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Notes

The First Structurally Alternating Copper(II) Chain with Alternate Single End-on and End-to-End Azido Bridging: A Synthesis, Crystal Structure, and Low-Temperature Magnetic Study

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Introduction

The μ-azido ligand has been investigated as a very efficient superexchange pathway for propagating magnetic interactions between paramagnetic centers. This versatile ligand has been widely used to design molecular based magnets[1−3] because its diverse binding modes lead to variation in magnetic properties that depend on its orientation with respect to magnetic centers.[4] The structural variety of azido complexes includes dinuclear,[5] tetranuclear,[6]cubane,[7] 1-D,[8] 2-D,[9] and 3-D[10] compounds. In general, the coordination modes observed for the bridging azido group are end-to-end[11−13] with antiferromagnetic interaction and end-on with ferromagnetic interaction.[14−16] Moreover the magnetic properties for end-on bridged metal complexes are also dependent on the M−N−M angle.[17−19,27,28] For the copper(II) system, it is observed that when this angle is less than 108°, the complex shows ferromagnetic property; when it is larger than 108°, the magnetic interaction between the paramagnetic centers is anti-ferromagnetic in nature.

After outstanding research on azido-bridged binuclear transition metal complexes[5] for the last 2 decades, the magnetochemical research is presently concentrated mainly on multinuclear mono- and multidimensional systems. To our knowledge, only five azido-bridged uniform and alternating chains are reported to date for copper(II) and nickel(II) metal ions.[4,20−22] From all the previous reported azido-bridged complexes it is observed that single end-to-end azido bridging mode is quite common,[23] but whenever an azide bridges two metals in end-on fashion, it is always associated with another bridging moiety (type 1)[24]. This shows that only a single azide flanked between two metals in end-on fashion is still lacking. We, in the present paper, first report the synthesis, interesting crystal structure, and low-temperature magnetic properties of a 1-D copper(II) chain $[Cu(L)(\mu\text{-}1,1\text{-}N_3)(\mu\text{-}1,3\text{-}N_3)]_n$ (L = homopiperazine) with alternate single end-on and single end-to-end azido bridging has a new mode of coordination (type 2) and a very high M−N−M bond angle (129.98°) for end-on azido bridging mode; this is very rare because only one example is reported[24b] to date where such a bond angle is larger than 125°. Magnetic measurements indicate that, in agreement with the structural data, the chain shows a regular alternation of two different types of antiferromanetic interactions.

Experimental Section

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

Synthesis. To an aqueous solution of 1 mmol of $Cu(NO_3)_2\cdot3H_2O$

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(where X = N_3^-, HO^-, CH_3COO^- etc.).

was added 2 mmol of NaN_3 dissolved in 10 mL of water. A brown solid appeared which, on treatment with excess NaN_3, transformed into a brown solution. To the solution, 5 mL of an aqueous solution of homopiperazine (1 mmol) was added drop by drop, resulting a deep-green solution. After a few days in a desiccator, suitable single crystals for X-ray determination were obtained from the solution. Anal. Calcd for $C_5H_{12}N_8Cu$: C, 24.2; H, 4.84; N, 45.18. Found: C, 24.4; H, 4.73; N, 45.89. IR: $\nu(N_3)$, 2037, 2048, 2067, 2085 cm^{-1}; ν(N−H), 3330 cm^{-1}.

Spectral and Magnetic Measurements. IR spectra were recorded on a Nicolet 520 FTIR spectrometer. Magnetic measurements were performed on a microcrystalline sample using a SQUID magnetometer operating in the 2−300 K temperature range with an applied field of 5 kOe

Crystal Data Collection and Refinement. A crystal suitable for X-ray analysis was mounted on an Enraf−Nonius CAD4 diffractometer equipped with a graphite monochromator and Cu Kα (λ 1.5418 Å) radiation. The unit cell parameter and orientation matrix were determined by least-squares refinements of the setting angles of 25 reflections (10° < θ < 30°). Crystal and instrument stabilities were monitored with a set of three standard reflections measured over 100 reflections; in all cases, variations were insignificant. The collected intensity data were corrected for Lorentz polarization effect, and an empirical absorption correction was also employed (T_{min}/T_{max} = 0.7325/0.9971). A total of 4053 reflections were measured and 3799 were assumed observed applying the condition $I > 2\sigma(I)$. The structure was solved by Patterson synthesis and refined through full matrix least-squares on F^2 using SHELXL 93 [25] with an anisotropic thermal parameter for all non-hydrogen atoms. Hydrogen atoms were constrained to ride on the respective carbon and nitrogen atoms (C−H, 0.97 Å; N−H, 0.90 Å). The refinement converged to residual indices R1 = 0.0478; wR2 = 0.1278 with $I > 2\sigma(I)$. The final difference Fourier map showed maximum and minimum peak heights of 0.579 and −1.133 e $Å^{-3}$, respectively. All calculations were carried out using SHELXS 97,[25] SHELXL 93,[25] ZORTEP,[25] and PLATON 99 [25] programs. The crystallographic data are given in Table 1.

