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Linear trinuclear and one-dimensional copper(II) complexes containing co-bridging end-on azido and triazole ligands. Crystal structures and magnetic properties of $[Cu_3(atrz)_2(N_3)_6]$ and $[Cu(atrz)_2(N_3)]NO_3$ (atrz = 4-amino-1,2,4-triazole)

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New complexes with 1,2,4-triazole and end-on azido bridging ligands, $[Cu_3(atrz)_2(N_3)_6]$ **1** and $[Cu(atrz)_2(N_3)]NO_3$ **2** (atrz = 4-amino-1,2,4-triazole), have been prepared and structurally determined. Complex **1** has a linear trinuclear copper(II) structure with bridging bond angles Cu–N–N (atrz) [119.3(3) and 123.4(3)°], and larger Cu–N–Cu [118.7(2)°]. In **2** the copper(II) ions are linked by one end-on azido and two triazole bridges forming a cationic chain with Cu–N–N (equatorial atrz) [121.0(2) and 122.3(2)°] and Cu–N–Cu 104.05(12)°. The nearest-neighbour Cu · · · Cu distances are 3.4496(7) Å for **1** and 3.5034(6) Å for **2**. The copper(II) ions are strongly antiferromagnetically coupled with $J = -108.8$ cm^{-1} for **1**, and weakly with $J = -17.7$ cm^{-1} for **2**. The nature and the magnitude of the antiferromagnetic exchange of both complexes are discussed based on their structures.

There has been a great and growing interest in the coordination chemistry of 1,2,4-triazole and its derivatives due to the fact that it acts as a bridging group through its two nitrogen atoms (N1 and N2) in polymeric compounds with transition-metal ions, and can effectively transmit magnetic interaction between paramagnetic centres.[1–11] Furthermore, its iron(II) complexes have been found to show an interesting spin-crossover behaviour.[12,13] Two general kinds of bridging mode are allowed by these ligands in the form of only triazole bridges or containing second small bridging anions. For the latter kind of complexes, successful magneto-structural correlations have been achieved only for the bridging ions Cl^-, F^- or NCS^-.[10,11] However, the 1,2,4-triazole complex with N_3^- bridging anions has not been reported until now. As is well known, the bridging azido ligand stabilizes either end-on or end-to-end coordination modes to the paramagnetic metal centres, generally giving ferro- or antiferro-magnetic interactions respectively.[13] In particular, a recent study on end-on azide-bridged dicopper(II) complexes with Cu–N–Cu angles in the range 98.3–124.1°, which contain a bridging network formed by the azide together with a diazine-based ligand, has revealed a marked dependence on Cu–N–Cu bridging angle and shown antiferromagnetic interactions for angles greater than 108.5°.[14,15] In order to examine some copper(II) complexes with these two types of bridging modes, here we report the synthesis, structure and magnetic properties of both linear trinuclear $[Cu_3(atrz)_2(N_3)_6]$ **1** and one-dimensional chain $[Cu(atrz)_2(N_3)]NO_3$ **2** (atrz = 4-amino-1,2,4-triazole).

Experimental

Materials

All chemicals were commercial products of reagent grade used without purification, except that 4-amino-1,2,4-triazole was prepared by literature methods.[16]

Measurements

Analyses of C, H and N were determined on a Perkin-Elmer 240C elemental analyser. The infrared spectra were recorded on a Nicolet-170 SX FT-IR spectrometer with KBr pellets in the range 4000–200 cm^{-1}. Magnetic susceptibilities on powder samples were measured with a Quantum Design MPMS SQUID magnetometer in the temperature range 5–300 K. The applied magnetic field was 10000 G and the data were corrected for diamagnetism using Pascal's constants and the temperature independent paramagnetism was estimated at 60×10^{-6} emu mol^{-1} per copper(II) ion.

Preparations

$[Cu_3(atrz)_2(N_3)_6]$ 1. To a stirring aqueous solution (40 ml) containing atrz (170 mg, 2 mmol) and $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1 mmol) was added dropwise an aqueous solution of sodium azide (33 mg, 0.5 mmol). The resulting black green solution was filtered, and after several days the dark brown compound crystallized upon slow evaporation of the solvent at room temperature. Yield 20 mg (Found: C, 7.91; H, 1.40; N, 59.33. Calc. for $C_4H_8Cu_3N_{26}$: C, 7.86; H, 1.32; N, 59.62%). IR (KBr): $\nu_{asym}(N_3)$ 2094vs, 2073vs and 2030vs; $\nu_{sym}(N_3)$ 1342ms and 1291ms; $\delta(N_3)$ 617m cm^{-1}.

$[Cu(atrz)_2(N_3)]NO_3$ 2. To a stirring aqueous solution (20 ml) of atrz (127.5 mg, 1.5 mmol) was added an aqueous solution (5 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (120 mg, 0.5 mmol), followed dropwise by a solution of NH_4N_3 (18 mg, 0.3 mmol) in the minimum of distilled water, and the resulting deep green solution was filtered. After several days, green single crystals were harvested by slow evaporation of the filtrate at room temperature. Yield 50 mg (Found: C, 14.27; H, 2.40; N, 49.84. Calc. for $C_4H_8CuN_{12}O_3$: C, 14.31; H, 2.40; N, 50.06%). IR (KBr): $\nu_{asym}(N_3)$ 2056vs; $\nu_{sym}(N_3)$ 1289ms; $\delta(N_3)$ 618m; $\nu_3(NO_3)$ 1384vs; $\nu_2(NO_3)$ 824ms cm^{-1}.

