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# Structure of Two Azide Salts of a Copper(II) Macrocycle and Magnetic Properties of Cu(14ane)Cu($N_3$)$_4$

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Synthesis of azide complexes with the copper(II) macrocycle complex Cu(14ane)$^{2+}$ (where 14ane = 1,4,8,11-tetraazacyclothetradecane) has yielded two compounds. Cu(14ane)Cu($N_3$)$_4$ contains $\mu$(1,3)-azido bridged chains of Cu(14ane)$^{2+}$ cations and Cu($N_3$)$_4^{2-}$ anions. Magnetic studies reveal the presence of ferromagnetic interactions within the chains with $J/k = 0.635(4)$ K. [Cu(14ane)$N_3$]$BF_4$ contains [Cu(14ane)$N_3$]$^+$ cations with elongated square pyramidal geometry. The $BF_4^-$ anions are weakly coordinated in the sixth coordination site of the cations.

The design and characterization of low dimensional magnetic systems continues to be an area of scientific interest. A simple strategy to obtain such systems is to couple molecular "bricks" via "mortar" elements, one or both of which may be paramagnetic. One way to implement this strategy is to utilize coordinately unsaturated paramagnetic "bricks" that can be linked together by either diamagnetic or paramagnetic "mortar" units. Examples of the former include the Haldane gap systems, such as [Ni(pn)$_2$($NO_2$)]X or [Ni(14ane)$N_3$]X, where the nitrito or azido groups link planar four-coordinate complexes into chains.[1] Paramagnetic mortar units, such as halometalate ions or TCNQ anions, have been used to form chains and layers with copper(II) macrocycle bricks.[2]

Azido-based systems are interesting since the azide ion can bridge between metal ions either in an end-on (EO) fashion or in an end-to-end (EE) manner.[3,4] Most of the initial systems studied contain bibridged EO configurations, and magnetostructural correlations determined that the coupling is ferromagnetic for bridging Cu−N−Cu angles <108°.[5] More recently, emphasis has been placed on EE bridged systems, particularly monobridged chains. With copper(II) exhibiting its common elongated octahedral or elongated square pyramidal coordination geometry, the EE linkage can occur via two very different routes. In the equatorial−equatorial configuration (ee), where the azido group coordinates via the equatorial bonds to both copper atoms, strong antiferromagnetic coupling can occur since the $\sigma$ orbitals on the azido group couple directly with the unpaired electron density in the $d_{x^2-y^2}$ orbitals.[6] In contrast, if the bridging

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conformation involves an equatorial linkage to one of the copper ions and an axial linkage to the second (ea), the coupling is expected to be weak, since there is little overlap of the azido $\sigma$ and $\pi$ orbitals with the magnetic $d_{x^2-y^2}$ orbital via the axial interaction. De Munno et al. reported the first single EE-ea bridged chain in 1998, in which antiferromagnetic interactions were observed.[7] In 2001, the first examples of ferromagnetic chains containing monobridged EE linkages were reported, follow rapidly by several reports on other systems.[8] Other combinations of EE and EO linkages have been observed, including alternating antiferromagnetic chains, alternating ferro/antiferromagnetic chains, ferromagnetic layers, etc.[9]

In this paper, we report the investigation of two compounds that were obtained in attempts to prepare chain systems based on azido linked copper(II) macrocycle complexes. The macrocycle ligand chosen was 1,4,8,11-tetraazatetradecane (henceforth 14ane). In one case, a novel alternating site chain system containing Cu(14ane)$^{2+}$ cations and Cu(N$_3$)$_4{}^{2-}$ anions is obtained; in the other, the structure contains isolated monomeric species.

