polycrystalline samples, using a Beckman DK-2A spectrometer. The room-temperature magnetic moment was measured on a Gouy balance using [Ni(en)$_3$][S_2O_3] (en = ethylenediamine) as a standard.

Table 3. Selected bond lengths (Å) and angles (°) with standard deviations in parentheses

	Complex	
	(**1**)	(**2**)
Cu(1)–Cu(2)	2.471(1)	2.468(1)
Cu(1)–N(2)	1.953(4)	1.998(9)
Cu(1)–N(5)	1.977(4)	1.936(9)
Cu(2)–Cl(Br)	2.465(1)	2.640(1)
Cu(2)–N(1)	2.050(4)	2.090(8)
Cu(2)–N(4)	2.071(4)	2.045(8)
Cu(2)–Cu(1)–Cu(2')	178.12(1)	178.51(2)
N(2)–Cu(1)–Cu(2)	91.3(1)	90.8(3)
N(5)–Cu(1)–Cu(2)	89.2(1)	89.4(3)
N(5)–Cu(1)–N(2)	90.1(1)	89.9(2)
Cl(Br)–Cu(2)–Cu(1)	178.3(1)	178.6(1)
N(1)–Cu(2)–Cu(1)	80.0(1)	80.3(2)
N(1)–Cu(2)–Cl(Br)	100.2(1)	99.1(2)
N(4)–Cu(2)–Cu(1)	81.3(1)	81.3(2)
N(4)–Cu(2)–Cl(Br)	97.0(1)	97.5(2)
N(4)–Cu(2)–N(1)	88.5(2)	88.0(3)

Results and Discussion

Crystal Structures.—The crystal structures of complexes (**1**) and (**2**) both involve two [Cu_3(bipyam–H)$_4$$X_2$] units and two water molecules in the unit cell, Figure 2. Both trimers involve an almost linear Cu_3 unit, with a Cu(2)–Cu(1)–Cu(2') bond angle of 178.12(1) and 178.51(2)° for (**1**) and (**2**), respectively. The central Cu(1) atom occupies a two-fold special position, while the two terminal Cu(2) atoms are in general positions. The two halogen atoms in (**1**) and (**2**) bond to the terminal copper atoms, essentially collinear with the Cu_3 axis, Figure 1. The three copper(II) ions of both complexes are bridged by the central deprotonated amine nitrogen atoms and two pyridine nitrogen atoms of the four bipyam–H ligands, with almost equal Cu–Cu distances of 2.471(1) and 2.468(1) Å, respectively. If these separations are ignored, the central Cu(1) atoms in both structures are four co-ordinate, square coplanar, with a slight rhombic component, consisting of the four bridging nitrogen atoms of the four independent, deprotonated, central nitrogen atoms of the bipyam–H ligands. The terminal Cu(2) atoms in both structures are five-co-ordinate with a square-based pyramidal geometry, again with a slight rhombic component, to give a CuN_4X chromophore. The basal plane consists of the four terminal pyridine nitrogen atoms of the four independent bipyam – H ligands, while the axial co-ordination sites are occupied by a chloride anion in (**1**) and a bromide anion in (**2**), at distances of 2.465(1) and 2.640(1) Å, respectively. The mean central Cu(1)–N distances are below 2.0 Å, Table 3, while the mean Cu(2)–N distances are greater than 2.0 Å, consistent with the rhombic coplanar[10] and square-based pyramidal[11] geometries, Table 3. In the latter, the Cu(2) atom is lifted out of the plane of the four co-ordinating nitrogen ligands, by distances of 0.2336 and 0.2309 Å, for (**1**) and (**2**), respectively, in a direction towards the terminal halide ligands, as normally found for the square-pyramidal copper(II) stereochemistry.[12,13] The copper–halogen distances are *ca.* 0.1 Å longer than the normal Cu–Cl, 2.30 Å, and Cu–Br distance, 2.40 Å, consistent with the fifth-ligand elongation of a square-based pyramidal stereochemistry.[12]

The bipyam–H ligands act as tridentate nitrogen ligands in

Table 4. Some relevant mean-plane data (root-mean-square deviations, r.m.s.d., in Å) with significant deviations (Å) of atoms from the planes given in square brackets

(*a*) $[Cu_3(bipyam-H)_4Cl_2]\cdot H_2O$ (**1**)