X-Ray crystallography

A summary of the crystal data and data collection and refinement parameters for compounds **1** and **2**, respectively, is given in Table 1. Data were collected at 293 K on a Siemens P4 four-

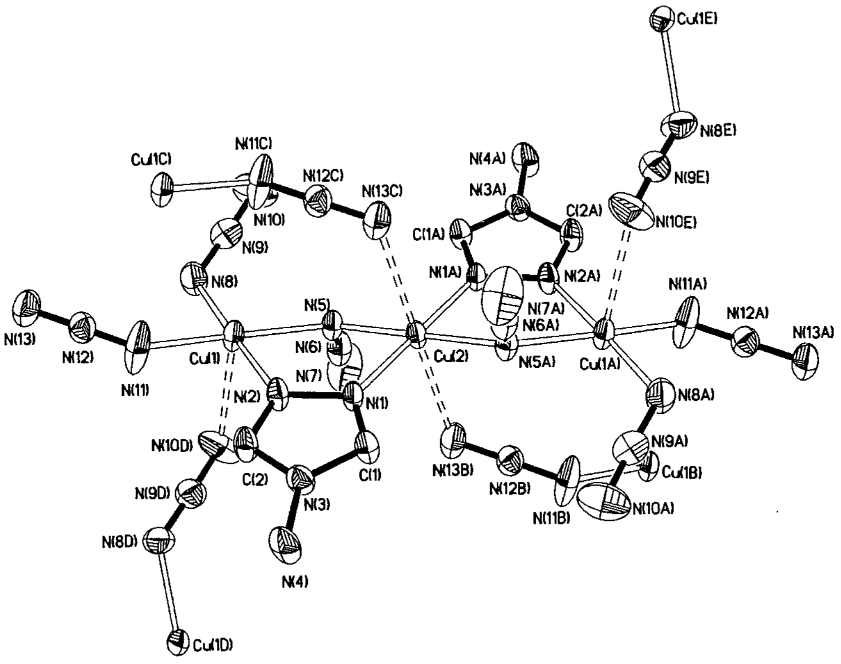

Fig. 1 Structure of [$Cu_3(atrz)_2(N_3)_6$] **1**. Symmetry codes are A ($-x + 2$, $+y + 0.5$, $-z$), B ($+x + 1$, $+y$, $+z$), C ($-x + 1$, $-y + 2$, $-z$), D ($+x$, $-y + 1.5$, $+z - 0.5$) and E ($-x + 2$, $+y - 0.5$, $-z + 0.5$).

circle diffractometer with monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation using the ω–2θ scan mode with a variable scan speed 4.0–40.0° min^{-1} in ω. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2. Hydrogen atoms were placed in their calculated positions (C–H 0.96 and N–H 0.90 Å), assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. Computations were carried out on a PC-586 computer using the SHELXTL-PC program package.[17]

CCDC reference number 186/1481.

See http://www.rsc.org/suppdata/dt/1999/2337/ for crystallographic files in .cif format.

Results and discussion

Crystal structures

[$Cu_3(atrz)_2(N_3)_6$] 1. Fig. 1 shows the principal structural features with the atom labelling scheme, Fig. 2 shows stereoviews of the crystal structure, and Table 2 gives the bond distances and angles relevant to the copper co-ordination spheres. This complex has a centrosymmetric linear trinuclear structure. Three essentially square-planar copper centres are bridged equatorially by the atrz and the 1,1-azide. The central copper(II) ion Cu(2) lies on an inversion centre and shows an elongated octahedron with four short equatorial Cu–N bonds (<2.01 Å) and two much longer axial Cu–N [2.531(4) Å]. Each external copper(II) ion Cu(1) is strongly co-ordinated by four short equatorial N (Cu–N < 2.01 Å), and weakly by an axial N(10D) [Cu(1)–N(10D) 2.525(4) Å; D $+x$, $-y + 1.5$, $+z - 0.5$]. However, the longer Cu(1)–N(11C) [C $-x + 1$, $-y + 2$, $-z$] distance [3.042(4) Å] does not generate a significant bridging interaction, so the local environment around Cu(1) might be best described as a distorted square pyramid. The Cu(2) equatorial plane and Cu(1) basal plane make a dihedral angle of 26.2°, and form two dihedral angles of 17.8 and 18.9° with the atrz mean plane, respectively.