Crystals of Cu(14ane)Cu(N$_3$)$_4$ were obtained by slow evaporation of a solution of acetonitrile containing stoichiometric quantities of Cu(NO$_3$)$_2$·$n$H$_2$O, 14ane, and NaN$_3$. Similarly, stoichiometric amounts of Cu(NO$_3$)$_2$·$n$H$_2$O, Cu(BF$_4$)$_2$, 14ane, and NaN$_3$ were dissolved in acetonitrile to prepare the compound [Cu(14ane)N$_3$]BF$_4$. X-ray diffraction data[10,11] were collected at 295 K on a Bruker three-circle platform diffractometer equipped with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) and a CCD detector.[12-14] The structures were solved by the direct method and refined by the least-squares method on $F^2$.[15,16] Figure 1 illustrates the molecular species for Cu(14ane)Cu(N$_3$)$_4$ and the relevant distances and angles are given in the figure caption.

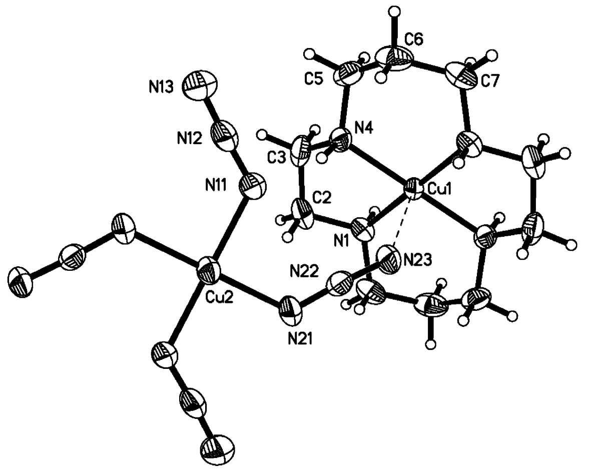

**Figure 1.** Illustration of the molecular units in Cu(14ane)Cu(N$_3$)$_4$. Thermal ellipsoids shown at 50% probability. Relevant structural parameters: Cu1−N1, 2.025(3); Cu1−N4, 2.015(2); Cu2−N11, 1.976(3); Cu2−N21, 1.983(3); Cu1−N13, 2.535(3); N11−N12, 1.198(4); N12−N13, 1.149(4); N21−N22, 1.191(3); N22−N23, 1.157(3) Å; Cu1−N13−N12, 123.5(2); Cu2−N11−N12, 122.8(2); N11−N12−N13, 177.1(3); Cu2−N21−N22, 123.0(2); N21−N22−N23, 176.9(3)°.

Variable temperature susceptibility measurements were carried out on Cu(14ane)Cu(N$_3$)$_4$ in the temperature range 2−300 K at a magnetic field of 0.1 T on ground polycrystalline samples with a SQUID magnetometer (Quantum Design MPMS-XL-5). The susceptibility data were corrected for the diamagnetic contributions of the polyanions as deduced by using Pascal's constant tables. Isothermal magnetization and hysteresis measurements were made at different temperatures, after zero field cooling, between 0 and 9 T. Variable temperature AC susceptibility studies were performed in the SQUID magnetometer with an alternating field of 0.395 mT at different frequencies (between 1 and 332 Hz) in the temperature range 1.8−10 K.

The syntheses yield two compounds; the first contains alternating site chains in which the Cu(14ane)$^{2+}$ bricks are joined by paramagnetic Cu(N$_3$)$_4{}^{2-}$ linkers while the second contains [Cu(14ane)N$_3$]$^+$ monomeric units. Both compounds contain Cu(14ane)$^{2+}$ cations in which the copper(II) ion has a planar coordination geometry. The macrocycle in both cases assumes the low energy trans conformation in which the six-membered rings have a boat conformation and the five membered rings have a twisted conformation. Bond distances and angles within the two cationic species are very similar.

