Synthesis, crystal structure, and magnetic properties of two new Cu(II) complexes with end-to-end azido bridging ligands

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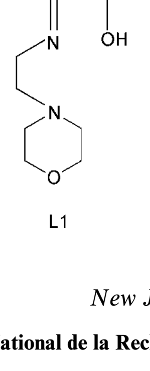
Two new copper(II) complexes, derived from an end-to-end azido linker and two different tridentate Schiff base ligands, have been synthesised and their crystal structures determined by X-ray diffraction methods. They are the single azido-bridged $[Cu(L1-H)(\mu\text{-}1,3\text{-}N_3)]_n(H_2O)_{2n}$ (**1**) chain and the dinuclear $[Cu_2(L2)_2(\mu\text{-}1,3\text{-}N_3)_2(ClO_4)_2]$ (**2**) where L1 and L2 are two different tridentate Schiff bases obtained by condensation of salicylaldehyde with 4-(2-aminoethyl)morpholine and of pyridine-2-aldehyde with *N*,*N*-dimethylpropane-1,3-diamine, respectively. Structural results show that each copper(II) centre in **1** is in a square pyramidal geometry while in **2** the geometry of copper(II) is octahedral with one coordinated perchlorate in both copper(II) complexes. Variable temperature magnetic susceptibility data in the range of 300–2 K for **1** reveal the existence of intrachain weak antiferromagnetic interactions through the end-to-end azido coupler, while the data for **2** show the existence of unusual intradimer ferromagnetic interactions through the end-to-end azido pathway, which almost always leads to an anti-parallel spin orientation. Fitting of the data for **1** using the Bonner–Fisher model for an antiferromagnetically coupled chain of $S = 1/2$ local spins resulted in the parameters $J = -4.3\ \text{cm}^{-1}$, $g = 2.1$ and $R = 4.0 \times 10^{-4}$. Temperature dependent susceptibility data for **2** were fitted using the Bleaney–Bowers expression for a Cu(II) dimer, which led to the parameters $J = +2.4\ \text{cm}^{-1}$, $g = 2.11$ and $\rho = 0.003$.

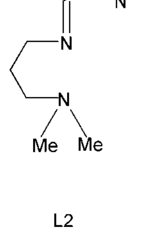
The magnetic study of molecular based magnetic materials has become an area of enchanting interest to physicists, material chemists and inorganic chemists.[1–8] To design magnetic materials, the proper choice of bridging ligand is a major task as it influences the magnetic strength and behaviour by affecting the magnetic pathways between the paramagnetic centres, resulting in low as well as high dimensional materials.

The azido ligand has been extensively used as it is an efficient superexchange pathway between magnetic centres and it displays a huge structural variety, ranging from dinuclear, tetranuclear, cubane, one-dimensional, two-dimensional to three-dimensional compounds.[9–14] This versatile ligand has been widely used to design molecular based magnets because its diverse binding modes lead to variation in magnetic properties that depend on its orientation with respect to the magnetic centres.[15] The flexidentate azido ligand bridges metal centres in two different fashions: one is end-on (μ-1,1) and the other is end-to-end (μ-1,3). In the former mode the magnetism depends largely on the angle it subtends at the two metal centres. Dicopper(II) systems with smaller Cu–N–Cu bond angles ($<108°$) reflect a dominant ferromagnetic interaction while for larger angles ($>108°$) an antiferromagnetic interaction is favoured.[16–20] But in the end-to-end mode, superexchange is almost always antiferromagnetic[21,22] in nature with the exception of only three systems. Of these, two systems based on Ni(II) were reported recently, showing weak ferromagnetic interactions through the 1,3-azido pathway, while the third system, a 1,3-single azido-briged one-dimensional Cu(II) system, has been synthesised recently by our group and shows a ferromagnetic interaction.[23,24]