It is interesting that there are two distinct types of azido groups distinguished by the mode or strength of co-ordination to the metal: one acts as a intramolecular bridge between neighbouring copper atoms in μ-1,1 co-ordination mode, the other as an intermolecular bridge between external copper and external copper or centre copper originating from another trinuclear unit in μ-1,3 co-ordination mode (see Fig. 2). Furthermore, both azido groups on external copper are also different; N(12) and N(13) atoms are well in the Cu(1) basal plane with the largest deviation of 0.0696(6) Å, while N(9) and N(10) are not in the plane with deviations of 0.5711(6) and 1.1082(6) Å respectively. All Cu–N distances fall in the ranges 1.95–2.15 and 2.50–2.85 Å for short and long distances, respectively, very close to corresponding distances in other copper(II) azide complexes.[18] The N(5)–N(6) distance (1.241(6) Å) is slightly larger than that of N(6)–N(7) (1.148(7) Å), as is common for the end-on azide bridging mode. The azide groups are found to be

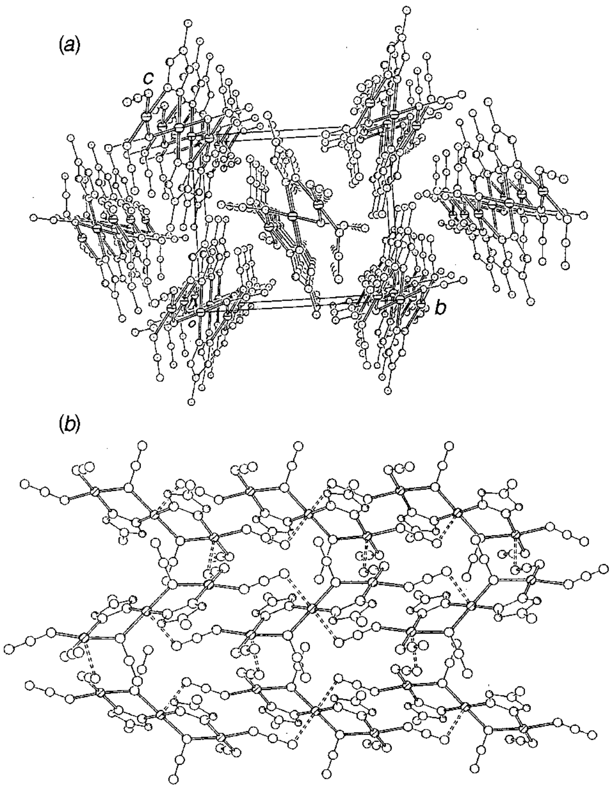

Fig. 2 Perspective view of compound **1** (*a*) along the *a* axis and (*b*) along the *c* axis.

Table 1 Summary of crystal data for compounds **1** and **2**

	1	**2**
Empirical formula	$C_4H_8Cu_3N_{26}$	$C_4H_8CuN_{12}O_3$
M	610.98	335.76
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	8.444(2)	7.0069(11)
b/Å	11.1376(13)	8.533(2)
c/Å	9.994(2)	11.013(2)
α/°	—	70.95(2)
β/°	98.48(2)	84.824(13)
γ/°	—	74.25(2)
U/Å^3	929.6(3)	599.1(2)
Z	2	2
D_c/g cm^{-3}	2.183	1.861
F(000)	602	338
μ/mm^{-1}	3.464	1.857
Reflections collected	1744	2632
Independent reflections	1630 (R_{int} = 0.0312)	2073 (R_{int} = 0.0208)
No. parameters	151	184
Goodness of fit on F^2	1.058	1.051
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0374, 0.0882	0.0466, 0.1312
Largest difference peak and hole/e Å^{-3}	0.492 and −0.706	0.905 and −0.892

Table 2 Selected bond distances (Å) and angles (°) for compound **1**

Cu(1)–N(8)	1.952(4)	Cu(1)–N(11)	1.973(5)
Cu(1)–N(5)	2.002(4)	Cu(1)–N(2)	2.004(4)
Cu(1)–N(10D)	2.525(4)	Cu(2)–N(1)	1.993(4)
Cu(2)–N(5)	2.008(4)	Cu(2)–N(13B)	2.531(4)
N(1)–N(2)	1.370(5)	N(5)–N(6)	1.241(6)
N(6)–N(7)	1.148(7)	N(8)–N(9)	1.185(6)
N(9)–N(10)	1.162(6)	N(11)–N(12)	1.172(6)
N(12)–N(13)	1.164(6)		
N(8)–Cu(1)–N(11)	92.8(2)	N(8)–Cu(1)–N(5)	94.4(2)
N(11)–Cu(1)–N(5)	171.6(2)	N(8)–Cu(1)–N(2)	177.4(2)
N(11)–Cu(1)–N(2)	87.1(2)	N(5)–Cu(1)–N(2)	85.5(2)
N(2)–Cu(1)–N(10D)	89.3(2)	N(5)–Cu(1)–N(10D)	90.8(2)
N(8)–Cu(1)–N(10D)	93.2(2)	N(11)–Cu(1)–N(10D)	93.1(2)
N(1)–Cu(2)–N(1A)	180.0	N(5)–Cu(2)–N(5A)	180.0
N(1)–Cu(2)–N(5A)	92.9(2)	N(1)–Cu(2)–N(5)	87.1(2)
N(1)–Cu(2)–N(13B)	92.6(2)	N(1)–Cu(2)–N(13C)	87.4(2)
N(5)–Cu(2)–N(13B)	88.9(2)	N(5)–Cu(2)–N(13C)	91.1(2)
N(13C)–Cu(2)–N(13B)	180.0	Cu(1)–N(5)–Cu(2)	118.7(2)
Cu(1)–N(2)–N(1)	123.4(3)	Cu(2)–N(1)–N(2)	119.3(3)
Cu(1)–N(5)–N(6)	114.3(3)	Cu(2)–N(5)–N(6)	117.3(3)
Cu(1)–N(10D)–N(9D)	113.1(2)	Cu(2)–N(13C)–N(12C)	112.3(2)
Cu(1)–N(8)–N(9)	120.4(4)	Cu(1)–N(11)–N(12)	125.8(4)
N(5)–N(6)–N(7)	178.7(6)	N(8)–N(9)–N(10)	177.1(6)
N(11)–N(12)–N(13)	177.8(5)		

Symmetry codes: (A) 2 − x, 0.5 + y, −z; (B) 1 + x, y, z; (C) 1 − x, 2 − y, −z; (D) x, 1.5 − y, −0.5 + z.