Plane	R.m.s.d.
(1) N(1), C(1)—C(5)	0.0116
(2) C(6)—C(10), N(3)	0.0068
(3) N(1)—N(2)—N(3)	0.4051
[N(1) −0.4902, C(3) 0.5579, C(4) 0.5333, C(7) −0.5718, C(8) −0.5708, C(10) 0.4619, N(3) 0.5070]	
(4) N(4), C(11)—C(15)	0.0141
(5) C(16)—C(20), N(6)	0.0060
(6) N(4)—N(5)—N(6)	0.4020
[N(4) −0.4953, C(13) 0.5604, C(14) 0.4520, C(17) −0.5963, C(18) −0.5703, C(20) 0.4954, N(6) 0.5026]	
(7) Cu(2), N(1), N(6), N(3′), N(4′)	0.1434
[Cu(2) 0.2336]	
(8) Cu(1), N(2), N(5), N(2′), N(5′)	0.0234
[Cu(1) 0.0386]	

Dihedral angles (°) between the mean planes:
1—2, 48.21; 4—5, 48.07; 7—8, 3.91

(*b*) $[Cu_3(bipyam-H)_4Br_2]\cdot H_2O$ (**2**)

Plane	R.m.s.d.
(1) N(1), C(1)—C(5)	0.0109
(2) C(6)—C(10), N(3)	0.0097
(3) N(1)—N(2)—N(3)	0.4113
[N(1) −0.5040, C(3) 0.5787, C(4) 0.5211, C(7) −0.5665, C(8) −0.5963, C(10) 0.4568, N(3) 0.5250]	
(4) N(4), C(11)—C(15)	0.0311
(5) C(16)—C(20), N(6)	0.0041
(6) N(4)—N(5)—N(6)	0.3991
[N(4) −0.5200, C(13) 0.5400, C(14) 0.4550, C(17) −0.5830, C(18) −0.5724, C(20) 0.5026, N(6) 0.5000]	
(7) Cu(2), N(1), N(6), N(3′), N(4′)	0.1421
[Cu(2) 0.2309]	
(8) Cu(1), N(2), N(5), N(2′), N(5′)	0.0169
[Cu(1) 0.0276]	

Dihedral angles (°) between the mean planes:
1—2, 49.17; 4—5, 47.43; 7—8, 3.32

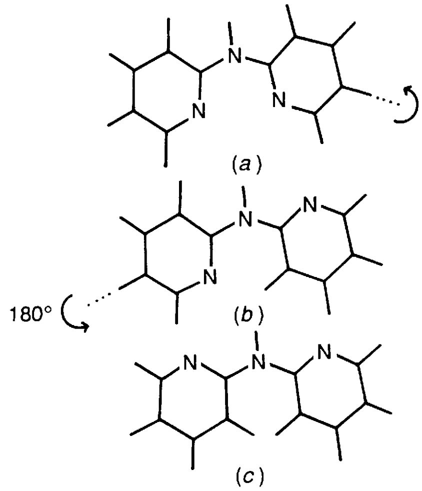


Figure 3. The three conformations of the bipyam and bipyam–H ligands: (*a*) *cis*-N; (*b*) *trans*-N; and (*c*) aligned N atoms

both complexes, rather than the usual bidentate function of the bipyam[14,15] or bipyam–H ligands,[2] previously reported. In the bidentate mode of co-ordination, Figure 3(*a*), the nitrogen atoms of each pyridine ring are arranged in a *cis* conformation, to allow bidentate chelate bonding to a metal. This contrasts with the *trans* conformation found in the crystal structure[16] of the free ligand, Figure 3(*b*), and is related to the *cis* conformation by a rotation of 180° of *one* pyridine ring, about the ring carbon to back-nitrogen bond. The only example of the bipyam ligand co-ordinating in this *trans* conformation is in $[W(CO)_5(bipyam)]$[17] and this *trans* conformation is unknown in the co-ordinated bipyam–H ligand. Rotation of the second pyridine ring by 180°, in the *trans* conformation, Figure 3(*b*), about the back C–N bond, gives a near linear array of nitrogen atoms for co-ordination to the metal atoms, Figure 3(*c*), but in which the pyridine rings involve a significant dihedral angle. There is no evidence for co-ordination of the bipyam ligand[14] in this conformation, but this conformation does occur with the bipyam–H ligand, as in the present complexes.

