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Unprecedented Low Cu–N(azide)–Cu Angles in End-On Double Azido Bridged Copper(II) Complex

Subratanath Koner,*,† Sandip Saha,† Tallal Mallah,‡ and Ken-Ichi Okamoto§

Department of Chemistry, Jadavpur University, Jadavpur, Calcutta 700 032, India, Université Paris-Sud, Bat. 420, Laboratoire de Chimie Inorganique UMR CNRS, 8613 91405 Orsay, France, and Department of Chemistry, Tsukuba University, Tsukuba, Ibaraki 305-8566, Japan

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A rare asymmetric end-on double azido-bridged copper(II) complex has been synthesized and characterized structurally and magnetically. The Cu–N(azide)–Cu angle in this complex is calculated to be 89.1°. This is unusually low in comparison to the same angle in other end-on azido-bridged binuclear complexes reported so far. Though a strong ferromagnetic interaction between the metal centers is expected in the complex, the coupling has actually been found to be antiferromagnetic, instead.

Investigation into the structural and magnetic properties of the polynuclear transition metal complexes has become a fascinating subject in the field of coordination chemistry, materials chemistry, and condensed matter physics.[1] A lot of complexes having a metal−metal bridge have been synthesized in the past decade.[2] The pseudohalogens are found to be the versatile ligands for making such a bridge.[2a,3] Among them, azide ion is the most efficient ligand as regards the superexchange pathways between paramagnetic centers.[3a,b] The versatility and efficiency of azido ligand lies in its functionality as a bridging bi-, tri-, and tetradentate ligand.[3b] Depending on the steric and electronic requirement of the other coligands present in the complex, the azide can form bridges in end-on ($\mu_{1,1}$) or end-to-end ($\mu_{1,3}$) fashion.[3a] It is well established that the nature of magnetic interaction depends on the mode of coordination between the metal ions and bridging azido group.[3a] In symmetric bibridged end-on azido dimers, the interaction is strongly ferromagnetic[4] while with one or more symmetric end-to-end azido bridges the interaction is strongly antiferromagnetic.[5] Complexes with asymmertic[6] end-to-end azido bridges are usually weakly antiferromagnetic[4b] whereas complexes with asymmetric end-on azido bridges are rare and show a weak to moderately strong ferromagnetic interaction.[7] The studies concerning magneto-structural correlation including theoretical calculations of this type of complexes have been done by several group of researchers.[8−10] Various factors like strict and accidental orthogonality of magnetic orbitals,[8,9] spin polarization,[3a,8] and delocalization of unpaired electrons[8,10] including charge transfer[2e,11] are found to have considerable influence in determining the characteristic of the magnetic coupling between paramagnetic centers. It is noteworthy that all the end-on azido bridged copper(II) dimers reported so far have shown ferromagnetic coupling only.[4,7,12]

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* To whom correspondence should be addressed. E-mail: skoner55@hotmail.com.

† Jadavpur University.

‡ Université Paris-Sud.

§ Tsukuba University.

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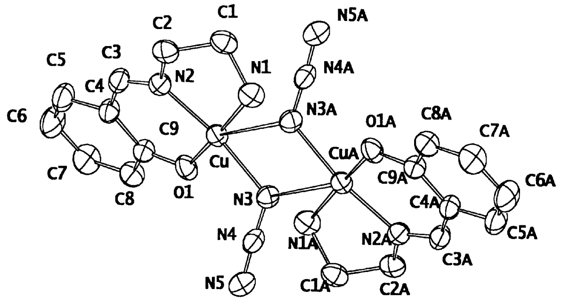

Figure 1. The ORTEP diagram of the complex $[Cu_2L_2(N_3)_2]$ with atom numbering scheme. Intermolecular distances (Å): Cu−O1 1.905(2), N3−N4 1.187(4), Cu−N1 2.019(3), Cu−N2 1.934(3), N2−C3 1.276(4).

We report here the synthesis and structural and magnetic study of a novel asymmetric end-on double azido-bridged copper(II) complex. Among the azido-bridged binuclear metal compounds, the complex reported here is showing, for the first time, unusually low Cu−N(azide)−Cu angles.

