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Ferromagnetic Ordering in a Two-Dimensional Copper Complex with Dual End-to-End and End-On Azide Bridges[**]

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The construction of multidimensional magnetic materials with ferromagnetic ordering is one of the major challenges in magneto chemistry.[1] Azide-bridged metal complexes have attracted much attention because of the structural diversity of azide compounds and the electronic versatility of the two bridging modes, end-on (EO) and end-to-end (EE), which mediate ferro- and antiferromagnetic exchange interactions, respectively. The dinuclear azide-bridged copper(II) complexes with both kinds of bridging mode were the first to be studied and well-documented,[2] then trinuclear,[3] tetranuclear,[4] one-dimensional (1D) (uniform[5] and alternating[6]), and even alternating two-dimensional (2D)[7] polymeric complexes have also been characterized structurally and magnetically in recent years. Ferromagnetic interactions were found in EO-bridged dinuclear compounds.[2a–d,g,h]The 1D and 2D compounds reported are antiferro-[5a,b, 6a,b,d, 7a] or ferrimagnetic[6c]. Herein, we report the synthesis, structure, and magnetic properties of the ferromagnetically coupled 2D Cu^{II} compound $[\{Cu(L)(N_3)_2\}_n]$ (**1**) (L = benzylamine) (order at $T_c = 7$ K) with both EO and EE bridging modes. Two-dimensional systems that are ordered at low temperatures and contain both azide coordination modes, have only been reported for Mn[8] and Ni[9] compounds, in which the ordering was attributed to canting phenomena. Noteworthy is that 2D Cu^{II}-azide compounds are much rarer than Ni and Mn-azide complexes.

The crystal structure of **1**[10] shows it to be a neutral sheetlike molecule in which each Cu^{II} ion is five-coordinate in the form of a slightly distorted square-based pyramid, CuN_5 (Figure 1). The apical position is occupied by one nitrogen atom N(3A) of the azide bridge in the EE mode (Cu–N apical bond of 2.332 Å) and the equatorial plane is formed by nitrogen atoms from the amine ligand (N(7)), two EO azide bridges (N(4), N(4B)) and a second EE azide bridge (N(1)). The average Cu–N bond length in the basal plane is 2.005 Å. The maximum deviation from the mean plane of N(1)-N(4)-N(4B)-N(7) is 0.017 Å and the copper atom lies 0.236 Å above this plane. Each Cu^{II} center is bonded to another Cu^{II} center by two EO azide bridges, giving an asymmetrical planar entity (Cu(1)-N(4)-Cu(1B)-N(4B)); the EO bridging azides, which are quasi-linear (N(4)-N(5)-N(6), 179.5(5)°), slightly deviate (up and down) from this plane. The two Cu^{II} ions are related by an inversion center. This feature has been found in several dinuclear Cu^{II} complexes in which the Cu^{II} ions are linked by two EO N_3^- ions.[2a,d] In **1** each dinuclear entity is further linked through EE azide bridges to four neighboring dimers, leading to a neutral network (Figure 2). The Cu⋯Cu separation through the EO azide bridges is 3.129 Å, and through the EE bridges is 5.751 Å. The Cu(1)-N(4)-Cu(1B) angle in the EO bridge is 102.0(2)°, which lies in the typical range for this type of bridge. For the EE bridges, the Cu(1)-N(1)-N(2) angle is 121.5(3)° and the Cu(1)-N(3A)-N(2A) is 144.6(3)°.

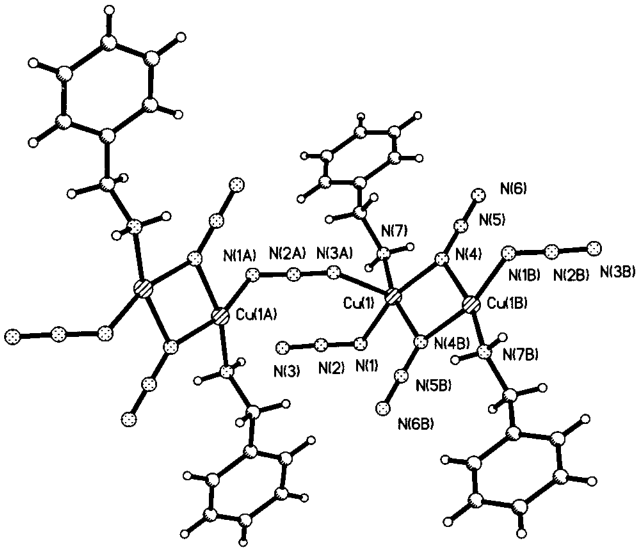

Figure 1. The molecular structure of **1** showing the atom-numbering scheme.