Each tridentate bipyam–H ligand is not flat, but twisted about the central nitrogen–carbon bonds, with an average dihedral angle between the planes of the two pyridine rings of 48°, Table 4, for both complexes (**1**) and (**2**). This results in a spiral structure for the trimer, which is best appreciated when viewed down the Cu(2)–Cu(1)–Cu(2′) direction, Figure 4. This arises mainly from the interaction between the two ring hydrogen atoms, for example, H(4) and H(7), of the coplanar tridentate bipyam–H ligand, Figure 1. Notwithstanding this novel tridentate mode of co-ordination, there are no unusual bond lengths or angles in the bipyam–H ligands.[15,16] However, the short Cu–Cu separation is largely determined by the small N ··· N bite distances, 2.44 Å, of the twisted and co-ordinated bipyam–H ligands. A further consequence of the spiral conformation of the $[Cu_3(bipyam-H)_4X_2]$ units is that they are inherently optically active and that in the centrosymmetric space group, *Pnn*2, both the D and L conformations of (**1**) and (**2**) are present ($Z = 4$).

In both complexes the water molecules are disordered with site occupation factors of 0.5 and are more than 3.0 Å from the copper atom, too far even for weak semi-co-ordination.[12]

Structural Comparison with Other Relevant Complexes.—The most significant feature of the copper trimers is the almost linear Cu_3 unit and the short Cu–Cu distance of 2.47 Å. Table 5 lists the known $[M^{II}_3(bipyam-H)_4X_2]$ complexes, six of which are of known crystal structure[18–20] and all of which contain the same essentially isostructural trimer unit. All the M–M separations are slightly shorter than the corresponding separations in the pure metals,[21] Cu 2.54 and Ni 2.49 Å, respectively, but the Cu–Cu separations of 2.47—2.48 Å are all slightly longer than the corresponding Ni–Ni separations, 2.42—2.45 Å, and reflect the differences in these distances in the pure metals. In the six complexes the dihedral angles between the pyridine rings of the individual bipyam–H ligands are about 50°, with the values for the nickel complexes above 52° and the two copper 'halides' *ca.* 48°, a difference that suggests that the M–M separation determines the dihedral angles of the bipyam–H ligands in these trimers.

The bipyam–H ligand also forms a complex[22] with copper(I) $[Cu^I_2(bipyam-H)_2]$ (**3**), in which the ligand is tridentate to give an infinite chain of distorted trigonal-planar CuN_3 chromophores, linked into an infinite chain of Cu atoms, with a Cu–Cu distance of 2.67 Å, significantly longer than that in the copper(II) trimers, 2.475 Å, and greater than that in copper metal, 2.54 Å. The only other linear Cu_3-containing complex[23] is also of copper(I), $[\{Cu^I(MeC_6H_4NNNNNC_6H_4Me)\}_3]$ (**4**), and involves an even shorter Cu–Cu separation of 2.35 Å. Comparable Cu–Cu distances are known in dimeric copper complexes, as in the classical $[\{Cu^{II}(MeCO_2)_2(OH_2)\}_2]$,[24] (**5**), 2.62 Å, but lower values are observed in $[\{Cu^{II}(dpt)_2\}_2]$,[25] (**6**), 2.44 Å, and in $[\{Cu^I(dpt)\}_2]$,[26] (**7**), 2.45 Å, where dpt = 1,3-diphenyltriazenide.

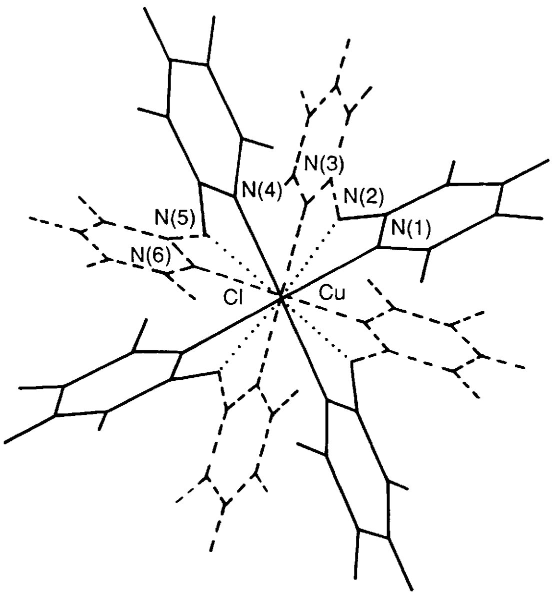


Figure 4. The molecular structures of complexes (**1**) and (**2**) viewed down the Cu_3 direction

