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Inorganic Chemistry
Note

Ferromagnetic Coupling in a Ladder-Type Copper(II) Complex with Single End-to-End Azido Bridges

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Introduction

The design and synthesis of molecular-based magnetic materials with ferromagnetic coupling is one of the major challenges in magnetochemistry.[1] Azido-bridged complexes have attracted considerable attention due to their structural diversity, which gives rise to a broad range of magnetic couplings. Magnetostructural correlations for azido-bridged complexes have shown that the end-to-end (EE) bridge mode predominantly leads to antiferromagnetic coupling and the end-on (EO) mode to ferromagnetic interaction. A large number of complexes with azido ligands, from dimers to three-dimensional networks, have been structurally and magnetically characterized in recent years.[2–6] However, examples exhibiting ferromagnetic coupling for end-to-end azido-bridged copper(II) complexes are scarce. Here we report a ladder-type copper(II) complex with single end-to-end azido bridges. Magnetic measurements indicate that the exchange coupling between two copper(II) ions through a single end-to-end azido bridge is a ferromagnetic interaction.

Table 1. Crystallographic Data for **1**

empirical formula	$C_{34}H_{24}Cl_2Cu_2N_{12}O_8$
fw	926.63
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	8.6986(10)
b, Å	11.3571(13)
c, Å	19.416(2)
α, deg	97.326(2)
β, deg	99.090(2)
γ, deg	101.251(2)
V, Å^3	1832.7(4)
Z	2
T, K	298(2)
λ(Mo Kα), Å	0.71073
μ(Mo Kα), mm^{-1}	1.377
ρ_{calcd}, g cm^{-3}	1.679
$R_1{}^a$	0.0423
$wR_2{}^b$	0.1180

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = (\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2)^2$; $w = 1/[\sigma^2(F_o{}^2) + (0.0764P)^2 + 0.8720P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Experimental Section

Preparation of $[Cu_2(phen)_2(N_3)_2(4,4'\text{-bipy})](ClO_4)_2$ (1). Single crystals of **1** were grown in a water−methanol (1:1) solution by a slow diffusion method using an H-shaped tube. The starting solution was $Cu(phen)(ClO_4)_2$ (phen = 1,10-phenanthroline) in one arm and a mixture of NaN_3 and 4,4′-bipy (bipy = bipyridine) in the other arm. After a few weeks, two kinds of crystals, dark green $[Cu(phen)(N_3)_2]$[7] (yield 50%) and bright green **1** (yield 30%), were separated. Anal. Calcd for $C_{34}H_{24}N_{12}Cl_2O_8Cu_2$ (**1**): C, 44.07; H, 2.61; N, 18.13. Found: C, 43.72; H, 2.60; N, 17.73.

X-ray Crystallography. A single crystal (0.20 × 0.25 × 0.30 mm^3) of **1** was selected and mounted on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were collected at room temperature to a θ_{max} value of 26.43° with a total of 8615 reflections collected, including 7358 independent reflections (R_{int} = 0.0160). A summary of the crystallographic data is given in Table 1. The structure was solved with direct methods using the SHELXS-97 program.[8] The H atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for **1**

Cu(1)−N(6)	1.955(3)	Cu(1)−N(2)	2.019(2)
Cu(1)−N(1)	2.039(2)	Cu(1)−N(3)	2.347(3)
Cu(1)−N(12A)	2.068(2)	Cu(2)−N(9)	2.023(2)
Cu(2)−N(10)	2.033(3)	Cu(2)−N(8)	2.322(3)
Cu(2)−N(11)	2.038(2)		
N(6)−Cu(1)−N(2)	162.73(12)	N(6)−Cu(1)−N(1)	88.69(11)
N(2)−Cu(1)−N(1)	81.52(10)	N(6)−Cu(1)−N(12A)	90.73(11)
N(2)−Cu(1)−N(12A)	100.57(10)	N(1)−Cu(1)−N(12A)	173.55(10)
N(6)−Cu(1)−N(3)	102.92(14)	N(2)−Cu(1)−N(3)	90.63(11)
N(4)−N(3)−Cu(1)	135.5(2)	N(7)−N(6)−Cu(1)	127.9(2)
N(9)−Cu(2)−N(10)	81.57(10)	N(9)−Cu(2)−N(11)	175.41(10)
N(10)−Cu(2)−N(11)	97.25(10)	N(9)−Cu(2)−N(8)	94.00(10)
N(10)−Cu(2)−N(8)	95.77(10)	N(11)−Cu(2)−N(8)	90.54(10)
N(7)−N(8)−Cu(2)	116.4(2)	N(3)−N(4)−N(5)	175.3(3)
N(8)−N(7)−N(6)	176.7(3)		

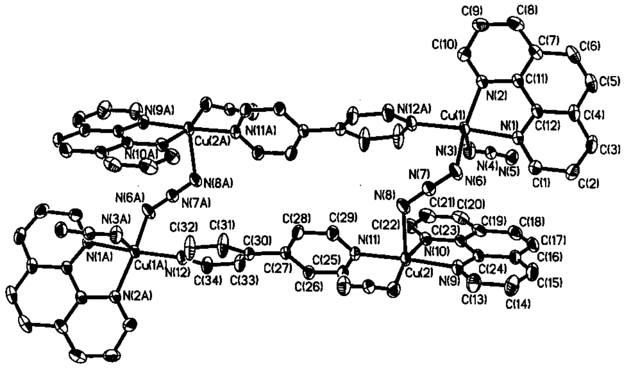

Figure 1. Perspective view of the ladder-type structure of **1** with atom labeling. Thermal ellipsoids at the 30% level are shown, and the perchlorate anions are omitted.