In Cu(14ane)Cu(N$_3$)$_4$ both the Cu(N$_3$)$_4{}^{2-}$ anions and the Cu(14ane)$^{2+}$ cations sit on centers of inversion, so the copper ions lie in the coordination planes. The swastika-shaped anion is nearly planar (the two independent N−Cu−N−N torsion angles are 7.3° and 3.6°). The Cu−N distances are somewhat shorter in the anion (1.980 Å, average) than in the cation

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(10) Crystal data. Cu(14ane)Cu(N$_3$)$_4$: formula, C$_{10}$H$_{24}$Cu$_2$N$_{16}$; fw, 495.53; triclinic, space group $P\bar{1}$; $a$ = 7.674(3) Å, $b$ = 7.703(3) Å, $c$ = 8.476(3) Å, $\alpha$ = 95.746(6)°, $\beta$ = 102.678(5)°, $\gamma$ = 97.648(5)°, $V$ = 480.1(3) Å$^3$, $Z$ = 1, $\rho_{calc}$ = 1.714 Mg/m$^3$, $\mu$ = 2.250 mm$^{-1}$, $T$ = 293 K, independent reflections 1679[$R$(int) = 0.0318], final $R$ indices [$I > 2\sigma(I)$], R$_1$ = 0.0277, wR$_2$ = 0.0550.

(11) Crystal data. [Cu(14ane)N$_3$]BF$_4$: formula, C$_{10}$H$_{20}$BCuF$_4$N$_7$; fw, 388.68; monoclinic, space group $P2_1/n$; $a$ = 8.638(1) Å, $b$ = 13.981 (2) Å, $c$ = 14.089(2) Å, $\beta$ = 99.710(2) °, $V$ = 1677.0(3) Å$^3$, $Z$ = 4, $\rho_{calc}$ = 1.539 Mg/m$^3$, $\mu$ = 1.349 mm$^{-1}$, $T$ = 293 K, independent reflections 2967[R (int) = 0.0248], final $R$ indices [$I > 2\sigma(I)$], R$_1$ = 0.0344, wR$_2$ = 0.1036.

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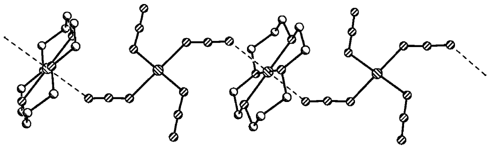

**Figure 2.** Illustration of the chain structure in Cu(14ane)Cu($N_3$)$_4$.

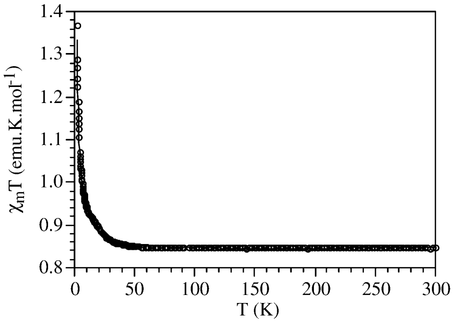

**Figure 3.** Plot of $\chi_M T$ vs $T$ for Cu(14ane)Cu($N_3$)$_4$. The solid line is the calculated curve (see text).

(2.020 Å, average). The Cu−N−N angles in the anion average 122.9°. The semicoordinate bonds formed between Cu1 and the terminal nitrogen atoms (N23) of the anions link the cations and anions together into a one-dimensional system (Cu1−N23 = 2.535 Å, Cu1−N23−N22 = 123.5°), as shown in Figure 2. This semicoordinate Cu···N bond is nearly normal to the coordination plane (6.1°) while the N1−Cu1−N23−N22 torsional angle is quite large at 32.5°. The packing of the chains in Cu(14ane)Cu($N_3$)$_4$ is such that close N···N and N−H···N contacts between chains exist. All of these short contacts involve the nonbridging azide ions. The 14ane N1 atom is found to have interchain contacts of 3.409 and 3.491 Å with N11 and N12, respectively. Somewhat longer $\pi-\pi$ contacts of 3.542 Å (N13−N13) and 3.590 Å (N12−N13) are formed between the nonbridging azide ions.