Table 3 Selected bond distances (Å) and angles (°) for compound **2**

Cu(1)–N(1)	2.029(3)	Cu(1)–N(5)	2.011(3)
Cu(1)–N(9)	2.406(3)	Cu(2)–N(2)	2.402(3)
Cu(2)–N(6)	2.008(3)	Cu(2)–N(9)	2.029(3)
N(1)–N(2)	1.374(4)	N(5)–N(6)	1.387(4)
N(9)–N(10)	1.183(4)	N(10)–N(11)	1.146(6)
N(5)–Cu(1)–N(1)	90.49(11)	N(5)–Cu(1)–N(1A)	89.51(11)
N(5A)–Cu(1)–N(9)	97.64(10)	N(5)–Cu(1)–N(9)	82.36(10)
N(1A)–Cu(1)–N(9)	94.42(10)	N(1)–Cu(1)–N(9)	85.58(10)
N(5A)–Cu(1)–N(5)	180.0	N(1)–Cu(1)–N(1A)	180.0
N(9A)–Cu(1)–N(9)	180.0	N(6B)–Cu(2)–N(6)	180.0
N(6)–Cu(2)–N(2B)	92.36(11)	N(6)–Cu(2)–N(9B)	91.03(11)
N(6B)–Cu(2)–N(9)	91.03(11)	N(6)–Cu(2)–N(9)	88.97(11)
N(9)–Cu(2)–N(2B)	97.55(11)	N(6B)–Cu(2)–N(2)	92.36(11)
N(6)–Cu(2)–N(2)	87.64(11)	N(9B)–Cu(2)–N(2)	97.55(11)
N(9)–Cu(2)–N(2)	82.45(11)	N(2B)–Cu(2)–N(2)	180.0
Cu(1)–N(1)–N(2)	123.2(2)	Cu(2)–N(2)–N(1)	113.4(2)
Cu(1)–N(5)–N(6)	121.0(2)	Cu(2)–N(6)–N(5)	122.3(2)
Cu(1)–N(9)–N(10)	129.7(2)	Cu(2)–N(9)–N(10)	117.9(2)
Cu(1)–N(9)–Cu(2)	104.05(12)	N(9)–N(10)–N(11)	175.9(6)

Symmetry codes: (A) −x, −y, 1 − z; (B) 1 − x, −y, 1 − z.

almost linear, while the sum of the angles around N(5) (350.3°) indicates some trigonal pyramidal distortion at the μ-1,1-azido bridge. The bridging angle Cu(1)–N(5)–Cu(2) is 118.7(2)°, close to those found in binuclear copper complexes[14] containing a diazine-based bridging ligand [Cu_2(PPD3Me)(μ-N_3)Cl_3(H_2O)$_{1.5}$] [124.1(3)°] and [Cu_2(PAP)(μ-N_3)Cl_3]·CH_2Cl_2 [107.9(2)°] [PPD3Me = 3,6-bis(2′-pyridylamino)phthalazine, PAP = 1,4-bis(2′-pyridylamino)phthalazine]. The angles Cu(2)–N(1)–N(2) 119.3(3)° and Cu(1)–N(2)–N(1) 123.4(3)° are clearly smaller than those found in the double triazole bridging complexes [Cu_2(pt)$_2$(SO_4)(H_2O)$_3$]·3H_2O [124.4(3) and 139.8(3)°][4] and [Cu(aamt)(H_2O)$_2$]$_2$[SO_4]$_2$·4H_2O [132.9(8) and 135.1(8)°] [ptH = 3-pyridin-2-yl-1,2,4-triazole, aamt = 4-amino-3,5-bis(aminomethyl)-1,2,4-triazole].[6] The torsion angle Cu(2)–N(1)–N(2)–Cu(1) is 2.31(2)°.

The distances of Cu(1C), N(11C), N(12C) and N(13C) atoms to the Cu(2) equatorial plane are 4.2076(5), 3.4142(6), 2.9824(6) and 2.5283(7) Å, respectively; those of Cu(1D), N(8D), N(9D) and N(10D) to the Cu(1) basal plane are 5.0934(5), 3.4259(7), 3.0190(6) and 2.5695(6) Å, respectively. The metal–metal separations are 3.4496(7), 5.475(4) and 5.788(4) Å for Cu(1)···Cu(2), Cu(2)···Cu(1C) and Cu(1)···Cu(1D), respectively. The intramolecular Cu(1)···Cu(2) distance of 3.4496(7) Å is slightly larger than that of 3.405 Å for copper(II) ions linked by a single N^1,N^2-1,2,4-triazole bridge and two μ-chloride anions in the linear complex [Cu(trz)Cl_2]$_\infty$ (trz = 1,2,4-triazole),[19] but somewhat shorter than the 3.5682(5) Å for copper(II) ions linked by two N^1,N^2-1,2,4-triazole bridges and one μ-chloride anion in the linear trinuclear compound[10] [Cu_3(H_2ahmt)$_6$-Cl_4]Cl_2 (H_2ahmt = 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole).