Table 5. The range of $[M_3(bipyam\text{-}H)_4X_2]$ complexes

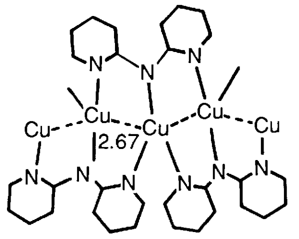
Complex	M-M distance (Å)	Mean dihedral angle (2θ,°)	Ref.
Cu-Cl	2.471(1)	48.14	Present work
Cu-Br	2.468(1)	48.30	Present work
Cu-NCO	2.48(1)	53.0	18
Ni-Cl	2.443(1), 2.431(1)	52	19
Ni-O_2CMe	2.449(3), 2.445(3)	52.55	20
Ni-ONO	2.443(1), 2.424(1)	53.10	20
Cu metal	2.54	—	21
Ni metal	2.494	—	21

M = Cu^{II}, X = Cl^-,* Br^-,* NCO^-,* NCS^-, or CN^-; M = Ni^{II}, X = Cl^-,* Br^-, NCS^-, O_2CMe^-,* ONO^-,* or NO_3^-; where the asterisk indicates crystal structure is known.

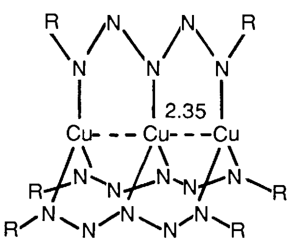
Infrared Spectrum.—The i.r. spectra of complexes (**1**) and (**2**) are dominated by the tridentate bipyam–H ligand.[27] The N-H stretching bands in the 3 300—3 400 cm^{-1} region of the bipyam ligand are absent and the highest-energy pyridine-ring vibrations show a significant shift from 1 650 to 1 600 cm^{-1} compared with that of the co-ordinated bipyam ligand.[27]

Magnetic Properties.—The observed magnetic moment at room temperature of complex (**1**) is 1.40 B.M. per copper(II) ion, significantly less than the spin-only value of 1.73 B.M. for the free copper(II) ion.[12] This suggests the presence of antiferromagnetic coupling[28] between the three copper(II) ions present, which might be anticipated from the short Cu–Cu separation of *ca.* 2.47 Å. However this may be reduced by the spiral twist of the planes of the three separate $Cu(1)N_4$ and $Cu(2)N_4X$ environments, 48°, which reduces the effective overlap of the $d_{x^2-y^2}$ orbitals of three respective copper(II) ions, see Figure 5. If the local molecular axes of the Cu(1) atom, Figure 5, are taken as x, y, and z, due to the spiral twist of the trimer, the local molecular axes of the Cu(2) atom, x'' and y'', are misaligned by $+24°$, and the x' and y' axes of the Cu(2′) atom are misaligned by $-24°$ relative to the x and y axes of the Cu(1) atom. For all three Cu atoms the individual z axes are virtually aligned, but the trimer axes of the two trimers per unit cell are also misaligned by $+24°$, Figure 2.

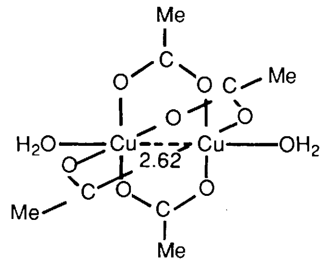
Complexes (**1**) and (**2**) are essentially e.s.r. silent, consistent with the reduced magnetic moment, due to the antiferromagnetic coupling associated with the short Cu–Cu separation of 2.47 Å. Both complexes have a very weak isotropic signal, but this is associated with a small amount of copper(II) impurity. The e.s.r. silence suggests that the antiferromagnetic coupling constant, J, is $> 500\ cm^{-1}$.



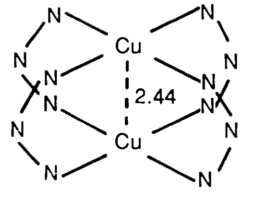
(**3**)



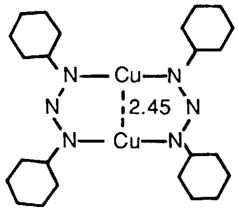
(**4**)



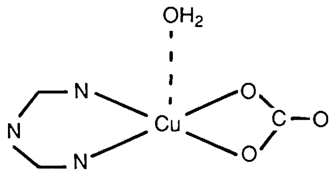
(**5**)



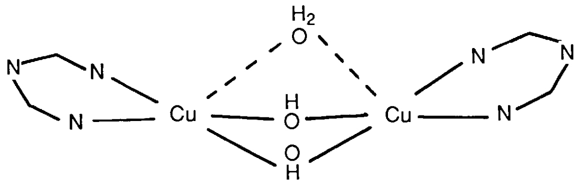
(**6**)



