

Structure and Magnetic Properties of the Ferromagnetic $\text{Cu}_3\text{Cl}_{12}^{6-}$ Trimer in $[(\text{NH}_3\text{C}_2\text{H}_4)_3\text{NH}]_2\text{Cu}_3\text{Cl}_{14}$

Mingyi Wei and Roger D. Willett*

Department of Chemistry, Washington State University, Pullman, Washington 99164

Carlos J. Gómez-García

Instituto de Ciencia Molecular, Universidad de Valencia, Dr. Moliner 50, 46100 Burjasot, Valencia, Spain

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The crystal structure consists of a strongly hydrogen bonded network of tris(*N*-ethylammonium)ammonium cations, $\text{Cu}_3\text{Cl}_{12}^{6-}$ trimeric species, and Cl^- anions. The $\text{Cu}_3\text{Cl}_{12}^{6-}$ trimers are formed by two distorted tetrahedral CuCl_4^{2-} anions linked to a central square planar CuCl_4^{2-} anion via semicoordinate $\text{Cu}-\text{Cl}\cdots\text{Cu}$ μ_1 bridges. The central copper ion shows only small deviations from ideal D_{4h} symmetry, while the terminal copper ions show a mild distortion from D_{2d} symmetry with an average trans $\text{Cl}-\text{Cu}-\text{Cl}$ angle of 136.0° . The semicoordinate linkages provide a ferromagnetic exchange pathway between the copper ions with $J/k = 6.91(3)$ K. Short $\text{Cl}\cdots\text{Cl}$ contacts (3.67–3.90 Å) lead to very weak antiferromagnetic coupling between the ferromagnetically coupled trimers.

examining the structures of oligomeric and polymeric species.^{1b,4} Here a wide variety of bridging geometries can be observed, involving either the normal $\text{Cu}-\text{X}$ bonds or the elongated semicoordinate $\text{Cu}\cdots\text{X}$ bonds in μ_1 , μ_2 , or μ_3 bridges. Many oligomers are based on stacked arrangements of pseudoplanar $\text{Cu}_n\text{X}_{2n+2}^{2n-}$ anions ($n = 2, 3, \dots, 7, 10$).⁵ Also, a number of isolated nonplanar $(\text{CuX}_3)_n^{n-}$ anions are known ($n = 2, 3$, or 4).⁶ In this communication, we report on a new type of trimeric halocuprate anion with stoichiometry $\text{Cu}_3\text{Cl}_{12}^{6-}$, the first $(\text{CuCl}_4)_n^{2n-}$ oligomeric species reported. We also examine the magnetic coupling within this anion.

Red-orange crystals of $[(\text{NH}_3\text{C}_2\text{H}_4)_3\text{NH}]_2\text{Cu}_3\text{Cl}_{14}$ were initially obtained⁷ as a byproduct in our study of $[(\text{NH}_3\text{C}_2\text{H}_4)_3\text{NH}]_2(\text{CuCl}_6)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$.^{3f} The crystal structure^{8,12} consists of

The structural chemistry of copper(II) halides is exceedingly diverse. Typically, monomeric CuX_4^{2-} species have compressed tetrahedral geometries, with the trans $\text{X}-\text{Cu}-\text{X}$ angles generally in the range 125 – 145° , although square planar ions are also known.¹ A few monomeric CuX_5^{3-} species with either square pyramidal or a folded $4+1$ geometry² are known as well as elongated octahedral CuCl_6^{4-} ions.³ The structural diversity is particularly evident when

* Author to whom correspondence should be addressed. E-mail: rdw@mail.wsu.edu.

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- (7) The compound $(\text{TAEA})_2\text{Cu}_3\text{Cl}_{14}$ was prepared by mixing stoichiometric quantities of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and tris(*N*-ethylamine)amine in sufficient hot dilute (1 M) hydrochloric acid solution to completely dissolve the components. Upon cooling, red-orange crystals of the compound were obtained. Chemical analysis: C 14.41 (14.59%); H 4.68 (4.49%); N 10.96 (11.34%).
- (8) X-ray diffraction data for the structure determination at room temperature were collected with a Syntex $P2_1$ diffractometer, upgraded to Siemens P4 specifications, and equipped with a graphite monochromator.⁹ Data collection parameters and refinement results are given

