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First observation of a ferromagnetic interaction through an end-to-end azido bridging pathway in a 1D copper(II) system

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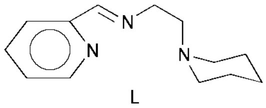
A novel one-dimensional copper(II) compound [Cu(L)($\mu_{1,3}$-N_3)(ClO_4)]$_n$ [L = tridentate Schiff base, formed by condensation of pyridine-2-aldehyde and 1-(2-aminoethyl)-piperidine] has been synthesized and structurally characterized; it exhibits ferromagnetic interaction *via* end-to-end azido ($\mu_{1,3}$-N_3) linkages, as rationalised by DFT calculation.

The investigation of magnetic properties of molecule-based magnetic materials (1D, 2D and 3D) has become a fascinating subject in the fields of condensed matter physics, material chemistry as well as inorganic chemistry.[1] Considerable efforts have been directed in preparing and characterizing molecular systems which can exhibit ferromagnetic properties.[2] Bridging ligands play a central role since they transmit the electronic information between the paramagnetic centres; among these the azido ligand has been proved to be efficient. The versatility of the azido ligand lies in its diverse bridging modes that lead to binuclear,[3a] tetranuclear,[3b] cubane-like,[3c] 1D,[3d] 2D[3e] and 3D[3f] compounds. In general, the coordination modes observed for the bridging azido group are end-to-end (μ-1,3) with antiferromagnetic interaction[4] and end-on (μ-1,1) with ferromagnetic interaction.[3a] However, in copper(II) systems where the azido ligand adopts the end-on mode, antiferromagnetic interaction is observed when the bridging M–N–M angle is $> 108°$.[3d] Ribas and coworkers showed, on the basis of theoretical calculations, that there is also a possibility of ferromagnetic interaction between paramagnetic centres when the azido ligand binds in μ-1,3 fashion.[5] Only one compound based on nickel(II) and displaying the end-to-end azido bridging mode exhibiting a ferromagnetic interaction is reported in the literature.[6] To the best of our knowledge, such a magnetic behaviour in 1D copper(II) systems has not been reported to date. Here we report the synthesis and crystal structure of a new one-dimensional (1D) compound, [Cu(L)($\mu_{1,3}$-N_3)(ClO_4)]$_n$ **1**† and the first observation of ferromagnetic interaction through end-to-end azido bridges in copper(II) systems.



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The IR spectrum of **1** shows two very strong bands assigned to the asymmetric stretching vibrations of N_3 [$\nu_{as}(N_3)$] centred at 2073 and 2050 cm^{-1} and the stretching vibrations of C=N bond of Schiff base [ν(C=N)] at 1603 cm^{-1}.

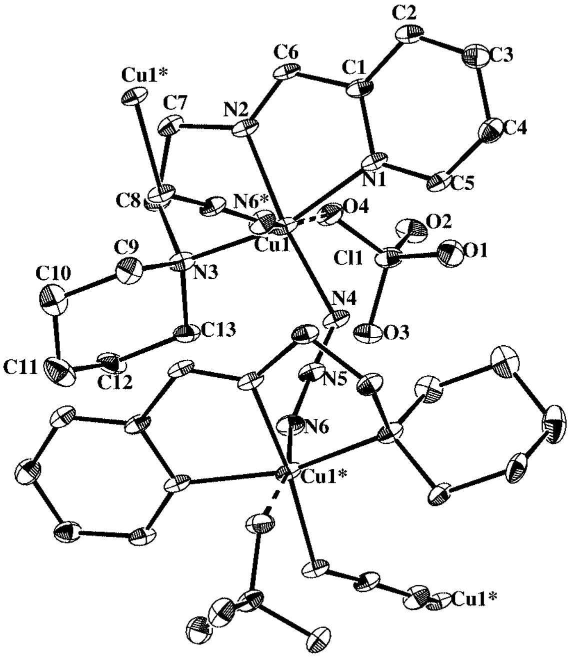

Fig. 1 ZORTEP plot with labelled scheme of [Cu(L)($\mu_{1,3}$-N_3)(ClO_4)]$_n$ **1** (thermal ellipsoids are drawn at 50% probablity). Selected bond lengths (Å) and angles (°): Cu1–N1 2.046(6), Cu1–N2 1.948(6), Cu1–N3 2.080(6), Cu1–N4 1.936(7), Cu1–N6* 2.486(7), Cu1–O4 2.691(7), N4–Cu1–N6*, 88.0(3), N1–Cu1–N4 94.6(3), N1–Cu1–N3 163.2(2), N1–Cu1–N2 80.1(2), Cu1–N4–N5 125.6(5), N4–N5–N6 177.1(8).