Results and Discussion

Synthesis. In general, for synthesizing this type of complex, an appropriate amount of NaN_3 is added to the resultant mixture of Cu(II) salt and amine. However, addition of homopiperazine ligand to Cu(II) salt produced a red solid which did not react further with NaN_3. We have overcome this by adding homopiperazine to the brown solution produced on mixing $Cu(NO_3)_2\cdot 3H_2O$ and excess NaN_3.

Table 1. Crystal Data and Details of the Structure Determination for $[Cu(L)(\mu\text{-}1,1\text{-}N_3)(\mu\text{-}1,3\text{-}N_3)]_n$

chemical formula	$C_{10}H_{22}N_{16}Cu_2$	fw	493.54
a (Å)	12.440(2)	space group	$P21/n$ (No. 14)
b (Å)	11.4250(10)	temp (K)	293
c (Å)	13.869(2)	λ (Å) (Cu Kα)	1.54180
α, β, γ (deg)	90, 93.140(10), 90	μ (cm^{-1})	30
V ($Å^3$)	1968.2(5)	ρ_{calc} (g/cm^3)	1.666
Z	4	$R(F_o)$ [a]	0.0478
		$R_w(F_o)$ [b]	0.1278

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

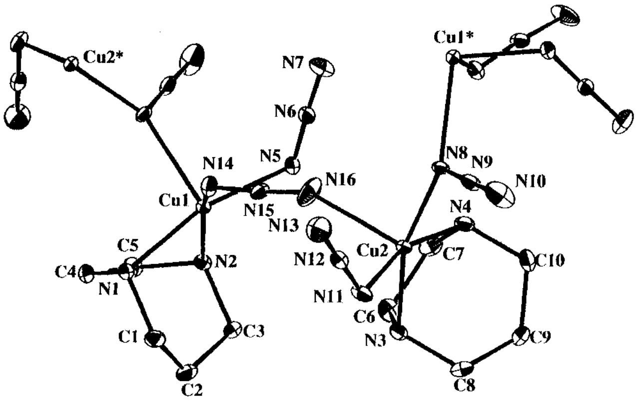

Figure 1. ORTEP diagram of $[Cu(L)(\mu\text{-}1,1\text{-}N_3)(\mu\text{-}1,3\text{-}N_3)]_n$ with atom labeling scheme showing 50% probability thermal ellipsoids for all non-hydrogen atoms.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of $[Cu(L)(\mu\text{-}1,1\text{-}N_3)(\mu\text{-}1,3\text{-}N_3)]_n$

Cu(1)−N(1)	2.005(2)	N(8)−N(9)	1.201(4)
N(9)−N(10)	1.146(5)	Cu(1)−N(2)	2.011(3)
Cu(1)−N(5)	1.991(2)	Cu(1)−N(8)	2.276(3)
Cu(1)−N(14)	2.013(3)	Cu(2)−N(3)	2.020(3)
Cu(2)−N(11)	1.978(3)	Cu(2)−N(8)	2.007(2)
Cu(1)−N(1)	2.005(2)	Cu(1)−N(2)	2.011(3)
Cu(2)−N(4)	2.021(3)	Cu(2)−N16_b	2.295(4)
N(1)−Cu(1)−N(2)	77.79(10)	Cu(1)−N(8)−Cu(2)	129.98(14)
Cu(2)−N(11)−N(12)	118.90(2)	Cu(1)−N(14)−N(15)	122.20(2)
Cu(1)−N(8)−N(9)	113.20(2)	Cu(2)−N(8)−N(9)	115.40(2)
N(3)−Cu(2)−N(4)	77.06(12)	Cu(2)−N(16)−N(15)	151.40(3)
N(1)−Cu(1)−N(5)	164.62(10)	N(1)−Cu(1)−N(8)	98.36(10)
N(1)−Cu(1)−N(14)	91.02(12)	N(2)−Cu(1)−N(5)	92.30(10)
N(2)−Cu(1)−N(14)	158.68(11)	N(5)−Cu(1)−N(8)	95.02(10)
N(5)−Cu(1)−N(14)	94.43(12)	N(4)−Cu(2)−N(8)	91.18(11)