We in the present paper report the syntheses, crystal structures and low temperature magnetic behaviour of a one-dimensional chain $[Cu(L1-H)(\mu\text{-}1,3\text{-}N_3)]_n(H_2O)_{2n}$ (**1**) and a dinuclear complex $[Cu_2(L2)_2(\mu_2\text{-}1,3\text{-}N_3)_2(ClO_4)_2]$ (**2**) in which L1 and L2 are two different tridentate Schiff base ligands obtained by the condensation of salicylaldehyde with 4-(2-aminoethyl)morpholine and of pyridine-2-aldehyde with *N*,*N*-dimethylpropane-1,3-diamine. A variable temperature magnetic study in the range of 300–2 K reveals the existence of the usual antiferromagnetic interaction through the 1,3-azido pathway in **1** whereas complex **2** shows an unusual ferromagnetic interaction through the 1,3-azido pathway. To the best of our knowledge complex **2** is the first example of a doubly azido-bridged metal complex showing a ferromagnetic interaction through the 1,3-azido pathway because all of the three previously reported 1,3-azido-bridged ferromagnetic complexes are single azido-bridged.[23,24]



L1



L2

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Experimental

Materials and methods

High purity *N*,*N*-dimethylpropane-1,3-diamine and 4-(2-aminoethyl)morpholine were purchased from Fluka and Aldrich Chemical Company Inc., respectively, and were used as received. All other reagents were of analytical grade.

Elemental analyses (C, H, N) were performed using a Perkin–Elmer 240 elemental analyser. IR spectra (4000–600 cm^{-1}) were taken in Nujol and hexachlorobutadiene mulls using a Jasco FT-IR (model 300E). The magnetic susceptibility data were measured on a Quantum Design MPMS-5XL 5T SQUID at 1000 Oe applied field. Diamagnetic corrections were made using Pascal's constants.

Synthesis

Caution! The reported azido and perchlorate complexes are potentially explosive. Only small amounts of the materials should be handled, and with care.

L1 and L2 ligands. The Schiff bases L1 and L2 were prepared by reflux of salicylaldehyde with 4-(2-aminoethyl)morpholine (2 mmol each) and pyridine-2-aldehyde with *N*,*N*-dimethylpropane-1,3-diamine (2 mmol each), respectively, in 15 cm^3 of methanol using literature methods.[25,26]

$[Cu(L1-H)(\mu\text{-}1,3\text{-}N_3)]_n(H_2O)_{2n}$ (1). A methanolic solution (10 cm^3) of copper(II) perchlorate hexahydrate (2 mmol) was added to a hot methanolic solution (10 cm^3) of L1 (2 mmol) and refluxed for 30 min. The deep blue solution obtained was cooled to room temperature and 5 cm^3 of an aqueous solution of sodium azide (2 mmol) was added dropwise with continuous stirring and then filtered. Suitable green single crystals for the structure determination were obtained by slow evaporation of the resulting green solution in air. Yield: 60%. Anal. calc. for $C_{13}H_{21}CuN_5O_4$: C, 41.65; H, 5.60; N, 18.69; found: C, 41.39; H, 5.54; N, 19.01%.

$[Cu_2(L2)_2(\mu\text{-}1,3\text{-}N_3)_2(ClO_4)_2]$ (2). A methanolic solution (10 cm^3) of copper(II) perchlorate hexahydrate (2 mmol) was added to a hot methanolic solution (10 cm^3) of L2 (2 mmol). To the cold blue solution, 5 cm^3 of an aqueous solution of sodium azide (2 mmol) was added dropwise with continuous stirring. Diffraction quality single crystals were obtained after a week by slow evaporation of the resulting dark green solution in a refrigerator. Yield: 55%. Anal. calc. for $C_{11}H_{17}ClCuN_6O_4$: C, 33.33; H, 4.29; N, 21.21; found: C, 33.13; H, 4.36; N, 21.46%.

