Ferromagnetic Coupling in a One-Dimensional Molecular Railroad Copper(II) Azido Compound Containing a Defective Double Cubane Motif

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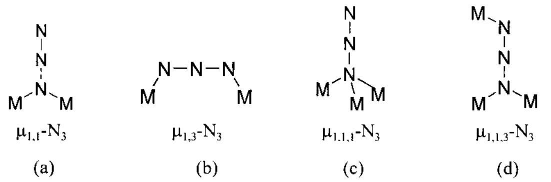
Introduction

During the past 15 years, the amount of work concerning magnetostructural studies of azido-bridged compounds with first-row transition metal ions is really impressive.[1] The two main reasons for this interest are (i) first, the remarkable ability of the azido ligand to transmit large ferro-[2] or antiferromagnetic interactions[3] when adopting the end-on ($\mu_{1,1}$-) (Chart 1a) or end-to-end ($\mu_{1,3}$-) (Chart 1b) bridging modes, and (ii) second, its great versatility as a ligand which affords a great variety of structural types spanning from discrete molecules to three-dimensional compounds.[4] Whereas a great number of compounds containing the two first bridging modes of the azido group in Chart 1 are known, examples of metal ions bridged by the azido ligands with the bridging modes of Chart 1c,d are very rare.

Chart 1



A recent communication by Cortés and Rojo et al. reported on a dicubane-like nickel(II) azido complex exhibiting a ferromagnetic coupling.[5] The structure shows the occurrence of tetrameric nickel(II) units with $\mu_{1,1}$-N$_3$ azido and dpk molecules (dpk = di-2-pyridyl ketone) as bridges. To our knowledge, no cubane-like azido-containing copper(II) complexes are reported to date. In the framework of our research efforts devoted to the magnetostructural studies of the azido-bridged metal compounds, we have prepared the first one-dimensional molecular railroad azido-containing copper(II) compound of formula $[\mathrm{Cu_4(bpm)_2(N_3)_8}]_n$ **1** (bpm = bis(pyrazol-1-yl)methane), which contains the $\mathrm{Cu_4N_6}$ defective double cubane unit. In this work, we present its preparation, X-ray crystal structure determination, and magnetic study. Interestingly, three different coordination modes of the azide group, namely, the $\mu_{1,1}$-, $\mu_{1,1,1}$-, and $\mu_{1,1,3}$-N$_3$ bridging modes, occur in **1** corresponding thus to an unprecedented situation in the Cu(II) chemistry. In addition, the Cu−N(azido)−Cu angles vary in the range 93.80(10)−102.31(9)°, values which lie within the domain where the magnetic coupling for azido-bridged copper(II) compounds is ferromagnetic.[1b]

Experimental Section

Spectral and Magnetic Measurements. Infrared spectra (4000−500 cm^{-1}) were recorded from KBr pellets on a Nicolet 560 FTIR spectrophotometer. Susceptibility measurements were performed on the polycrystalline sample with a Quantum Design instrument with a superconducting quantum interference device (SQUID) detector working in the temperature range 300−1.8 K.

Synthesis. Complex **1** was synthesized by slow diffusion in an H-shaped tube of methanolic solutions of NaN$_3$ (0.130 g, 2 mmol) on one arm, and $\mathrm{Cu(ClO_4)_2 \cdot 6H_2O}$ (0.370 g, 1 mmol) and bpm (0.150 g, 1 mmol) on the other one. Deep green crystals, suitable for X-ray determination, were formed after 3 weeks. IR peaks: 2084s and 2041s cm^{-1} (ν_{as} N$_3^-$) and 1286 cm^{-1} (ν_s N$_3^-$). Anal. Calcd for $\mathrm{C_7H_8Cu_2N_{16}}$: C, 19.0; H, 1.8; N, 50.6; Cu, 28.7. Found: C, 19.1; H, 2.2; N, 50.4; Cu, 28.3.

CAUTION! *Azido complexes of metal ions in the presence of organic ligands are potentially explosive. Only a small amount of material should be handled, and it should be handled with care.*

X-ray Crystallography. The X-ray single-crystal data for complex **1** were collected on a Siemens SMART CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The crystal dimensions were 0.35 × 0.30 × 0.25 mm. The $\omega-2\theta$ scan