Description of the Structure. The structure determination reveals that the copper atoms are bridged singly and alternately by end-on and end-to-end azido ligands with the occurrence of a 1-D polymeric infinite chain. A ZORTEP drawing of the chain with the atom labeling scheme is shown in Figure 1; selected bond lengths and angles are given in Table 2. Each copper atom possesses distorted square pyramidal geometry. Two nitrogen atoms of the terminal amine ligand (N1, N2), one nitrogen atom (N5) of the pendant azide ligand, and one nitrogen (N14) of the end-to-end bridged azido ligand define the basal plane for the Cu1 atom. The apical position is occupied by one nitrogen atom (N8) of the end-on bridged azido ligand. Similarly, the two nitrogen atoms of the amine (N3, N4), one nitrogen atom (N8) of the azido ligand, and one nitrogen atom (N11) of the pendant azido ligand define the basal plane for Cu2. Here the apical position is occupied by the nitrogen atom (N16) of the

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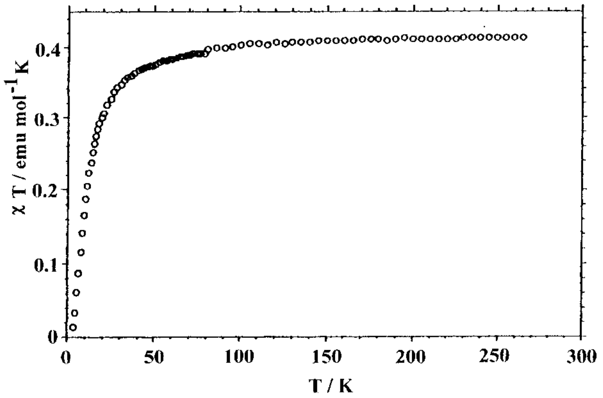

Figure 2. Temperature dependence of $\chi_M T$ for $[Cu(L)(\mu\text{-}1,1\text{-}N_3)(\mu\text{-}1,3\text{-}N_3)]_n$.

end-to-end bridged ligand. It is interesting to note that the N8 atom occupies the apical position for the coordination sphere of Cu1 whereas the same atom belongs to the base of the pyramid for Cu2. Each Cu center is linked to one neighboring Cu center by an azide in end-on fashion and another Cu atom through end-to-end fashion to form the 1-D alternate chain. Deviation of the Cu1 and Cu2 atoms from the mean plane formed by the four basal nitrogen atoms is about 0.28 Å and 0.26 Å, respectively. The basal bond distances around the Cu atoms are very close, in the 1.978(3)−2.021(3) Å range. The apical bond distances are Cu1−N8, 2.276(3) Å and Cu2−N16, 2.295(3) Å. The Cu−N−N angles are Cu1−N14−N15, 122.2(2)° and Cu2−N16−N15, 151.4(3)°. The Cu1−N8−Cu2 angle is 129.98(14)°. The unique single end-on azido bridging mode and very high Cu1−N8−Cu2 bond angle may be a consequence of using an uncommon ligand which produces two different sized rings on coordination to metal.

Magnetic Results. The $\chi_M T$ value (0.413 cm^3 mol^{-1} K) at $T = 270$ K corresponds to that of an isolated Cu(II) ion with a *g*-value of 2.1 (Figure 2). Upon cooling, $\chi_M T$ decreases and reaches a value very close to zero at $T = 2$ K. This behavior indicates an overall antiferromagnetic interaction between the Cu(II) ions within the chain. The presence of two kinds of bridges (1,1-N_3 and 1,3-N_3) is consistent with the presence of two different exchange-coupling parameters within the chain. Two hypotheses are then possible: (i) alternating ferro−antiferromagnetic (F/AF) interactions where the ferromagnetic coupling may be dominant or nondominant and (ii) alternating antiferro−antiferromagnetic (AF/AF) interactions. Since there is no maximum in the $\chi_M T = f(T)$ curve, we can rule out the possibility of a dominant ferromagnetic coupling in the former hypothesis. The fit of the $\chi_M T = f(T)$ data with either of the theoretical laws (F/AF or AF/AF) leads to reasonable results in the high-temperature region but is poor below $T = 30$ K.[26] Nevertheless, the fit at high-temperature allows an accurate *g*-value of 2.125 to be obtained, which was used later. The next step consists of fitting the $\chi_M = f(T)$ data, where the presence of a maximum should lead to a better agreement at low temperature and should allow one of the two hypotheses to be ruled out. The calculated curves for three different (J_{AF}, $\alpha = J_F/|J_{AF}|$) values in the case of a F/AF coupling scheme are made in comparison to the experimental data. No reasonable fit could be reached when considering this hypothesis. The results indicate that the antiferromagnetic coupling parameter J_{AF} has a value close to -12 cm^{-1}. When the theoretical law corresponding to a AF/AF alternating chain is considered, a rather good fit is obtained for $J_{AF} = -11.5$ cm^{-1}, $\alpha = 0.23$, $g = 2.125$, and an agreement factor $R = 10^{-4}$. Only in the AF/AF case can the position of the maximum of the $\chi_M = f(T)$ curve (Figure 3) be properly reproduced.