Crystal data collection and refinement

A suitable single crystal of complex **1** was mounted on an AFC7S diffractometer whereas that of complex **2** was mounted on an Enraf-Nonius CAD4 diffractometer, both equipped with a graphite monochromator and Mo-Kα radiation ($\lambda = 0.7107$ Å). The unit cell parameters and orientation matrix were determined by least squares refinements. Crystal data and refinement details are given in Table 1. Crystal and instrument stabilities were monitored with a set of three standard reflections measured every 100 reflections; in all cases variations were insignificant. The collected intensity data were corrected for Lorentz and polarisation effects and an empirical absorption correction was also employed. The structure was solved by Patterson synthesis and refined through full matrix least squares on F^2 using SHELXL-93[27] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens on the water oxygen atoms [O(3) and O(4)] were located from a difference map and their positional parameters were refined with four SADI restraints for complex **1**. All calculations were carried out using SHELXL-93,[27] SHELXS-97,[28] ZORTEP,[29] PLATON99[30] programs. Selected bond lengths and angles for **1** and **2** are presented in Tables 2 and 3, respectively.

Table 1 Crystal data and structure determination for complexes **1** and **2**. $R = \sum\|F_o| - |F_c\|/\sum|F_o|$; $wR = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

	1	2
Empirical formula	$C_{13}H_{21}CuN_5O_4$	$C_{11}H_{17}ClCuN_6O_4$
FW	374.90	396.30
T/K	293	294
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	9.497(6)	9.0852(10)
b/Å	9.410(2)	16.2398(18)
c/Å	18.232(8)	10.8913(12)
β/°	100.01(3)	96.881(2)
U/Å^3	1604.5(13)	1595.3(3)
Z	4	4
μ/mm^{-1}	1.389	1.565
Reflect. collected	6242	9550
Unique reflect.	5727	3611
Obs. reflect. [$I > 2\sigma(I)$]	2744	2571
R_1 [$I > 2\sigma(I)$]	0.0422	0.0434
wR_2 [$I > 2\sigma(I)$]	0.1857	0.1161
R(int)	0.017	0.030

CCDC reference numbers 167671 and 167672. See http://www.rsc.org/suppdata/nj/b1/b104596m/ for crystallographic data in CIF or other electronic format.

Results and discussion

The IR spectrum of **1** shows two very strong bands, centred at 2062 and 2048 cm^{-1}, assigned to the asymmetric stretching vibrations of the bridging azido while the stretching vibration of the C=N bond of the Schiff base is at 1607 cm^{-1}. Corresponding peaks for **2** appear at 2057, 2046 and 1604 cm^{-1}, respectively; in addition to this a broad peak near 998–1160 cm^{-1} in the IR spectrum of **2** is due to the presence of perchlorate.

Table 2 Selected bond lengths (Å) and bond angles (°) in complex **1**. Symmetry codes: a = 2 − *x*, 1/2 + *y*, 1/2 − *z*; b = 2 − *x*, −1/2 + *y*, 1/2 − *z*

Cu–O(1)	1.920(3)	Cu–N(1)	1.948(3)
Cu–N(2)	2.089(3)	Cu–N(3)	1.960(4)
Cu–N(5a)	2.563(4)	N(3)–N(4)	1.192(5)
N(4)–N(5)	1.154(5)		
O(1)–Cu–N(1)	92.79(14)	O(1)–Cu–N(2)	175.09(13)
O(1)–Cu–N(3)	92.01(17)	O(1)–Cu–N(5a)	95.96(13)
N(1)–Cu–N(2)	84.31(14)	N(1)–Cu–N(3)	168.11(19)
N(1)–Cu–N(5a)	84.77(13)	N(2)–Cu–N(3)	90.11(17)
N(2)–Cu–N(5a)	87.74(12)	N(3)–Cu–N(5a)	105.55(18)
Cu–N(3)–N(4)	129.0(4)	N(3)–N(4)–N(5)	177.6(4)
Cu(b)–N(5)–N(4)	122.6(3)		