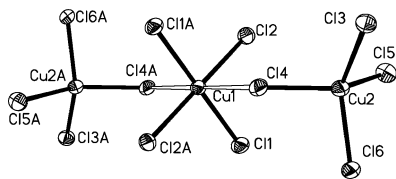


Figure 1. Illustration of the $\text{Cu}_3\text{Cl}_{12}^{6-}$ trimer species. $\text{Cu1}-\text{Cl1} = 2.3146(8)$, $\text{Cu1}-\text{Cl2} = 2.2969(8)$, $\text{Cu1}-\text{Cl4} = 2.931(1)$, $\text{Cu2}-\text{Cl3} = 2.2652(9)$, $\text{Cu2}-\text{Cl4} = 2.245(9)$, $\text{Cu2}-\text{Cl5} = 2.256(1)$, $\text{Cu2}-\text{Cl6} = 2.242(1)$ Å; $\text{Cl1}-\text{Cu1}-\text{Cl2} = 97.97(3)$, $\text{Cu1}-\text{Cl4}-\text{Cu2} = 117.81(4)$, $\text{Cl4}-\text{Cu2}-\text{Cl5} = 138.81(4)$, $\text{Cl3}-\text{Cu2}-\text{Cl6} = 113.15(4)^\circ$.

a strongly hydrogen bonded network involving the tris(*N*-ethylammonium)ammonium cations (henceforth TAEA⁴⁺), trimeric $\text{Cu}_3\text{Cl}_{12}^{6-}$ anionic species (shown in Figure 1) and lattice chloride ions. The strength of the interlocking network of hydrogen bonds is demonstrated by the very small values of room temperature thermal displacement parameters for all atoms in the structure ($U_{\text{iso}}(\text{av}) = 0.026 \text{ \AA}^2$).

The presence of this extensive hydrogen bond network has a second consequence: the stabilization of the highly negatively charged $\text{Cu}_3\text{Cl}_{12}^{6-}$ anions. This species, seen in Figure 1, consists of three CuCl_4^{2-} anions, one with square planar geometry and two with distorted tetrahedral geometry. The central square planar CuCl_4^{2-} anion completes its typical elongated octahedral geometry by the formation of $\mu_1 \text{Cu1} \cdots \text{Cl4}-\text{Cu2}$ linkages to the terminal anions, where the semicoordinate $\text{Cu1} \cdots \text{Cl4}$ distance is $2.932(1)$ Å and the bridging angle is $117.81(4)^\circ$. The plane of the bridging linkage nearly bisects the $\text{Cl1}-\text{Cu1}-\text{Cl2}$ angle, a fact important in the determination of the magnetic properties of the trimer species.

The central NH^+ moiety of the TAEA⁴⁺ cation forms strong hydrogen bonds to a lattice chloride ion, with a $\text{N} \cdots \text{Cl}$ distance of 3.109 Å. In contrast, each terminal NH_3^+ group forms hydrogen bonding interactions with a variety of chloride ions at distances ranging from 3.123 to 3.431 Å. The hydrogen bonding network forces the trimers to lie roughly in a rhombohedral network, as seen in Figure 2. However, relatively short $\text{Cl} \cdots \text{Cl}$ contacts between trimers, ranging from 3.66 to 3.90 Å, exist with four neighboring trimeric species, forming a network lying parallel to the *ac* plane. These contacts can provide for the weak intertrimer exchange coupling observed in the magnetic studies reported below.

Since the crystal structure contains discrete centrosymmetric $\text{Cu}_3\text{Cl}_{12}^{6-}$ trimeric species, the magnetic susceptibility can be modeled, to a first approximation, by the Hamiltonian

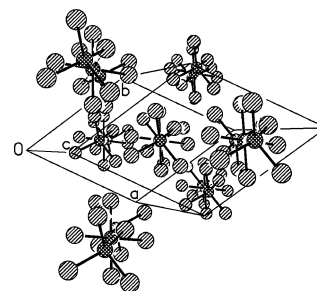


Figure 2. Illustration of the pseudorhomboidal packing of the $\text{Cu}_3\text{Cl}_{12}^{6-}$ trimers.