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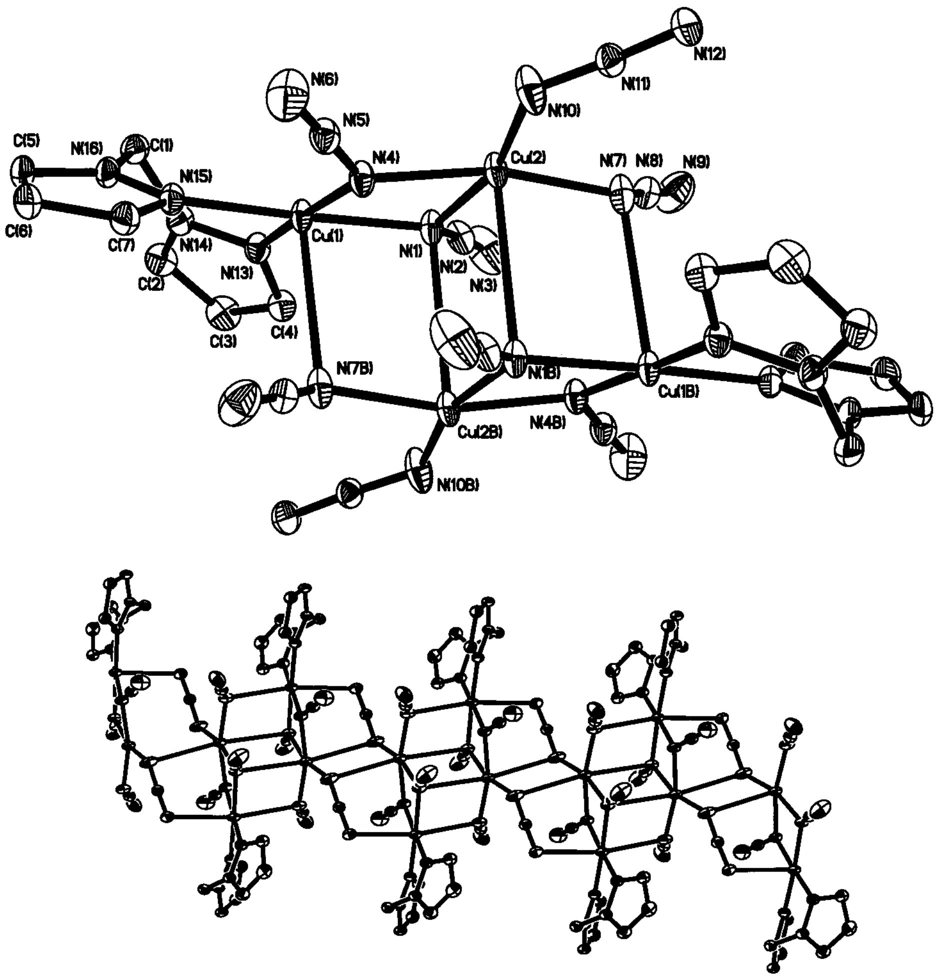

Figure 1. Top: ORTEP drawing of asymmetric unit of $[Cu_4(bpm)_2(N_3)_8]_n$ **1** along with the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted for clarity. Bottom: Perspective view of the railroad copper(II) chain of **1** showing the connection of the defective dicubane-type units.

Table 1. Crystallographic Data and the Structure Determination for $[Cu_4(bpm)_2(N_3)_8]_n$ **1**

chemical formula	$C_7H_8Cu_2N_{14}$
fw	443.37
space group	$P\bar{1}$
a, Å	7.4073(6)
b, Å	9.8470(8)
c, Å	11.9043(10)
α, deg	110.756(2)
β, deg	97.626(1)
γ, deg	103.771(2)
V, Å^3	765.75(11)
Z	2
temp, K	293(2)
λ(Mo Kα), Å	0.71073
ρ_{calcd}, g cm^{-3}	1.923
μ(Mo Kα), mm^{-1}	2.810
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0301, 0.0860
R1,[a] wR2[b] (for all data)	0.0328, 0.0882

[a] $R1(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F_o)^2 = \{\sum[w((F_o)^2 - (F_c)^2)^2]/\sum[w(F_o)^4]\}^{1/2}$.

mode was used for data collection in the range 1.88° $\leq \theta \leq$ 26.37°. A total of 3589 reflections were collected, and 3082 of them were independent ($R_{int} = 0.0141$) and used in the refinement process. Data were integrated by the program SAINT and corrected for absorption using SADABS.[6] The structure was solved by direct methods and successive Fourier difference syntheses using the SHELXL-97 package.[7] The refinement was done through full-matrix least-squares techniques based on F^2, all non-hydrogen atoms being anisotropically refined. The hydrogen atoms were placed at calculated positions and refined isotropically. The number of refined parameters was 259. Maximum and minimum peaks in the final difference Fourier synthesis were 0.460 and −0.426 e Å^{-3}. A summary of the crystallographic data and refinement results of **1** are given in Table 1.