Table 3 Selected bond lengths (Å) and bond angles (°) in complex **2**

Cu–O(2)	2.434(3)	Cu–N(1)	2.037(3)
Cu–N(2)	2.015(3)	Cu–N(3)	2.058(3)
Cu–N(4)	1.968(3)	Cl–O(1)	1.420(4)
N(4)–N(5)	1.188(4)	N(5)–N(6)	1.152(4)
O(2)–Cu–N(1)	91.66(12)	C(10)–N(3)–C(11)	108.0(3)
O(2)–Cu–N(2)	92.42(11)	Cu–N(4)–N(5)	123.0(2)
O(2)–Cu–N(3)	97.00(12)	N(4)–N(5)–N(6)	176.7(4)
O(2)–Cu–N(4)	89.99(12)	N(1)–Cu–N(2)	80.59(12)
N(1)–Cu–N(3)	170.70(11)	N(1)–Cu–N(4)	89.81(12)
N(2)–Cu–N(3)	95.60(12)	N(2)–Cu–N(4)	170.17(13)
N(3)–Cu–N(4)	93.56(13)	O(1)–Cl–O(2)	108.4(2)

Structure description

$[Cu(L1-H)(\mu\text{-}1,3\text{-}N_3)]_n(H_2O)_{2n}$ (1). The structure determination reveals that neutral $Cu(L1-H)(N_3)$ units are linked by single end-to-end azide ligands, forming a 1-D infinite chain. The tridentate NNO donor Schiff base ligand acts as a chelating ligand. A ZORTEP drawing of the chain with the atom labeling scheme is shown in Fig. 1. The co-ordination environment of each copper atom is best described by a distorted square pyramidal geometry. Two nitrogen atoms and one oxygen atom of the Schiff base ligand [Cu–N(1), Cu–N(2), Cu–O(1) = 1.948(3), 2.089(3), 1.920(3) Å, respectively] and one nitrogen atom of the bridging azido ligand [Cu–N(3) = 1.960(4) Å] define the basal plane around the Cu atom. The apical site is occupied by a nitrogen atom of another bridging azido ligand and shows a longer bond distance [Cu–N(5a) = 2.563(4) Å, a = $2-x$, $0.5+y$, $0.5-z$]. The average value of the angles N(5a)–Cu–N(basal) is 93.51(14)°, while the *trans*-basal angles are O(1)–Cu–N(2) = 175.09(13) and N(1)–Cu–N(3) = 168.11(19)°. The basal atoms are coplanar with the maximum deviation being 0.056(3) Å for the N(1) atom. The copper atom is displaced 0.128(1) Å from this mean plane. The intrachain minimum Cu···Cu(b) (b = $2-x$, $-0.5+y$, $0.5-z$) distance is 5.638(12) Å. The dihedral angle between the equatorial planes of adjacent copper centres is 17.0(1)°. The bridging Cu–N(3)–N(4) and Cu–N(5a)–N(4a) angles are 129.0(4) and 122.6(3)°, respectively. The azide ligand is almost linear [N(3)–N(4)–N(5) = 177.6(4)°]. The other bond distances and angles are close to the expected values.

$[Cu_2(L2)_2(\mu\text{-}1,3\text{-}N_3)_2(ClO_4)_2]$ (2). In this crystal structure, copper-containing neutral units $[Cu(L2)(N_3)(ClO_4)]$ pair up to form centrosymmetric end-to-end azide-bridged dimers. A view of the dimeric unit of the complex with atom labelling scheme is depicted in Fig. 2. The co-ordination environment around each copper atom may be best described as pseudo-octahedral. The three nitrogen atoms of the L2 ligand and atom N(4) of the azide group are in the equatorial plane and form four short bonds to the copper atom [Cu–N(1), Cu–N(2), Cu–N(3), Cu–N(4) = 2.037(3), 2.015(3), 2.058(3), 1.968(3) Å, respectively]. The nitrogen from a second bridging azide [N(6c), c = $1-x$, $-y$, $2-z$] and a perchlorate oxygen atom occupy the axial positions, forming long bonds to copper [Cu–N(6c), Cu–O(2) = 2.950(5), 2.434(3) Å, respectively] with ∠O(2)–Cu–N(6c) = 163.2(1)°. Such long Cu–N(azide) bonds, ranging from 2.480 to 2.994 Å, are also observed in several systems.[31–43] The angles between the Cu atom and the four atoms of the equatorial plane deviate by 0.2–9.4° from 90°. The co-ordination may be considered as 4 + 1 + 1, as usually found in Jahn–Teller active copper(II) complexes. Deviation of the copper atom from the mean plane formed by the four equatorial atoms is about 0.102(1) Å and the maximum deviation from the mean plane is 0.056(2) Å for the N(1) atom. The intradimer Cu···Cu distance is 5.746(9) Å. In the dimer complex **2**, the adjacent equatorial planes are parallel. The six atoms of the two N_3 bridging ligands are in a plane. The dihedral angle between this plane and the N(4)–Cu–N(6c) plane is 21.7(1)°. This plane and the equatorial plane are orthogonal as the dihedral angle between them is 89.4(1)°. The bridging Cu–N(4)–N(5) and Cu–N(6c)–N(5c) angles are 123.0(2)° and 135.2(4)°, respectively. The azide ligand is almost linear [N(4)–N(5)–N(6) = 176.7(4)°]. The other bond distances and angles are in good agreement with those found in the literature.