To prepare the complex $[Cu_2L_2(N_3)_2]$ (L = 1-(*N*-salicylideneamino)-2-aminoethane), the methanolic solution of ethylenediamine (0.276 mL, 4.6 mmol) was added to a clear solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1 g, 4.14 mmol) dissolved in 25 mL of methanol, which produced immediately an intensely blue solution. The solution was then heated to boiling, and a methanolic solution of salicylaldehyde (0.44 mL, 3.6 mmol) was added dropwise slowly over 2 h in refluxing condition. After the completion of the addition of salicylaldehyde, the reflux was continued for another 45 min. On cooling the mixture, a green slurry was obtained. The resulting green mass was then filtered out, and an excess amount of sodium azide (1 g, 15.4 mmol) dissolved in a minimum volume of water was added to the filtrate. On slow evaporation of the resulting bluish-green solution, the dark green block shaped single crystals of the complex were separated out in 2 days. The crystals were filtered and washed with methanol and dried in air (yield ca. 90%).[13] A dark suitable green block crystal was selected for X-ray data collection. IR spectrum of the complex showed a strong absorption band at 2036 cm^{-1}. This is the characteristic ν_{as} stretching band of coordinated azido ligand. A strong absorption band around 1637 cm^{-1} in the IR spectrum can be assigned to be the band of azomethine group of Schiff base present in the complex. ***Caution!!*** *Azide derivatives are potentially explosive, only a small amount of materials should be prepared, and they should be handled with proper care.*

The complex $[Cu_2L_2(N_3)_2]$ features an azido-bridged Cu(II) dimer complex as shown in Figure 1.[14] The copper(II) ion has a distorted pentacoordinated geometry in which the basal plane is composed of the three nitrogen donor atoms and one oxygen atom. Among them, one nitrogen atom is from the bridging azide anion, and the other two nitrogen atoms are from the Schiff base. The remaining coordinate position is occupied by the phenoxo oxygen of tridentate Schiff base. The fifth coordination site of the square pyramid is occupied by the nitrogen atom of the symmetry related azide group (symmetry; $^1/_2 - x$, $^1/_2 + y$, $-z$) forming the Cu−Cu bridge (Cu−CuA distance = 3.1807(9) Å). The Cu−N3A−CuA (or CuA−N3−Cu) angle is found to be ca. 89.1° in this complex. To our knowledge, this complex is possessing the lowest Cu−N(azide)−Cu angle among the end-on double azido bridged binuclear complexes. It can be noted here that in the case of binuclear triple azido bridged nickel(II) complexes the Ni−N(azide)−Ni angle was found to be ca. 86°.[15] In the equatorial plane, the bond lengths of Cu−N3 (or CuA−N3A) and Cu−N3A (or CuA−N3) are 1.998(3), 2.505(3) Å, respectively. This inequality in bond lengths gives the azido complex a rare variety of asymmetric end-on double-bridged structure. The Cu−N3A bond is showing little longer distance but is not unusual as quite a few end-on azido bridged copper(II) complexes possess Cu−N(azide) bond length of the order of 2.5 Å.[3b,12]

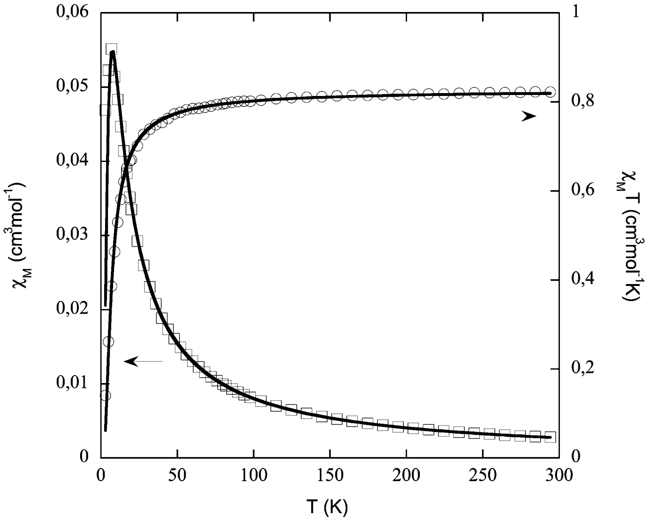

Figure 2. χ_MT product vs T (○) and χ_M vs T (□) under an applied magnetic field of 1.0 T for $[Cu_2L_2(N_3)_2]$. Solid lines represent the best fit of the data with the model described in the text.

The magnetic susceptibility of the complex has been measured in the temperature range 300−3 K.[16] The temperature dependence of χ_M and χ_MT product of the Cu_2 unit is shown in Figure 2. Upon cooling, χ_M increases, reaching a 5.54×10^{-2} cm^3 mol^{-1} maximum around 6 K, and then rapidly decreases with temperature. The χ_MT product at room temperature, 0.82 cm^3 mol^{-1} K, is slightly larger than the

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(13) Anal. Calcd for $C_9H_{11}N_5OCu$: C, 40.2; H, 4.12; N, 26.1. Found: C, 40.1; H, 4.2; N, 25.8%.