Results and Discussion

Description of the Structure. The structure determination of complex **1** reveals that it is a railroad chain with a defective double cubane repeating unit (Figure 1, top) which is linked by $\mu_{1,1,3}$-azido bridges (Figure 1, bottom). The tetranuclear Cu_4N_6 unit, Cu(1)Cu(2)Cu(1B)Cu(2B)N(1)N(4)N(7)N(1B)N(4B)N(7B), can be viewed as two face-sharing Cu_3N_4 cubane units with one copper site being vacant. There are two crystallographically independent six-coordinated copper(II) ions, Cu(1) and Cu(2), which have elongated octahedral environments built by six nitrogen atoms. The equatorial Cu−N bond distances (values ranging from 1.951(2) to 2.023(2) Å) are significantly shorter than the axial Cu−N ones (values comprised between 2.643(3) and 2.967(2) Å), this trend being as expected in six-coordinated copper(II). The Cu−N−Cu angles varying from 93.80(10)° to 102.31(9)° are close to the characteristic

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_4(bpm)_2(N_3)_8]_n$[a]

Cu(1)−N(1)	2.004(2)	Cu(1)−N(4)	1.989(2)
Cu(1)−N(13)	1.998(2)	Cu(1)−N(15)	1.999(2)
Cu(1)−N(7B)	2.703(2)	Cu(1)−N(12A)	2.643(2)
Cu(2)−N(1)	2.023(2)	Cu(2)−N(4)	2.012(2)
Cu(2)−N(7)	1.951(2)	Cu(2)−N(10)	1.965(2)
Cu(2)−N(1B)	2.868(2)	Cu(2)−N(10A)	2.967(2)
N(1)−N(2)	1.224(3)	N(2)−N(3)	1.131(4)
N(4)−N(5)	1.215(3)	N(5)−N(6)	1.137(4)
N(7)−N(8)	1.209(3)	N(8)−N(9)	1.145(4)
N(10)−N(11)	1.187(3)	N(11)−N(12)	1.147(3)
Cu(1)···Cu(2)	3.116(2)	Cu(1)···Cu(1B)	5.690(2)
Cu(1)···Cu(2B)	3.608(2)	Cu(1)···Cu(2A)	5.436(2)
Cu(2)···Cu(2B)	3.617(2)	Cu(2)···Cu(2A)	3.848(2)

N(4)−Cu(1)−N(13)	174.60(8)	N(4)−Cu(1)−N(15)	95.53(9)
N(13)−Cu(1)−N(15)	89.60(9)	N(1)−Cu(1)−N(4)	77.89(9)
N(1)−Cu(1)−N(13)	96.97(9)	N(1)−Cu(1)−N(15)	173.42(8)
N(7)−Cu(2)−N(10)	94.87(10)	N(7)−Cu(2)−N(4)	165.78(10)
N(10)−Cu(2)−N(4)	90.33(9)	N(7)−Cu(2)−N(1)	99.60(10)
N(10)−Cu(2)−N(1)	164.43(10)	N(4)−Cu(2)−N(1)	76.96(8)
N(2)−N(1)−Cu(1)	127.34(18)	N(2)−N(1)−Cu(2)	127.60(18)
N(5)−N(4)−Cu(1)	127.02(18)	N(5)−N(4)−Cu(2)	125.56(17)
Cu(1)−N(1)−Cu(2)	101.40(9)	Cu(1)−N(4)−Cu(2)	102.31(9)
N(8)−N(7)−Cu(2)	126.0(2)	N(11)−N(10)−Cu(2)	127.2(2)
N(1)−N(2)−N(3)	176.4(3)	N(4)−N(5)−N(6)	178.7(3)
N(7)−N(8)−N(9)	174.7(3)	N(10)−N(11)−N(12)	176.1(3)

[a] Symmetry code: A = $-x - 1, -y, -z + 1$; B = $-x, -y, -z + 1$.

Cu−N−Cu bond angle around 100° for bis($\mu_{1,1}$-N_3)-bridged compounds, indicative of ferromagnetic interactions between the copper centers in agreement with previous magnetostructural data which have been substantiated by DFT-type calculations.[1b] The copper−copper separation wthin the double cubane unit varies between 3.116(2) [Cu(1)···Cu(2) = Cu(1B) = Cu(2B)] and 5.690(2) Å [Cu(1)···Cu(1B)] (see Table 2), whereas the intercubane ones are 3.848(2) [Cu(2)···Cu(2A)] and 5.436(2) Å [Cu(1)···Cu(2A)]. It is emphasized that the coordination preference of the metal ion is crucial for the formation of the novel structure given that a compound with a different structure exhibiting a regular alternation is obtained in the parent Mn(II) species.[8]

Although a good number of azido-bridged copper(II) complexes involving just $\mu_{1,1}$-N_3 and a combination of $\mu_{1,1}$-N_3 and $\mu_{1,3}$-N_3 bridges have been structurally determined,[2a,4a,b,d,9] to our knowledge, complex **1** constitutes the first example containing a Cu_4N_6 dicubane-type motif with two missing vertexes where three different bridging modes of the azido group occur.