The structure determination‡ reveals that the copper atoms are bridged by azido units in an end-to-end fashion with the occurrence of a 1D polymeric infinite chain along the *a*-axis. A ZORTEP view of the asymmetric unit with the symmetry related fragment is shown in Fig. 1. In the chain each copper atom occupies a pseudo octahedral environment with a CuN_5O chromophore. The three nitrogen atoms (N1, N2 and N3) from the tridentate Schiff base ligand and N4 from the bridging azido ligand form the equatorial plane around Cu1 atom. One nitrogen atom (N6*) from another bridging azido ligand and oxygen atom (O4) of the perchlorate anion are in *trans* axial position around Cu1. The equatorial Cu–N bond distances are in the range [1.936(7)–2.080(6) Å]. The deviation of Cu1 from the mean plane formed by the four equatorial nitrogen atoms is *ca.* 0.076(3) Å while the maximum deviation of any equatorial atom (N2) from the mean plane is 0.032(3) Å. The equatorial least squares planes of the two copper atoms are not parallel and form a dihedral angle of 29.4(7)°. For two adjacent copper(II) atoms within the chain (Cu1 and Cu1*), one nitrogen (N4) of the bridging azido is linked to the equatorial base of Cu1 whereas the other nitrogen (N6) of the same azido is linked in an axial fashion to Cu1*. The torsion angle Cu1–N4–N5–N6–Cu1* is 91.6(8)° while the shortest Cu···Cu separation is 5.773(2) Å within the one-dimensional chain and 8.117(3) Å between two adjacent chains.

Magnetic studies were performed using a SQUID magnetometer on a crystalline sample in the temperature range 300–2 K in an applied field of 1 kOe. The $\chi_M T = f(T)$ plot (Fig. 2) indicates the occurrence of a ferromagnetic interaction between the Cu(II)

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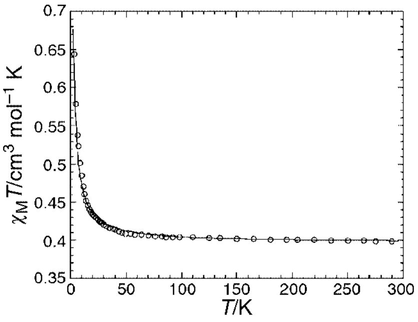

Fig. 2 $\chi_M T$ *vs.* T plot for **1**. The solid line corresponds to the best fit.

ions *via* the end-to-end azido bridge. A fit of the experimental data [where the susceptibility was corrected for TIP (55×10^{-6} cm^3 mol^{-1} per Cu)] was performed using a high-temperature series expansion of the susceptibility;[1a,7] this led to the following parameters: $J = +1.36$ cm^{-1} and $g = 2.06$ with an agreement factor R (defined as $\Sigma[(\chi_M T)_{calc} - (\chi_M T)_{obs}]^2/\Sigma[(\chi_M T)_{obs}]^2$) equal to 10^{-4}. No interchain interaction was included in the fit procedure.