SHELXL-97,[9] and the goodness of fit on F^2 was 1.015. The final agreement factor values are R1 = 0.0423 and wR2 = 0.1180 ($I > 2\sigma(I)$). Selected bond distances and angles are given in Table 2.

Physical Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out on a Model 240 Perkin-Elmer elemental analyzer. Variable-temperature magnetic susceptibilities were measured on an MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms, and the magnetic moments were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}}T)^{1/2}$. Experimental susceptibilities were also corrected for temperature-independent paramagnetism (60×10^{-6} cm^3 mol^{-1} per Cu(II)).

Result and Discussion

Description of the Structure. The molecular structure of **1** and a view of the ladder-type structure in the unit cell are shown in Figures 1 and 2, respectively. The crystal structure consists of infinite ladders (Figure 1). The side pieces of such a ladder are made of [Cu(phen)(N$_3$)]$^+$ units in which copper ions are bridged by single azido ligands in an end-to-end mode, and the rungs are made up of 4,4′-bipy units that bridge two copper atoms belonging to either side piece of the ladder. Each copper atom is in a 4 + 1 distorted-square-pyramidal environment. The apical position is occupied by one nitrogen atom N(3) of the azido bridge (Cu(1)−N(3) = 2.347(3) Å). The equatorial plane is formed by nitrogen atoms from the 4,4′-bipy bridge (N(12A)), the phen terminal ligand (N(1), N(2)), and another azido bridge (N(6)). The Cu−N bond lengths in the basal plane range from 1.955(3) to 2.068(2) Å. The copper atom is displaced by 0.0607 Å below the basal plane. The 4,4′-bipy ligands are not coplanar, the Cu−N$_{\mathrm{bipy}}$ bond distances are inequivalent (2.068(2) and 2.038(2) Å), and the dihedral angle between two pyridyl rings is 24.6°. Each azido ligand links two copper atoms by equatorial−axial positions. The Cu(1)−N(6)−N(7) angle is 127.9(2)°, and the Cu(2)−N(8)−N(7) angle is 116.4(2)°. The azido ligands are quasi-linear; the N(3)−N(4)−N(5) and N(6)−N(7)−N(8) bond angles are 175.3(3) and 176.7(3)°, respectively. The perchlorate anions are disordered and weakly coordinate to the copper atom (Cu(1)−O(8′) = 2.837 Å). The Cu- - -Cu separations are 11.195 Å (via 4,4′-bipy), and 5.467 Å (via the azido bridge).

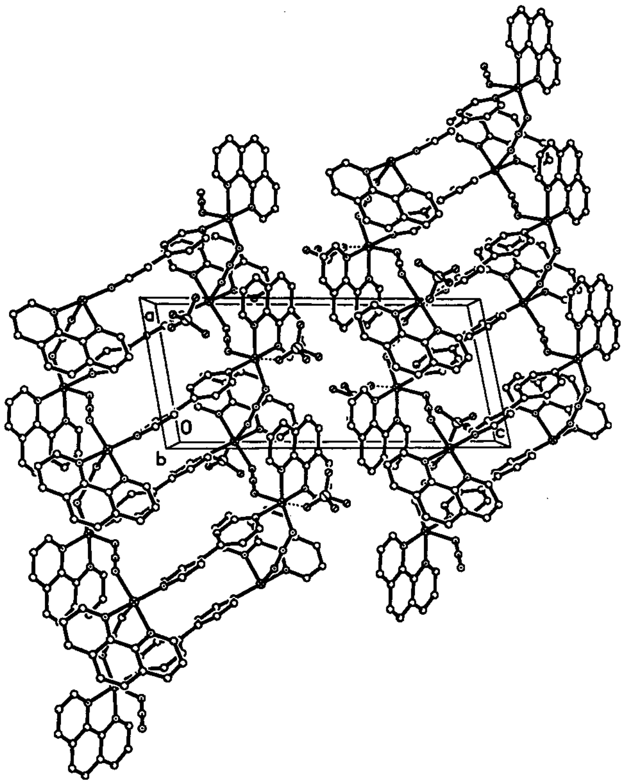

Figure 2. View of the ladder-type structure of **1** in the unit cell.