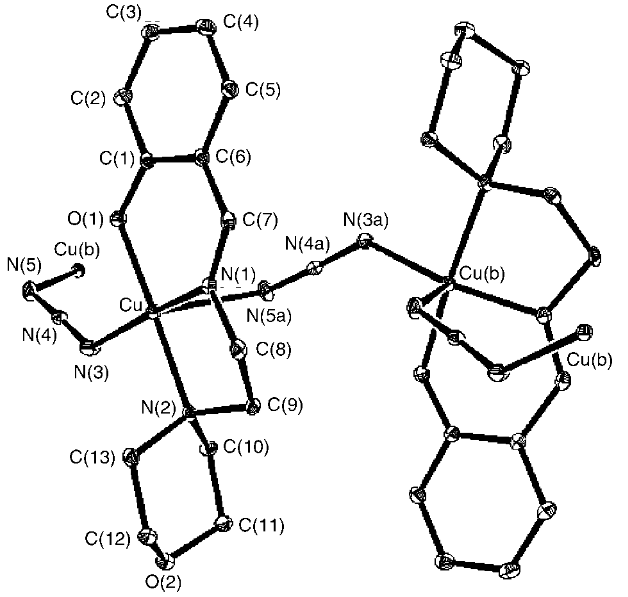

Fig. 1 ORTEP diagram of complex **1** with atom labelling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

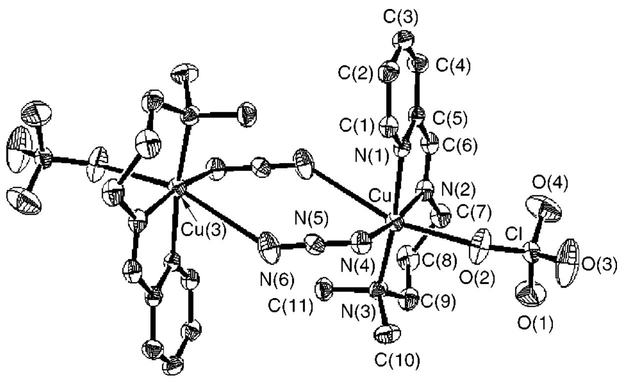

Fig. 2 ORTEP diagram of complex **2** with atom labelling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

Magnetic results

The variable temperature magnetic susceptibility data for complexes **1** and **2** were recorded between 300 and 2 K. Plots of χ_M *vs.* T for **1** and **2** are shown in Fig. 3 and 4, respectively. For complex **1** the molar susceptibility increases steadily with decreasing temperature. The $\chi_M T$ value at room temperature for **1** is 0.46 emu K mol^{-1} and it decreases slowly with decreasing temperature, tending finally to zero at the lowest temperatures. The overall behaviour of **1** corresponds to a weak antiferromagnetically coupled system. We followed two strategies to simulate the experimental data. First, we analysed the Curie–Weiss behaviour of the compound. The