In the present complex there appears to be a long N(4)···N(7) (−x + 2, +y − 0.5, −z − 0.5) contact of 3.201(7) Å, probably indicating the occurrence of a weak hydrogen bond between the amino group of the atrz ligand and bridging azide anion.

[Cu(atrz)$_2$(N_3)]NO_3 2. The structure of the complex **2** consists of polymeric cationic [Cu_2(atrz)$_4$(N_3)$_2$]$^{2+}$ units, and non-co-ordinated nitrate anions. One of the units is shown in Fig. 3, together with the atom-numbering scheme. Stereoviews of the crystal structure are shown in Fig. 4. Selected bond distances and angles are given in Table 3. In this case there is an inversion centre at the copper(II) atom Cu(1), giving a linear chain of equally spaced copper(II) ions (see Fig. 4). The copper(II) ions are linked by two bidentate bridging atrz groups and one end-on azide bridge. All copper(II) ions have elongated tetragonal octahedral (4 + 2) geometries. It is worth noting that two kinds of differently arranged CuN_6 cores alternate in the chain. The Cu(1) equatorial plane formed by four nitrogen atoms originates from atrz ligands [Cu–N 2.029(3)–2.011(3) Å]. Two ligand N (azide) atoms acting as axial ligands at slightly long distances [Cu–N 2.406(3) Å] fall in the range of 2.30–2.45 Å for medium strong Cu–N (azide) bonding interaction.[20] The Cu(2) equatorial plane formed by four nitrogen atoms, two from atrz ligands [Cu–N 2.008(3) Å], the others from azido ligands [Cu–N 2.029(3) Å]. Two nitrogen atoms of atrz ligands occupy axial positions with long contacts [Cu–N 2.402(3) Å], in good agreement with those observed in the similar complex [Cu(hyetrz)$_3$]-[ClO_4]$_2$·3H_2O [2.404(6) Å] [hyetrz = 4-(2-hydroxyethyl)-1,2,4-triazole].[8] Each copper(II) ion and four co-ordinated nitrogen atoms consist of a perfect plane. A dihedral angle of 52.9° was found between the planes from neighbouring copper atoms. All triazole rings are fairly planar. The dihedral angle between least-squares planes through the triazole ligands linking Cu(1) and Cu(2) is 114.7°.

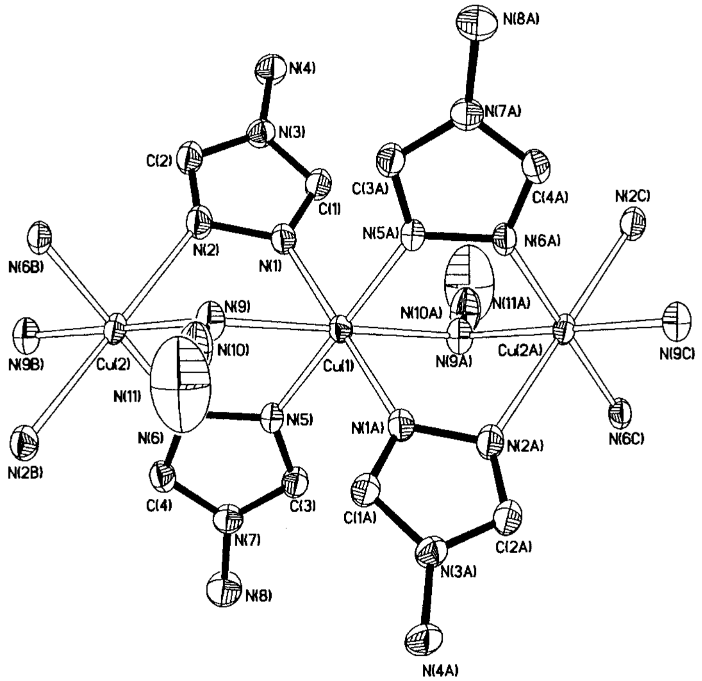

Fig. 3 Structure of $[Cu_2(atrz)_4(N_3)_2]^{2+}$ cation in compound **2**. Symmetry codes are A ($-x$, $-y$, $-z + 1$), B ($-x + 1$, $-y$, $-z + 1$) and C ($+x - 1$, $+y$, $+z$).