(14) Crystal structure analysis: Rigaku AFC7S diffractometer, graphite monochromatized Mo Kα radiation, $\lambda = 0.71069$ Å, 296 K. Lorentz-polarization and absorption corrections (ψ scan). $C_9H_{11}N_5OCu$, monoclinic, space group $P2_1/a$, $a = 14.855(2)$ Å, $b = 12.647(4)$ Å, $c = 5.9688(9)$ Å, $\beta = 98.37(1)°$, $U = 1109.4(4)$ Å^3, $Z = 4$, $D_c = 1.609$ g/cm^3, $F(000) = 548.00$. $\mu = 19.55$ cm^{-1}, crystal dimensions $0.56 \times 0.50 \times 0.34$ mm^3. 2960 reflections were collected of which 2558 were unique ($R_{int} = 0.028$). The refinement was done on the basis of 2558 observed reflections [$I > -10\sigma(I_0)$]. Structure was solved by direct methods (DIRDIF 94)[18] and refined on F^2 by full-matrix least squares to R1 = 0.043 (wR2 = 0.145).

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(16) The magnetic susceptibility of the complex was measured in the 300−3 K temperature range with a Quantum Design MPMS SQUID susceptometer under a 1 T magnetic field. The measured susceptibility was corrected for diamagnetism using Pascal constants and temperature independent paramagnetism (-60×10^{-6} cgs unit).

spin-only value of 0.75 $cm^3\ mol^{-1}$ K expected for two isolated copper(II) ions ($S = {}^1/_2$) assuming $g = 2.00$. As the temperature is lowered, $\chi_M T$ decreases slowly up to ca. 60 K then sharply to 0.14 $cm^3\ mol^{-1}$ K upon cooling to 3 K. This is characteristic magnetic behavior of antiferromagnetic coupling in the dimer. To estimate the magnitude of the antiferromagnetic coupling, the magnetic susceptibility data (300−3 K) were fitted to the modified Bleaney−Bowers equation for two interacting copper(II) ions ($S = {}^1/_2$) with the Hamiltonian in the form $H = -J\,\check{S}_1\cdot\check{S}_2$. The susceptibility equation for such a dimeric system can be written as follows[8a]

$$\chi = \frac{2Ng^2\beta^2}{kT}[3 + \exp(-J/kT)]^{-1}(1 - \rho) + \frac{Ng^2\beta^2}{2kT}\rho \quad (1)$$

where N, g, β, and ρ parameters in the equation bear their usual meaning.

The magnetic data were fitted in two steps. First, the g value was obtained from the high temperature $\chi_M T$ data, and then the $\chi_M = f(T)$ values in the temperature range 300−3 K were fitted leading to the following parameters: $J = -8.5(5)$ cm^{-1}, $g = 2.10(2)$, $\rho = 0.012$, and $R = 2 \times 10^{-4}$ (disagreement factor). Though it is well established that end-on double azido bridged copper(II) dimers are usually ferromagnetic, our measurement indicates that the coupling between two copper(II) ions in this complex is clearly to be antiferromagnetic. This is really unusual for a dimer of this kind.

A closer look into the structure, however, reveals the probable cause for this unusual magnetic behavior. The magnetic orbitals describing the single electron on Cu and CuA are mainly of a $x^2 - y^2$ type extended along the basal plane of the copper ions. The azido group connecting Cu and CuA through an end-on bridge, for example, the N3 atom of N3−N4−N5, belongs to the basal plane of Cu but occupies axial coordination position of square pyramidal geometry of CuA. The situation is the same for another azide group, viz. N3A−N4A−N5A in the dimeric molecular entity. Consequently, the interaction between the Cu and CuA magnetic orbitals is expected to be very weak leading to a small exchange coupling parameter. This type of situation is also observed in an oxalato bridged copper(II) dimer system earlier.[17] Besides, the CuA−N3 distance [2.505(3) Å] is significantly higher than the cutoff distance (2.05 Å) for the interaction being ferromagnetic.[10] Most probably due to these reasons the overall interaction is found to be antiferromagnetic in nature in the complex.

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Supporting Information Available: Further details of structure determination, including tables of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles for the complex $[Cu_2L_2(N_3)_2]$. $\chi_M T$ product and their best fit data of $[Cu_2L_2(N_3)_2]$ at different temperatures (Table 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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