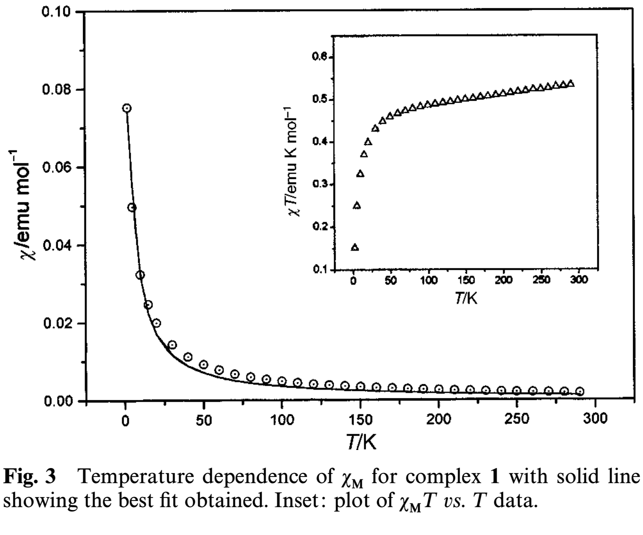

Fig. 3 Temperature dependence of χ_M for complex **1** with solid line showing the best fit obtained. Inset: plot of $\chi_M T$ *vs.* T data.

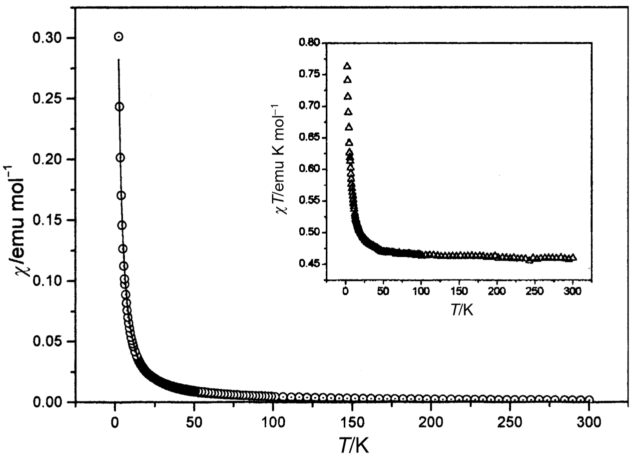

Fig. 4 Temperature dependence of χ_M for complex **2** with solid line showing the best fit obtained. Inset: plot of $\chi_M T$ *vs.* T data.

best fit parameters, $g = 2.29$ and the Weiss constant $\theta = -4.89$ K, correspond to weakly coupled copper(II) ions. On the other hand, taking into account that **1** is a uniformly spaced chain of copper(II) ions linked by single end-to-end azido groups, its magnetic data has been analysed using the Bonner–Fisher expression for antiferromagnetically coupled $S = 1/2$ spins.[44] The Hamiltonian for the isotropic interaction between nearest neighbour ions is $H = -J \sum S_i \cdot S_{i+1}$ and according to Bonner and Fisher[44,45] the molar susceptibility is given by

$$\chi = \frac{Ng^2\beta^2(0.25 + 0.074975x + 0.075235x^2)}{kT(1 + 0.9931x + 0.172135x^2 + 0.757825x^3)},$$

where $x = |J|/kT$ and J is the exchange coupling parameter describing the magnetic interaction between any two nearest neighbour $S = 1/2$ spins. The results of the best fit (Fig. 3) are $J = -4.3$ cm^{-1}, $g = 2.1$ and $R = 4.0 \times 10^{-4}$ (R is the agreement factor defined as $R = \sum[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2$).

For complex **2** the molar susceptibility gradually increases with decreasing temperature from room temperature to 2 K without any maximum in the χ_M *vs.* T plot (Fig. 4). The gradual increase in $\chi_M T$ values with decreasing T signals the existence of a global ferromagnetic interaction in **2**. The susceptibility data for **2** were fitted to the Bleaney–Bowers expression for the magnetic susceptibility[5,6] of isotropically coupled dinuclear $S = 1/2$ ions, derived from the Hamiltonian $H = -JS_1S_2$: $\chi_M = 2\ Ng^2\beta^2(1-\rho)[3 + \exp(-J/kT)]^{-1}/kT + Ng^2\beta^2\rho/2\ kT + N\alpha$. The result of the best fit, shown as the solid lines in Fig. 4, were $J = +2.4$ cm^{-1}, $g = 2.11$ and $\rho = 0.003$ with $R = 1.6 \times 10^{-5}$.