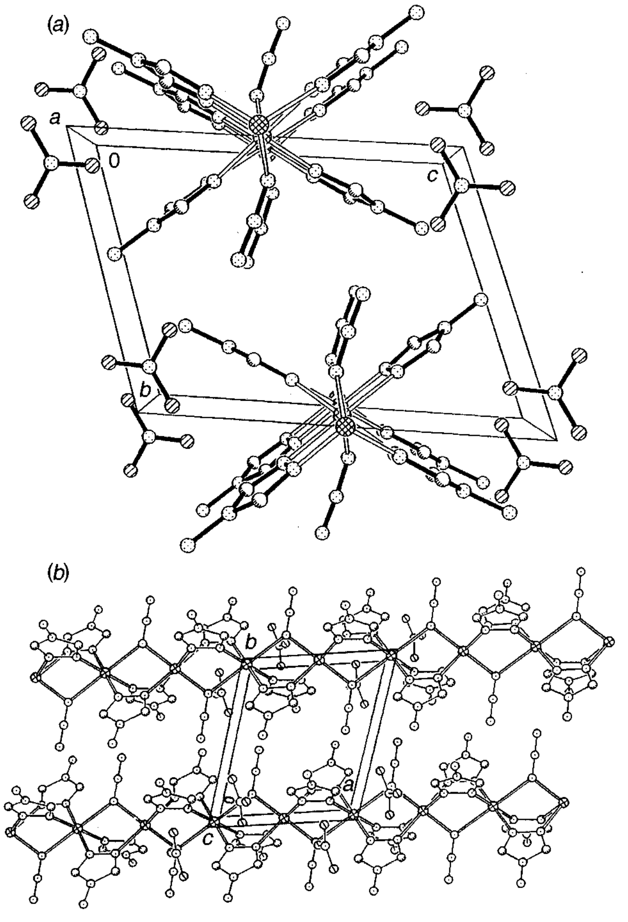

Fig. 4 Perspective view of compound **2** (*a*) along the *a* axis and (*b*) along the *c* axis.

The *cis* interligand angles at the copper atom display values in the range 82.36–97.64° at Cu(1), and 82.45–97.55° at Cu(2), respectively. The sum of the angles around N(9) is 351.6°, suggesting that there is also some pyramidal distortion at the azide bridge as found in complex **1**. The angle Cu(1)–N(9)–Cu(2) is 104.05(12)° in this complex containing two N–N *exo*-bidentate ligands and one end-on azide ligand. The two atrz bridging between neighbouring copper atoms are not the same. One links the metal atoms in the equatorial plane with Cu–N–N bond angles of 121.0(2) and 122.3(2)°, the other in equatorial and axial positions with Cu–N–N angles 123.2(2) and 113.4(2)°, very similar to those found in the tricopper complex[10] $[Cu_3(H_2ahmt)Cl_4]Cl_2$ [121.2(3) and 122.3(2), 124.3(3) and 116(2)°], somewhat smaller than those in $[Cu(hyetrz)_3][ClO_4]_2{\cdot}3H_2O$ [123.1(4)–129.9(4), 125.8(4)–118.1(4)°].[8] The former values are intermediate between 119.3(3) and 123.4(3)° found in complex **1**, but much smaller than those observed in the double triazole bridging complex[5] $[Cu(aamt)Br_2(H_2O)]_2{\cdot}Br_2{\cdot}H_2O{\cdot}CH_3OH$ [133.7(2) and 134(2)°]. The atrz bridging torsion angles Cu(1)–N(1)–N(2)–Cu(2) and Cu(1)–N(5)–N(6)–Cu(2) are −13.00 and −7.77°, respectively. The Cu ··· Cu separation of 3.5034(6) Å in the binuclear unit is slightly larger than that in complex **1** [3.4496(7) Å], and significantly longer than that in the bis(end-on μ-azido)copper(II) complex $[Cu_2(N_3)_4(C_{16}H_{34}N_2O_6)(H_2O)]$ [3.162(1) Å],[21] but much shorter than those found in triple triazole bridging complexes $[Cu_3(metrz)_6(H_2O)_4][CF_3SO_3]_6{\cdot}4H_2O$ [3.719(7) Å][22] (metrz = 3-methyl-4-ethyl-1,2,4-triazole) and $[Cu(hyetrz)_3][ClO_4]_2{\cdot}3H_2O$ [3.8530(8) and 3.8293(2) Å],[8] indicating that when a μ-1,1-azido ligand is replaced by 1,2,4-triazole bridging ligands the Cu ··· Cu distance tends to enlarge.

Magnetic properties

The $\chi_m T$ values of the two complexes decreased at low temperatures, showing that these two complexes are antiferromagnetic. A slight increase of $\chi_m T$ at low temperature for **1** implies the occurrence of intermolecular exchange interaction, probably due to the cross-linkage of this complex in the crystal. However, from the magnetic viewpoint, the linkage between copper ions through asymmetrical end-to-end bridging azides [N(11)–N(12)–N(13) and N(8)–N(9)–N(10)] can only propagate negligible exchange or very weak antiferromagnetic exchange interaction.[23] So that, as the first approximation, complex **1** can be treated as a symmetrical linear trinuclear complex with bridging triazole and azide between adjacent copper atoms, and the corresponding molar magnetic susceptibility is represented by eqn. (1)[24] [the Hamiltonian being $\boldsymbol{H} = -2J(\boldsymbol{S}_1{\cdot}\boldsymbol{S}_2 + \boldsymbol{S}_2{\cdot}\boldsymbol{S}_3)$],

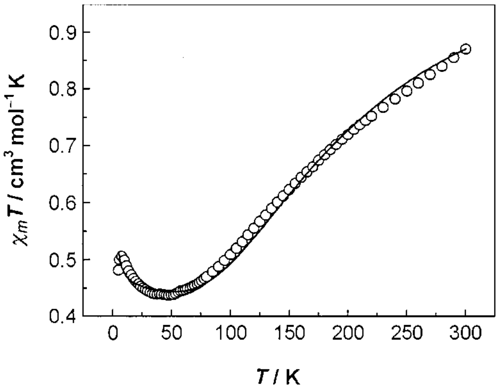

Fig. 5 Experimental (○) and calculated (−) temperature dependence of χ_mT for the trinuclear $[Cu_3(atrz)_2(N_3)_6]$ **1**.