The IR spectrum of **1** shows two sharp bands at 2094 and 2056 cm^{-1}, consistent with the presence of both EO and EE bridging azides.[6a] The X-band EPR spectra recorded at room temperature show a very broad feature centered at $g = 2.067$ and no signal at half-field. The spectra remain almost unchanged on lowering the temperature to 110 K, which

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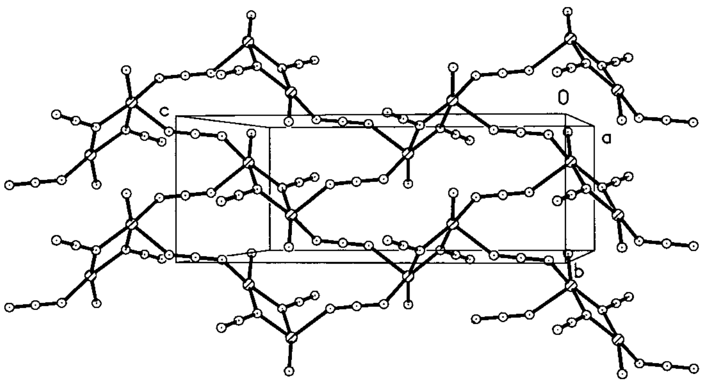

Figure 2. Arrangement of the 2D network of **1** in the *bc* plane (hydrogen and carbon atoms of the amine ligands have been omitted for clarity).

indicates that the square-pyramidal environment of the Cu^{II} ion does not alter to any great extent and the interaction between the Cu^{II} ions is rather weak, in the range of 300–110 K.

The $\chi_M T$ versus T plot of **1** is shown in Figure 3a(χ_M being the molar magnetic susceptibility per two Cu^{II} ions). At room temperature $\chi_M T$ is equal to 1.08 emu mol^{-1} K, which is slightly higher than that expected for two uncoupled Cu^{II} ions. It increases upon cooling and reaches a maximum at 9 K ($\chi_M T = 6.33$ emu mol^{-1} K) and then decreases to 2.06 emu mol^{-1} K at 2 K. No maximum was observed in the χ_M versus T plot. Apparently, short-range ferromagnetic correlation is present in the system, and it develops into a long range ordering state below 9 K. This is evidenced by zero field alternating current (AC) susceptibility shown in Figure 3b, from which $T_c = 7$ K was determined as the maximum of χ'_M. The plot also shows the appearance of nonzero χ''_M. The magnetization at 1.9 K (Figure 4a) increases very rapidly in low field, as expected for a magnet, and reaches 2.07 μ_B at 50 kOe, which corresponds to the theoretical saturation value for two ferromagnetically ordered $S_{Cu(dimer)} = 1$, $g = 2.07$. Furthermore, a characteristic hysteresis loop is observed at 1.9 K with a remanent magnetization (M_r) of 0.41 μ_B and a coercive field (H_c) of 135 Oe (Figure 4b). These results are all indicative of a long-range ordered ferromagnetic ground state. From a magnetic viewpoint, the double EO azide bridges should promote ferromagnetic interaction for angles between 100–105°, while asymmetric EE bridges with short equatorial Cu–N bonds and a long axial Cu–N bond could propagate negligible interaction for square-pyramidal geometry at the copper center.[2a] Thus, ferromagnetic coupling is predominant in compound **1**. To evaluate the super-exchange coupling constants in such a magnetic system we tried to simplify it by treating it as an interacting dimer, μ-(1,1-$N_3)_2Cu_2$, with the exchange through the EE azide bridges as an inter-dimer molecular field[6b] [Eq. (1)]. In this case J is the intra-dimer exchange constant through the double EO bridges, J' is the inter-dimer coupling constant transferred by the single EE azide group and z is 4.