Magnetic Properties. Variable-temperature magnetic susceptibility measurements were performed on a polycrystalline sample in the range 5−300 K, and the results are shown in Figure 3 in the form of χ_{M} and μ_{eff} vs T plots. At room temperature, the μ_{eff} value is 2.47 μ_{B}, which is close to the spin-only value of 2.45 μ_{B} expected for two uncoupled $S = {}^1/_2$ spin systems. As the temperature is lowered, the μ_{eff} value continuously increases and reaches a value of 3.32 μ_{B} at 5.00 K. Such magnetic behavior is characteristic of a dominant ferromagnetic interaction in complex **1**. For complex **1**, there are two kinds of magnetic interactions, namely (i) copper(II)−copper(II) through the azido bridge and (ii) copper(II)−copper(II) through the 4,4′-bipy bridge. The crystal structure shows that 4,4′-bipy ligand link two copper atoms by equatorial positions and produce an 11.195 Å separation. From a magnetic viewpoint, the exchange coupling through the 4,4′-bipy bridge should be a weakly

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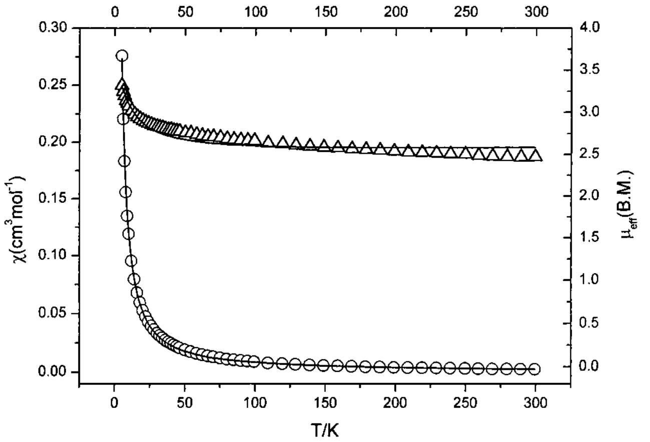

Figure 3. Plots of χ_M (○) and μ_{eff} (△) of complex **1** versus *T*. The solid lines correspond to the best theoretical fits.

antiferromagnetic interaction. Thus, the origin of ferromagnetic coupling is attributed to the magnetic interaction between copper(II) ions through azido bridges. Therefore, the magnetic behavior of **1** can be interpreted as two ferromagnetic chains with a weak antiferromagnetic interaction of interchain (intramolecule). The magnetic susceptibility data were fitted to Baker's expression[10] for an $S = {}^1/_2$ uniformly spaced ferromagnetic chain with a Hamiltonian in the form

$$\hat{H} = -J\sum_{i}^{n-1} \hat{S}_i\hat{S}_{i+1}$$

A molecular field (zJ'),[11] representing a magnetic interaction between copper(II) ions through the 4,4′-bipy ligand, was added to account for the actual nature of the complex.

The best-fit parameters were $g = 2.04$, $J = 5.52$ cm^{-1}, $zJ' = -0.90$ cm^{-1}, and $R = 5.29 \times 10^{-4}$ (R is the agreement factor, defined as $R = \sum[(\mu_{eff})_{obsd} - (\mu_{eff})_{calcd}]^2/\sum[(\mu_{eff})_{obsd}]^2$). The positive *J* valve suggests the presence of a ferromagnetic exchange coupling transmitted by a single end-to-end azido bridge. This is rather unexpected, and the ferromagnetic interaction in this complex can be explained on the basis of symmetry considerations.[12] In complex **1**, the azide group is quasi-linear (N(3)−N(4)−N(5) = 175.3(3)°) and the σ_x and π_z azide orbitals are strictly orthogonal. The unpaired electron of each copper(II) ion in a pyramidal environment is described by the $d_{x^2-y^2}$ type with a very small admixture of d_{z^2}. The σ_x and π_z orbitals of the azide ligand overlap with $d_{x^2-y^2}$ and d_{z^2} orbitals of two bridged copper(II) ions, respectively. Thus, the magnetic orbitals of two adjacent copper(II) ions are strictly orthogonal and a ferromagnetic interaction should be observed.[1] The ferromagnetic coupling is weak, due to ineffective transfer by azido bridges with short Cu−N bonds and a long axial Cu−N bond for square-pyramidal geometry at the copper(II) ion.[2a]

It is well-known that the magnetic coupling is highly sensitive to small structural changes for azido-bridged complexes.[13] The ferromagnetic coupling in **1** also can be understood by another possible mechanism. According to Kahn theory, the exchange coupling constant (*J*) may be expressed as a sum of the negative antiferromagnetic (J_{AF}) and positive ferromagnetic (J_F) contributions. In complex **1**, two adjacent copper(II) ions are bridged by a single azido ligand through equatorial−axial positions and the Cu- - -Cu distances through this kind of bridge are longer, 5.467 Å. Both of them reduce the overlap between the MO's bearing an unpaired electron, which will result in a reduction of the magnitude of J_{AF}. Therefore, the reduced antiferromagnetic interaction of J_{AF} is taken as evidence of ferromagnetic coupling of J_F.[14] The magnetostructural correlation for single end-to-end azido-bridged copper(II) complexes will be the subject of further work.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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