$$\chi'_m = \frac{Ng^2\beta^2}{4kT}\frac{1 + \exp(-2J/kT) + 10\exp(J/kT)}{1 + \exp(-2J/kT) + 2\exp(J/kT)} \quad (1)$$

in which the exchange constant between the terminal copper ions was taken as zero. The exchange interaction through axial azides, if it has any effect on the observed magnetic susceptibility, may be treated as an intermolecular exchange interaction zj by a molecular field model using eqn. (2).[25] The symbols

$$\chi_m = \frac{\chi'_m}{1 - (2zj\chi'_m/Ng^2\beta^2)} \quad (2)$$

in eqns. (1) and (2) have their usual meanings. The least-squares fitting of the experimental χ_mT [χ_m is the magnetic susceptibility per trinuclear copper(II) unit] gives $J = -108.8(2)$ cm^{-1}, $zj = 0.86(3)$ cm^{-1}, $g = 2.13(1)$ and $R = 1.35 \times 10^{-3}$ [$R = \Sigma|(\chi_mT)_{exp} - (\chi_mT)_{calc}|^2/\Sigma(\chi_mT)_{exp}{}^2$] (Fig. 5).

The small positive zj value of complex **1** implies the exchange interaction through axial asymmetrical end-to-end bridging azide is very weakly ferromagnetic. This is in conflict with those previously described. However, it is reasonable due to the characterization of this asymmetrical bridging azide which has been examined above. The exchange mechanism is similar to that in the complex $[Ni_2(en)_4(SCN)_2]I_2$.[26] It is noteworthy that although the angle Cu(1)–N(11C)–Cu(1C) is 86.6°, suggesting this linkage may transmit ferromagnetic exchange interaction between copper atoms due to an "accident orthogonality" in end-on bridging azide,[21,27] this pathway, if it has any role in exchange interaction, is not important bearing in mind the large distance of 3.04 Å between N(11C) and Cu(1) atoms. The intramolecular ferromagnetic exchange interaction in complex **1** is mainly due to the strict orthogonality of σ_x and π_z azide orbitals.

Complex **2** has an isolated linear structure. For simplicity, assuming the g factors of the two independent copper atoms [Cu(1), Cu(2)] are the same, the magnetic susceptibility of **2** may be treated by a uniform $S = 1/2$ infinite chain model with eqn. (3) [the Hamiltonian being $\boldsymbol{H} = -2J\Sigma(\boldsymbol{S}_i\cdot\boldsymbol{S}_{i+1})$] derived

$$\chi'_m = \frac{Ng^2\beta^2}{kT}\frac{0.25 + 0.14995X + 0.30094X^2}{1.0 + 1.9862X + 0.68854X^2 + 6.0626X^3} \quad (3)$$

by Bonner and Fisher,[28] when $X = |J|/kT$. Taking into account the possible chain breaking which maybe introduces some unlinked copper ions, the experimental χ_mT [χ_m is the magnetic susceptibility per copper(II) ion] of **2** is actually fitted by eqn. (4) in which x_p is the percentage of paramagnetic ions. The best

$$\chi_m = (1 - x_p)\chi'_m + \frac{Ng^2\beta^2}{4kT}x_p \quad (4)$$

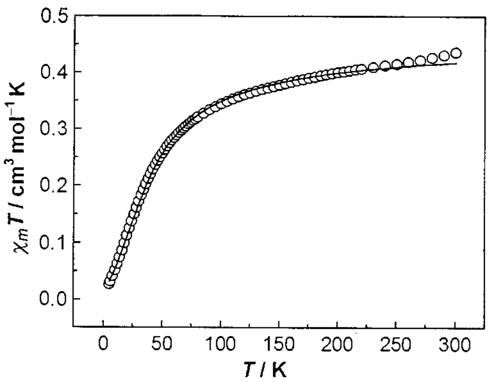

Fig. 6 Experimental (○) and calculated (−) temperature dependence of χ_mT for the one-dimensional $[Cu(atrz)_2(N_3)]NO_3$ **2**.

fit parameters are $J = -17.7(4)$ cm^{-1}, $g = 2.22(1)$, $x_p = 0.026(2)$ and $R = 2.16 \times 10^{-4}$ [$R = \Sigma|(\chi_mT)_{exp} - (\chi_mT)_{calc}|^2/\Sigma(\chi_mT)_{exp}{}^2$] (Fig. 6).

In complex **2** copper atoms are bridged by one end-on azide and two triazole bridges. Exchange interaction through the pathway provided by the large axial bonding [through N(2) and N(9) atoms] can be expected to be not relevant, due to the low unpaired electron density along the d_{z^2} orbital in the octahedral co-ordination around the copper atoms. The main pathway for the exchange interaction proceeds through one of the equatorially co-ordinated triazole ligands, the bridging geometry of this ligand being almost symmetric, with similar Cu–N–N angles (121.0 and 122.3°), but a torsion angle of about −7.77°.