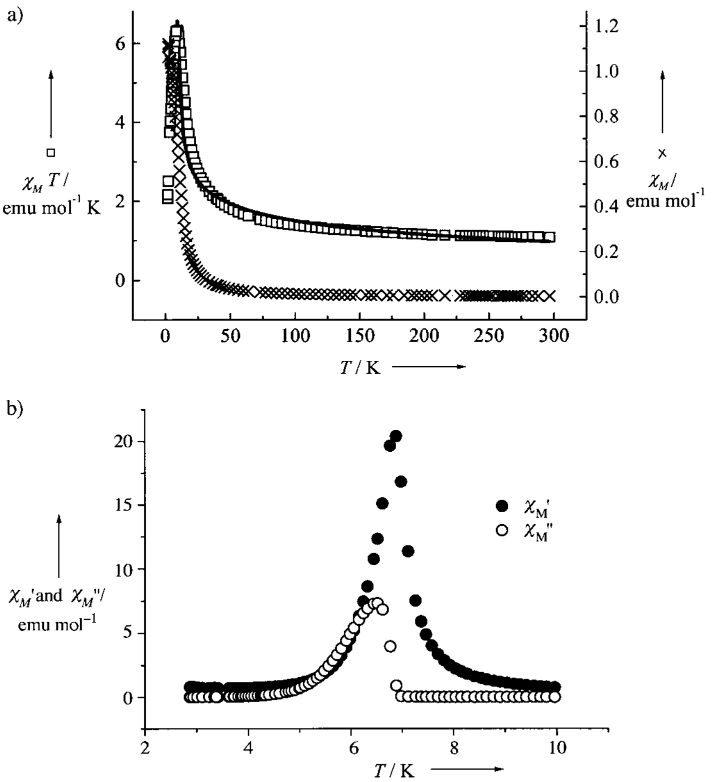

Figure 3. a) Plot of the temperature dependence of $\chi_M T$ (□) and χ_M (×) of **1** measured at 10 kOe field. The solid line corresponds to the best theoretical fit (see text); b) temperature dependence of AC susceptibility obtained at zero external magnetic field, $H_{AC} = 2$ Oe, 111 Hz.

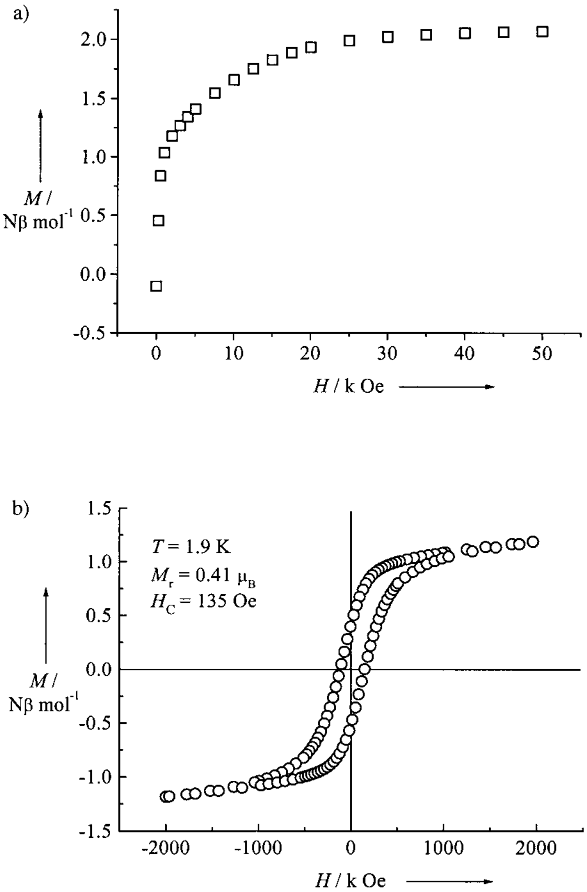

Figure 4. a) Magnetization versus field up to $H = 50$ kOe at 1.9 K for **1**; b) hysteresis loop in the ±2 kOe range at $T = 1.9$ K.