Superexchange mechanism

The end-to-end coordination mode of the azido bridge generally allows for antiferromagnetic coupling as in a large number of Cu(II), Ni(II), Co(II) and Mn(II) systems reported to date.[46,47] The magnitude of this coupling is strongly dependent on several factors such as the bond parameters in the bridging region, but in the case of the Cu(II) derivatives the atomic orbitals of the metallic ion become the most important factor. The coupling may even be strongly antiferromagnetic when the azido ligand is bonded to equatorial co-ordination sites of the two copper atoms, in which case the atomic orbitals involved in the superexchange mechanism are the two $d_{x^2-y^2}$ orbitals. In contrast, very low coupling interactions are expected when the interaction is between axial–equatorial co-ordination sites and the atomic orbitals involved are $d_{x^2-y^2}$ and d_{z^2}, respectively. The different magnetic behaviour is related to the low unpaired electronic density found in the d_{z^2} atomic orbitals in the square pyramidal or octahedrally co-ordinated copper atoms, the consequence of which is a good delocalisation of the unpaired electron from one copper while the delocalisation from the second copper is very poor as the bridging ligand is bonded in an axial position. Classical attempts to relate the magnitude of the superexchange coupling and the structural data for the axial–equatorial case concluded that a larger antiferromagnetic coupling for the trigonal bipyramidal arrangement should be found, in agreement with the greater mixing of the $d_{x^2-y^2}$ and d_{z^2} atomic orbitals.[48]

In our case, the geometry of the copper(II) in complexes **1** and **2** is square pyramidal and octahedral, respectively, and in both cases axial–equatorial bridging is involved, so extremely weak magnetic interactions are expected. The sign of this low interaction may be ferro- or antiferromagnetic, depending on the bond parameters in the bridging region. It has been well-established that for systems in which only the e_g atomic orbitals of the metallic ion are involved, the maximum antiferromagnetic interaction is expected for a M–N–N angle close to 110° and the antiferromagnetic interaction decreases very rapidly when increasing this angle.[47] Accidental orthogonality with a resulting ferromagnetic interaction may be found for large M–N–N bond angles or for torsion angles (τ) close to 45°.[47] In compound **1** the Cu–N–N angles are 129.0(4) and 122.6(3)°, respectively. The antiferromagnetic interaction in **1** is typical for an end-to-end azido pathway, but has a very weak coupling parameter due to the axial–equatorial bridging mode, large Cu–N–N bond angles as well as a long end-to-end coupling pathway. In compound **2** the Cu–N–N angles are 123.0(2) and 135.2(4)°, respectively and the torsion angle is 38.1(1)°, close to 45° where the accidental orthogonality with a resulting ferromagnetic interaction is expected. In this complex too the weak coupling is due to the large deviation of the Cu–N–N angle from 110°, axial–equatorial bridging mode of the azido, as well as a long length superexchange pathway. Thus, the weak but evident ferromagnetic interaction in **2** may be explained on the basis of these arguments.

Conclusion

We presented here the syntheses, single crystal structures and low temperature magnetic behaviour of two new copper(II) complexes **1** and **2** using two different tridentate Schiff base ligands. Compound **1** is a 1-D end-to-end azido-bridged copper(II) chain whereas **2** is a doubly end-to-end azido-bridged copper(II) dimer. Fitting of the temperature dependent susceptibility data for **1** using the Bonner–Fisher model shows the expected weak antiferromagnetic interaction ($J = -4.3$ cm^{-1}, $g = 2.1$ and $R = 4.0 \times 10^{-4}$) while that of **2** using the Bleaney–Bowers equation shows an unusual weak ferromagnetic ($J = +2.4$ cm^{-1}, $g = 2.11$ and $R = 1.6 \times 10^{-5}$) interaction through an end-to-end azido pathway, which usually mediates antiferromagnetic interactions. This unusual magnetic behaviour of **2** has been correlated with its structural parameters.

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