Recently, many polynuclear copper complexes containing triazole bridging ligands have been investigated. The J values in these complexes range from −0.59 cm^{-1} found in $[Cu(hyetrz)_3][ClO_4]_2\cdot3H_2O$ to −118 cm^{-1} found in $[Cu_2(bpt)_2(CF_3SO_3)_2(H_2O)_2]$ [bptH = 3,5-bis(pyridin-2-yl)-1,2,4-triazole].[1] A magneto-structural relationship between the symmetry of two bridging angles and the exchange interaction in triazole bridged dicopper complexes with a planar $Cu(N–N)_2Cu$ framework has been proposed: with one Cu–N–N angle close to 135°, the greater the symmetry of the two bridging angles of triazole (Cu–N$_\alpha$–N$_\beta$), the larger is the J value.[4] For example, the complex $[Cu_2(bpt)_2(CF_3SO_3)_2(H_2O)]$,[1] in which the two bridging angles are all close to 135°, has the largest exchange interaction (−118 cm^{-1}); and $[Cu_2(pt)_2(SO_4)(H_2O)_3]\cdot3H_2O$[4] which has two asymmetric bridging angles (Cu–N1–N2 124.4 and Cu–N2–N1 139.8°) has a J value of −49 cm^{-1}. Although variation of the structure of the complexes may induce a subtle change in J value, this simple correlation seems to apply to other triazole bridged copper complexes, such as **2** and $[Cu(hyetrz)_3][ClO_4]_2\cdot3H_2O$.[8] These two complexes have a chain-like structure and the Cu–N–N angles all deviate from 135°. Complex **2** has two symmetrical bridging angles in its exchange pathway (121.0, 122.3°). The fitted J value for it is −17.7 cm^{-1}. The bridging angles in $[Cu(hyetrz)_3][ClO_4]_2\cdot3H_2O$ are asymmetrical (123.1, 129.9, 124.0, 128.6°) and the exchange interaction is very weak (−0.59 cm^{-1}).

In complex **1** the unpaired electron of each copper(II) ion clearly resides in the ($d_{x^2-y^2}$) orbital, whose electron density is spread over the equatorial ligands, just including the azido and triazole bridges, and exchange interactions along the linear trinuclear molecules would be expected to depend predominantly on these bridges. However the two bridging angles of triazole are smaller than 124° and also have a large asymmetry (119.3 and 123.4°). According to the above analysis, with only this bridging group, there will be very weak antiferromagnetic exchange interaction. It is an interesting question as to what will happen in the presence of both triazole and azido bridges as in complex **1**.

For the end-on azido bridged copper complexes, experimental observation and theoretical analysis show that there is a critical bridging angle(Cu–N–Cu) of about 108.5°. With smaller angles accidental orthogonality of magnetic orbitals will lead to a ferromagnetic interaction between copper atoms, while with larger angles an antiferromagnetic exchange interaction is expected.[27] However, the most common kind of compound shows two azido bridges with M–N–M bond angles in the 100–106° range. More recently Thompson and co-workers[14,15] have obtained a series of binuclear compounds with two simultaneous bridges, one end-on azido bridge and one pyridazine bridge using tetradentate dinucleating diazine ligands, in which, some large Cu–N–Cu angles were observed in the range 98.3–124.1°. Furthermore, they also established a relationship between $2J$ values and Cu–N–Cu angles.[15] In complex **1**, we also found a large Cu–N–Cu angle of 118.7° beyond the critical point. Using Thompson's relationship, the $2J$ value of **1** would be -540 cm^{-1}, much larger than that found by magnetic susceptibility analysis (-217.6 cm^{-1}). Some reasons may be proposed to explain why this difference, such as the electronegative third N atom in triazole which will lower the HOMO relative to that of diazine, and the five-membered ring of triazole may increase the distance between copper ions bridged by it. In fact, in dicopper complexes having two bridges, those of triazole have smaller absolute J values than those of diazine.[29] The other possible factor reducing the antiferromagnetic exchange interaction in complex **1** is the deviation from coplanarity of the triazole and copper basal planes (dihedral angles 17.8 and 18.9° respectively). However, it has been shown in pyrazolate bridged dicopper complexes that the isotropic exchange interaction is rather insensitive to such geometrical distortions. Currently it is difficult to draw a definite conclusion on the difference between diazine/azido and triazole/azido doubly bridged complexes because there are many factors such as the R substituents of the ring to influence on the obtained J values and little structural and magnetic data on the complexes with triazole/azido bridges.

Conclusion

Triazole and azide ligands display abundant structural and magnetic chemistry with transition metal ions. In triazole bridged copper complexes the Cu–N–N bridging angles seem to control the exchange interaction. The larger the bridging angle, the stronger is the exchange interaction; and the more asymmetrical the bridging angles (a large difference in two bridging angles), the weaker is the exchange interaction. This is consistent with the calculation made by Escuer *et al.*[29] showing that the antiferromagnetic component of J reaches its maximum for the parameters M–N–N 135° and N–M–N 90°. In the first example of a copper complex with simultaneous triazole and azido bridges we obtained a bridging azide in end-on mode with a large Cu–N–Cu angle of 118.7°. Such a large angle has been found in Thompson's complexes containing both diazine and azido bridges. However, in comparison to their J values, a relatively weak exchange interaction was found in complex **1** with a large Cu–N–Cu angle.

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