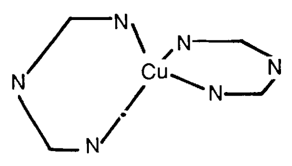
(**7**)



(**8**)



(**9**)



(**10**)

Electronic Properties.—The crystals of complexes (**1**) and (**2**) are dark purple, almost black. The observed electronic reflectance spectra, Figure 6, are the same and show a main peak at 15 200 cm^{-1} and a high-energy shoulder at 19 230 cm^{-1}. The latter is associated with the central rhombic coplanar CuN_4 chromophore of the trimer and the main band is associated with the square-based pyramidal CuN_4X chromophore of the trimer. The higher intensity[12,28] of the latter chromophore is then associated with the lack of a centre of symmetry and the one centrosymmetric, rhombic, coplanar chromophore, is

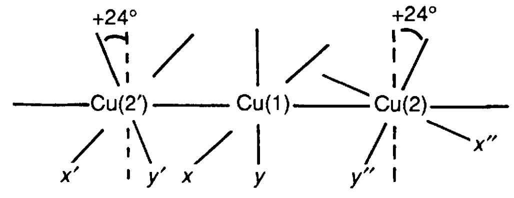


Figure 5. The local molecular axes of the three Cu atoms in complex (**1**)

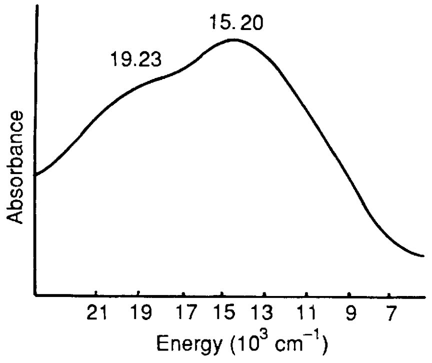


Figure 6. The electronic reflectance spectrum of the chloride trimer

then associated with the lower-intensity shoulder. The higher energy of the shoulder is then associated with the lower tetragonality[12] of the rhombic coplanar chromophore, relative to that of the square-based pyramidal chromophore (ref. 12, Figure 4).

Copper Metal Reduction.—The use of copper metal[29] as a means of reducing copper(II) complexes to the corresponding copper(I) complexes has been reported earlier in the preparation of $[Cu^I(MeCN)_4][ClO_4]$.[30] In this case the copper(I) complexes were stable in air and were readily isolated, but with $[Cu^I(bipyam)_2]X$ complexes,[1] while solid complexes could be isolated under nitrogen gas, in air reoxygenation to copper(II) species occurs, especially in solution. If the above copper metal reduction of $[Cu(bipyam)_2Cl]Cl$ is carried out in air,[31] without excess of bipyam, crystals of a carbonato species are obtained, $[Cu^{II}(bipyam)(O_2CO)(OH_2)]\cdot 2H_2O$,[32] (**8**). If CO_2-free air is involved, a dihydroxy bridged species is obtained, $[Cu^{II}_2(bipyam)_2(OH)_2(OH_2)]Cl_2\cdot 2H_2O$,[33] (**9**). Thus these copper metal reduction and reoxygenation reactions, without the presence of excess of bipyam, give evidence of the formation of the OH^- anion. This suggests that in the presence of copper metal a simple copper(II) reduction occurs [equation (1)].

$$Cu^0 + Cu^{II} \longrightarrow 2Cu^I \qquad (1)$$

Followed by the reoxygenation reaction [equations (2)—(4)].

$$2Cu^I + 2HOH + O_2 \longrightarrow 2Cu^{II} + 4HO^- \qquad (2)$$

$$2Cu^{II} + 2HO^- + 2\,bipyam \longrightarrow [\{Cu^{II}(bipyam)(OH)\}_2]^{2+} \qquad (3)$$

$$\text{Excess of bipyam} + HO^- \longrightarrow \text{bipyam–H} + H_2O \qquad (4)$$

The initial reoxygenation reaction involves traces of water as a source of hydrogen atoms to give the HO^- anions, which as good ligands form dihydroxy-bridged species, such as (**9**) above. In the presence of excess of bipyam these HO^- anions extract protons from the neutral bipyam ligand, to form bipyam − H and water; the latter is recycled in the reoxygenation reaction above and the bipyam − H can act as a ligand. Some evidence for this process can be observed[2] in the preparation of $[Cu^{II}(bipyam\text{-}H)_2]$, (**10**), with a compressed tetrahedral CuN_4 chromophore, directly, from the reaction of $Cu(OH)_2$ and bipyam.[2]

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