$$\chi_{\mathrm{dimer}} = N g^2 \mu_{\mathrm{B}}^2 S(S+1)\,(1+u)/3\,\mathrm{k}T \qquad (1\,\mathrm{a})$$

$$u = \coth[JS(S+1)/\mathrm{k}T] - \mathrm{k}T/J\,S(S+1) \qquad (1\,\mathrm{b})$$

$$\chi_{\mathrm{M}} = \chi_{\mathrm{dimer}}/[1-\chi_{\mathrm{dimer}}(2\,zJ'/Ng^2\mu_{\mathrm{B}}^2)] \qquad (1\,\mathrm{c})$$

The best fit for $\chi_{\mathrm{M}}T$ versus T in the range of 9–300 K (solid line shown in Figure 3a) leads to the following parameters: $J/k = 71.18$ K, $J'/k = 0.58$ K, $g = 2.07$ and $R = 2.0\times10^{-2}$ ($R = \Sigma[(\chi_{\mathrm{M}})_{\mathrm{obs}} - (\chi_{\mathrm{M}})_{\mathrm{calcd}}]^2/\Sigma[(\chi_{\mathrm{M}})_{\mathrm{obs}}]^2$). The small positive J' value implies that the exchange interaction through the axial asymmetrical EE bridging azide is very weakly ferromagnetic. This is mainly because of the strict orthogonality of σ_x and π_z azide orbitals.[3b] The low temperature magnetic data (2–20 K) measured at different external fields between 200 Oe to 10 kOe indicate that the value of $\chi_{\mathrm{M}}T$ increases greatly with decreasing magnetic field. This result suggest that the presence of field-saturation effects in addition to the possible weak inter-layer antiferromagnetic interaction may cause the decrease of $\chi_{\mathrm{M}}T$ below 9 K.

Very recently, Monfort et al.[11] reported a 2D molecular material with $\mathrm{Ni^{II}}$ centers and azide units that shows metamagnetic behavior. Our work supplies the first 2D metal–azide bridged compounds with long-range ferromagnetic ordering properties. Details of further magnetic measurements can be found in the Supporting Information.

Experimental Section

A solution of $\mathrm{CuCl_2\cdot 6\,H_2O}$ (1 mmol) in methanol (10 mL) was added to a solution of $\mathrm{NaN_3}$ (2 mmol) and the hydrobromide salt of benzylamine (1 mmol) in $\mathrm{H_2O}$ (25 mL). A Black-brown precipitate formed over several minutes. The solid was collected by filtration and washed with methanol and diethyl ether (yield ca. 75%). Elemental analysis calcd for $\mathrm{C_7H_9CuN_7}$ (%): C 32.97, H 3.53, N 38.47, Cu, 24.93; found: C 32.78, H 3.70, N 38.56, Cu 25.00; IR: $\tilde{\nu}_{\max} = 2094$, 2056 $\mathrm{cm^{-1}}$ (ν_{asym} $\mathrm{N_3}$). Black needles suitable for single-crystal X-ray analysis were obtained by slow evaporation of the filtrate in air.

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[10] Crystal data ($\mathrm{C_7H_9CuN_7}$): monoclinic, space group $P2_1/c$; $a = 13.664(1)$, $b = 5.4609(4)$, $c = 14.165(1)$ Å, $\beta = 96.395(1)°$, $V = 1050.38(13)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.611\ \mathrm{g\,cm^{-3}}$, $\mu = 2.058\ \mathrm{mm^{-1}}$, $F(000) = 516$, $\lambda = 0.71073$ Å, $T = 293$ K; 7132 reflections were measured on a Siemens SMART CCD area detector diffractometer and yielded 2586 unique data ($2\Theta_{\max} = 56.62°$, $R_{\mathrm{int}} = 0.0664$, semiempirical absorption corrections). The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXTL. R(on F^2) = 0.0504, ωR(on F^2) = 0.0827, 136 parameters. Largest difference peak/hole 0.751/−0.730 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142222. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Asymmetric Conjugate Addition of Azide to α,β-Unsaturated Carbonyl Compounds Catalyzed by Simple Peptides**

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Stimulated by the efficiency exhibited by enzymes, chemists have sought not only to understand the mechanistic basis for enzymatic reactions, but also to reproduce and even surpass their capabilities. The complementary fields of enzymatic catalysis and transition metal based asymmetric catalysis have recorded many successes in the field of enantioselective reaction development. One question at the interface of these

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