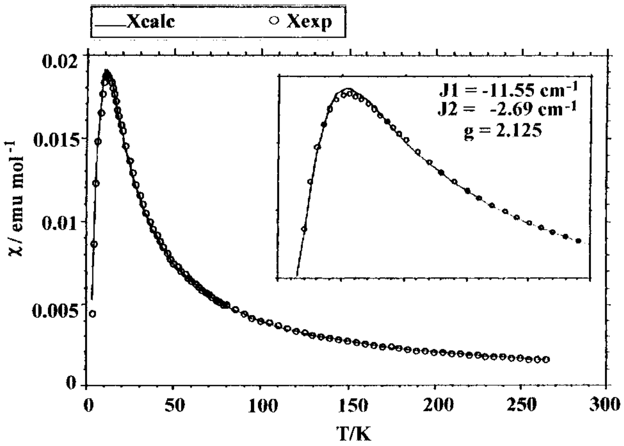

Figure 3. Demonstration of the fact that only in the AF−AF case can the position of the maximum of the χ_M vs T plot be properly reproduced.

Thompson and co-workers have already shown by comparing the magnetic behavior of several complexes that when the azido ligand bridges two Cu(II) ions in an end-on manner, the nature of the exchange coupling changes from ferromagnetic to antiferromagnetic when the Cu−N−Cu angle is around 108°.[19] The interaction is found to be ferromagnetic for lower angle values and antiferromagnetic for higher angle values. This empirical result was confirmed by a density functional study on an end-on azido-bridged Cu(II) binuclear model complex.[27] It was found that the critical Cu−N−Cu angle is equal to 104°. Thus, the end-on bridge angle Cu1−N8−Cu2 [129.98(14)°] produces an antiferromagnetic exchange coupling and is consistent with the derived magnetic results. However, the experimental values of the exchange coupling parameters reported by Thompson et al. are much larger for angles smaller than those found in our compound. For instance, *J* values of -107 and -778 cm^{-1} were found for Cu−N−Cu angles of 108.6(2)° and 124.1(3)°, respectively.[27,28] The origin of the smaller exchange coupling parameters in our compound can be easily accounted for when considering the geometry around the two copper atoms linked by the end-on azido bridge. The magnetic orbital describing the single electron on Cu2 and Cu1 is mainly of an x^2-y^2 type lying in the basal plane of the copper atoms and has only a small contribution on the axis perpendicular to the basal plane. The consequence is a good delocalization of the Cu2 electron density toward the bridging N8 atom, while the delocalization is poor from Cu1 because N8 occupies an apical position with a longer distance. It is worth noting here that polarized neutron diffraction on a binuclear end-on azido-bridged Cu(II) complex where the bridging nitrogen atoms are in the basal plane of the copper atoms has been performed.[28] It shows that the spin density on the nitrogen bridging atom has the same sign as that of the copper atom leading to the conclusions that (i) spin delocalization is important and (ii) spin delocalization predominates spin polarization. The overlap between the Cu1 and Cu2 magnetic orbitals is thus expected to be very weak, leading to a small exchange coupling parameter as observed.

The situation is very similar for the end-to-end bridge apart from the fact that the overlap should be even weaker because the bridging entity has three atoms instead of one in the previous case and because the metal−metal distance is 5.63 Å instead of 3.88 Å for the end-on bridge. So, we can safely assign the exchange coupling parameter values of -11.5 and -2.7 cm^{-1} to the end-on and to the end-to-end bridges, respectively.

Concluding Remarks

Structural characterization of a Cu(II) chain with alternate single end-on and single end-to-end azido bridging has been described. From a magnetic point of view, the chain shows an antiferromagnetic interaction which is in agreement with the previous theory.[27,28] The superexchange values are -11.5 and -2.7 cm^{-1} for end-on and end-to-end mode, respectively. In our opinion, a wide variety of M−N−M angles can be designed by single end-on coordination mode using a suitable terminal amine ligand. Thus, due to flexibility, the design of molecular based magnet will be easier when the azide bridge is present in single end-on fashion, and this mode may open up the new possibility in the field of molecular magnetism.

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Supporting Information Available: X-ray crystallographic data, in CIF format, and tables giving crystal data and details of the structure determination, bond lengths, bond angles, atomic and hydrogen coordinates, equivalent displacement parameters, and anisotropic parameters; also included are two plots of χ_M vs T. This material is available free of charge via the Internet at http://pubs.acs.org.

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