In [Cu(14ane)$N_3$]$BF_4$, the Cu(14ane)$^{2+}$ complex is coordinated in an end-on fashion by an azide ion, yielding an axially elongated five-coordinate geometry for the copper(II) ion. The Cu−N21 distance is 2.306(3) Å, and the Cu−N21−N22 angle is 124.8(2)°. The copper ion lies 0.156 Å out of the coordination plane defined by the four equatorial N atoms, and the Cu−N21 vector is essentially normal to it (174.8°). The N1−Cu−N21−N22 torsion angle is 25.9°. The $BF_4^-$ ion is tucked in on the back side of the resultant Cu(14ane)$N_3^+$ ion with a Cu−F3 contact distance of 2.886 Å. In addition, a relatively long, nearly linear N−H···F contact is formed with a N4−F4 distance of 2.968 Å and a N4−H4···F4 angle of 153°. These longer contacts tie the cations and anions together into chains running parallel to the *b*-axis.

Figure 3 shows a plot of $\chi_M T$ vs $T$ for Cu(14ane)Cu($N_3$)$_4$. The rapid increase of $\chi_M T$ at low temperature is indicative of ferromagnetic interactions within the material and can reasonably be associated with the Cu−$N_3$−Cu linkages in the chain shown in Figure 2. The small inflection near 15 K, and another anomaly near 3 K, is due to an unknown ferromagnetic impurity since its response is independent of field. The quantity is small enough that it was not possible to identify its source or the actual amount present. The magnetic susceptibility was fitted using a regular ferromagnetic $S = {}^1/_2$ chain model[17] with $x = J/2kT$. The data for the whole temperature range can be fitted quite accurately to the model for a one-dimensional spin ${}^1/_2$ Heisenberg system (solid line, Figure 3) with the parameters $g = 2.108(1)$ and $J/k = 0.635(4)$ K (0.441(3) cm$^{-1}$). Magnetization curves taken at 1.8 K showed no evidence of hysteresis, indicating that no long range order occurred above that temperature.

The properties reported here for Cu(14ane)Cu($N_3$)$_4$ are unique in several ways. Although two previous examples of [Cu($N_3$)$_4$]$^{2-}$ ions have been reported,[18] this is the first example where it functions as a bridging unit in a magnetic system. In addition, this is the first report of a ferromagnetic azido cuprate chain with uniform coupling but with alternating paramagnetic sites. The presence of weak coupling in Cu(14ane)Cu($N_3$)$_4$ is not surprising, given the EE-ea configuration. Relevant structural parameters that have been discussed in the role of the determination of the sign and strength of the coupling[19] include (a) the axial Cu···N distance, (b) the Cu−N−N and Cu···N−N angles, (c) the Cu−$N_3$···Cu torsion angle, and (d) the distortion of the primary Cu coordination geometry away from square planarity. The latter is not a factor in this case, since both copper species are situated on centers of inversion. The Cu···N distance is relatively long in this case (2.535 Å), 0.555 Å more than the equatorial bonds in the [Cu($N_3$)$_4$]$^{2-}$ anion. This should lead to weak coupling. The Cu−N−N and Cu···N−N angles (122.8° and 123.5°, respectively) are relatively small, favoring overlap between the azido $\pi$ orbitals with the copper orbitals. These are in the range normally associated with antiferromagnetic coupling. In contrast, the Cu−$N_3$···Cu torsion angle is 77.6°, which should favor ferromagnetic exchange. A further factor affecting the strength (and possibly sign) of the interaction is the dihedral angles between the in-plane Cu−N bonds and the bonds in the azido group. If this angle is 0° (or, equivalently, 90°, 180°, or 270°), the $\sigma$ and $\pi$ orbitals of the azido groups will have nonzero overlap with the Cu $d_{x^2-y^2}$ orbital. However, if it is 45° (or 135° etc.), the overlap will be zero by symmetry, leading to (weak) ferromagnetic coupling. In our case, this angle is 49.3°. Taking all these factors into account, the observed ferromagnetic coupling is reasonable.

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**Supporting Information Available:** Crystal data for both compounds in CIF format and an illustration of the structure of [Cu(14ane)$N_3$]$BF_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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