It has already been shown that the different orientations of the equatorial planes (*i.e.* the relative orientations of the $x^2 - y^2$ singly occupied orbitals) of two adjacent Cu atoms are at the origin of the nature and the strength of the magnetic interaction.[8] In order to rationalize the origin of the ferromagnetic interaction, we carried out two types of calculations using the DFT method.[9,12] § The calculation of the exchange parameter within a binuclear unit of the infinite chain leads to a positive J value of +1.6 cm^{-1} indicating that a weak ferromagnetic exchange interaction should be present as observed experimentally. The second calculation was carried out on a mononuclear fragment in order to visualize the magnetic orbital and to try to give a qualitative interpretation of the observed ferromagnetic interaction.[13] It has been found that the magnetic orbital has a contribution from the azido π orbital for the azido nitrogen atom located in the equatorial plane of copper Fig. 3(a)] while a very weak contribution from the σ-like orbital of the azido bridge is found for the nitrogen occupying the axial position as schematized in Fig 3(b). The origin of the ferromagnetic exchange interaction can thus be rationalized as due to the quasi-orthogonality of the magnetic orbitals of the two mononuclear fragments. It is worth noting that the presence of a contribution from the σ orbital of the azido bridge is due to the fact that for a Cu–$\mu_{1,3}$-N3–Cu torsion angle of 91.6(8)° (close to 90°) the Cu–N6–N5 angle [135.7(5)°] is rather large [Fig. 3(b)]. A zero delocalisation should theoretically be observed for a Cu–N6–N5 angle of 90° while it should be maximal for 180°. On the other hand, the fact that the Cu–N4–N5 angle [125.6(5)°] is closer to 90 than to 180° results in a rather large delocalisation of the metal electron density towards the π orbital of the azido bridge. The very weak coupling parameter is mainly due to the unusual axial–equatorial bridging mode of the azido ligand. The consequence is a good π-type delocalisation of the Cu1 electron density towards the bridging azido ligand nitrogen atoms N(4) and N(6), while the apical position of N(6) and the long Cu–N(6) distance results in a rather poor σ-type delocalisation from Cu1*. The overlap density which is mainly localized on N(6) is thus very small leading to a weak exchange coupling parameter.

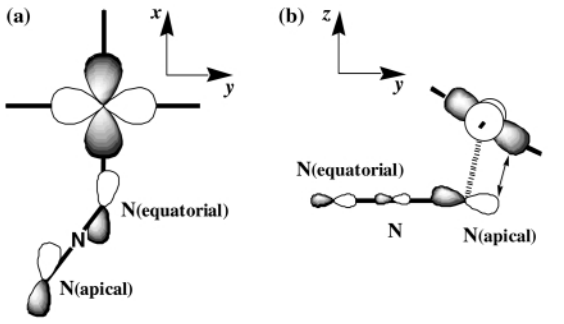

Fig. 3 The magnetic orbital of the copper fragment interacting with (a) the azido nitrogen in the equatorial plane and (b) the azido nitrogen in apical position.

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Notes and references

† **CAUTION**: perchlorate as well as azide salts should be used in small quantities and handled with care since explosion may occur.

A methanolic solution (5 cm³) of 1-(2-aminoethyl)piperidine (1 mmol, 0.128 g) was added to a methanolic solution (20 cm³) of pyridine-2-aldehyde (1 mmol, 0.106 g). The reaction mixture was refluxed for 1 h and evaporated on a water bath until the volume reduced to *ca.* 5 ml to obtain a viscous liquid which was added to the methanolic solution (10 cm³) of $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 0.370 g). The resulting reaction mixture was refluxed for 15 min. To it NaN_3 (1 mmol, 0.065 g) dissolved in methanol (5 cm³) was added and the resulting deep green solution was stirred for 1 h. This was then filtered and the filtrate kept in the open atmosphere. After a few days deep green shiny single crystals suitable for X-ray diffraction were obtained. (Yield 80%). Anal. Found (calc.): C, 36.89 (36.96); H, 4.50 (4.50); N, 19.89 (19.90); Cu, 15.00 (15.05)%.

‡ *Crystal data*: $C_{13}H_{19}ClCuN_6O_4$, $M_w = 422.34$, monoclinic, space group $P2_1/n$ (no. 14), $a = 20.685(4)$, $b = 7.337(2)$, $c = 11.692(2)$ Å, $\beta = 95.730(10)$, $V = 1765.6(7)$ Å^3, $Z = 4$, $D_c = 1.589$ g cm^{-3}, $F(000) = 868$, λ(Mo-Kα) = 0.710 70 Å, μ(Mo-Kα) = 1.420 mm^{-1}, crystal size = $0.10 \times 0.20 \times 0.43$ mm, $T = 296$ K, $\theta_{max} = 27.5°$, total data = 4566, unique data = 4052 (R_{int} 0.028), observed data [$I > 2\sigma(I)$] = 1984, $R = 0.0601$, $wR = 0.0676$, $S = 1.21$. CCDC 156831. See http://www.rsc.org/suppdata/cc/b1/b100529o/ for crystallographic data in .cif or other electronic format.

§ The methodology used to evaluate the coupling exchange constants is described in refs. 9 and 10. Calculations were carried out using the hybrid B3LYP (ref. 11) method as implemented in GAUSSIAN98, with the all-electron double-basis proposed by Ahlrichs, except for the metal atom, where we have used a triple-basis (ref. 12).

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