Magnetic Properties. Variable-temperature magnetic susceptibility measurements were performed on a polycrystalline sample of **1** under an applied magnetic field of 100 G. The temperature dependence of the $\chi_M T$ product (χ_M is the magnetic susceptibility per two copper(II) ions) is shown in Figure 2. The value of $\chi_M T$ at room temperature is 0.82 cm^3 mol^{-1} K, in agreement with the presence of two noninteracting spin doublets. Upon cooling, $\chi_M T$ continuously increases, reaching a maximum of ca. 0.98 cm^3 mol^{-1} K at 10 K, and further decreases to 0.74 cm^3 mol^{-1} K at 1.8 K. The shape of this curve is typical of a moderate ferromagnetic interaction between two copper(II) ions. The decrease at lower temperatures is due to zero-field splitting effects and/or intermolecular interactions. Looking at the structure shown in Figure 1, it is clear that the ferromagnetic coupling involves the Cu(1)N(1)N(4)Cu(2) unit: the magnetic orbital on each copper atom is located in the equatorial plane defined by the four short equatorial bonds (N(1)N(4)N(13)N(16) and N(1)N(4)N(7)N(10) sets of atoms at Cu(1) and Cu(2), respectively). The interactions between these dimers within the railroad chain structure, which occur through longer axial bonds (Cu(1)−N(1)−Cu(2B), Cu(1)−N(7B)−Cu(2B), Cu(1)−N(12A)−N(11A)−N(10A), Cu(2)−N(10)−Cu(2A), Cu(2)−N(10)−N(11)−N(12)−Cu(1A), and Cu(2)−N(1)−Cu(2B)), must be much weaker given the small spin density on the axial sites and in principle can be discarded. These considerations lead us to fit the magnetic behavior of **1** to a simple Bleaney−Bowers expression (the Hamiltonian used is $\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2$, J being the isotropic exchange coupling parameter). The zero-field splitting of the triplet spin state (D) and a molecular-field correction term (θ) to account for the weak interdimer interactions were introduced in the expression. The best fit parameters are $J = 11.7(1)$ cm^{-1}, $g = 2.07(1)$, $|D| = 2.0(1)$ cm^{-1}, $\theta = -0.40(1)$ K, and $R = 6.0 \times 10^{-6}$ (R is the agreement factor defined as $\sum_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]^2/\sum_i[(\chi_M T)_{obs}(i)]^2$). The theoretical curve matches very well the experimental data as shown in Figure 2. Other fits neglecting either D or θ were significantly worse. The interdimer interactions are very weak as predicted on the basis of the above considerations. The ferromagnetic coupling within the dimeric unit is as expected taking into account that the value of the angle at the end-on azido bridge (ca. 102°) lies within the experimental range (96−104°) for which a ground triplet spin state has been observed.[1b]

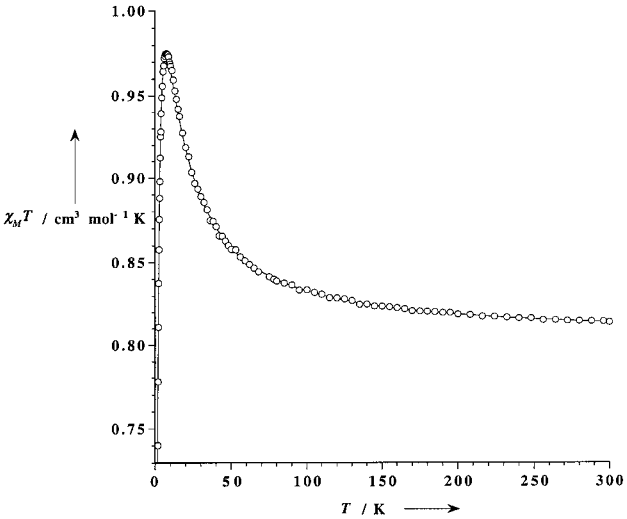

Figure 2. Thermal variation of $\chi_M T$ for $[Cu_4(bpm)_2(N_3)_8]_n$ **1**: (○) experimental data; (−) best fit (see text).

In conclusion, a new one-dimensional molecular railroad copper(II) azido complex containing a defective double cubane motif has been characterized from structural and magnetic points of view. The magnetic properties of **1** reveal a moderate ferromagnetic interaction between the copper(II) ions in agreement with previous studies concerning end-on azido-bridged copper(II) complexes which have been analyzed by DFT-type calculations.[1b] Finally, "cubane-like" systems showing ferromagnetic interactions are playing an important role in the field of molecular magnetism because of the interest in designing high-spin molecules.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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