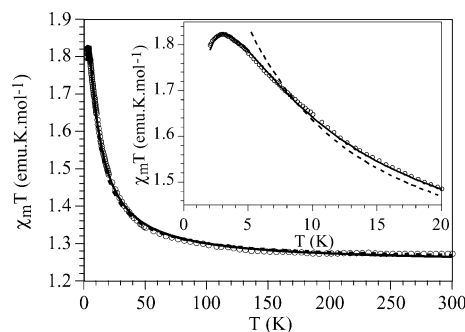


Figure 3. Plot of $\chi_{\text{m}}T$ vs T for $(\text{TAEA})_2\text{Cu}_3\text{Cl}_{14}$. Inset: Low-temperature regime with fit for isolated trimer model (dashed line) and mean field corrected trimer model (solid line).

$$H = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3)$$

This yields the following spin states and energies: $E_{3/2}/k = -J$; $E'_{1/2}/k = 0$; $E_{1/2}/k = 2J$. The magnetic studies¹³ reveal the presence of ferromagnetic coupling within the trimeric anionic species, as seen in the plot of $\chi_{\text{m}}T$ vs T shown in Figure 3. This indicates that the $S = 3/2$ state is the ground state. However, the value of $\chi_{\text{m}}T$ should extrapolate at $T = 0$ K to a value of $C_{3/2}$, the value of the Curie constant for a spin $3/2$ ground state (which should be approximately $2 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for $g = 2.10$). Rather, a turnover of the $\chi_{\text{m}}T$ is observed below 3 K (inset, Figure 3). The data over the whole temperature range (1.8 – 300 K) can be fit very accurately with the model for a ferromagnetic trimer with a mean field correction for the antiferromagnetic intertrimer exchange with $g = 2.1057(6)$, $J/k = 6.91(3)$ K, and $zJ'/k = -0.119(1)$ K. With the observed short $\text{Cl} \cdots \text{Cl}$ contacts to four nearest neighbor trimeric units, z can be taken as 4 , yielding an average intertrimer exchange constant of $J'/k = -0.030$ K. The isothermal magnetization data at 2 K, seen in Figure 4, can be fit accurately with the $S = 3/2$ Brillouin function with a reduced g factor of $1.9717(7)$. This reduced value confirms the presence of the intertrimer AF interactions.

Several tricuprate(II) species involving combinations of CuX_4^{2-} anions and ligand-coordinated Cu(II) ions have been

in the Supporting Information. Structure solutions and refinement were obtained using the SHELXTL package.^{10,11} Hydrogen atoms were included at calculated positions and refined assuming a riding model.

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 (12) Crystal data. $[(\text{NH}_3\text{C}_2\text{H}_4)_3\text{NH}]_2\text{Cu}_3\text{Cl}_{14}$; FW, 987.47; triclinic, space group $P-1$; $a = 10.0721(7)$ Å, $b = 10.0844(10)$ Å, $c = 11.2671(7)$ Å, $\alpha = 64.242(6)^\circ$, $\beta = 65.611(3)^\circ$, $\gamma = 61.971(5)^\circ$, $V = 877.90(12)$ Å³, $Z = 1$, $\rho_{\text{calc}} = 1.868 \text{ Mg/m}^3$, $\mu = 2.888 \text{ mm}^{-1}$, $T = 293$ K, independent reflections $2904[R(\text{int}) = 0.0257]$, final R indices $[I > 2\sigma(I)]$, $R_1 = 0.0291$, $wR_2 = 0.0710$.

- (13) Variable temperature susceptibility measurements were carried out 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 as deduced by using Pascal's constant tables and for the sample holders. Isothermal magnetization measurements were made at different temperatures, after zero field cooling, between 0 and 5 T.

Table 1. Structural Parameters for the $\text{Cu}_a\cdots\text{X}-\text{Cu}_b$ Linkages

compound ^a	$\text{Cu}\cdots\text{X}$ (Å)	$\text{Cu}\cdots\text{X}-\text{Cu}$ (deg)	τ (deg)	τ' (deg)	J/k (K)	ref
$(\text{TAEA})_2\text{Cu}_3\text{Cl}_{14}$	2.932	117.8	41.8	50.3	6.91	this work
$(\text{TEA})_2[\text{Cu}(\text{TIM})](\text{CuBr}_4)_2$	2.965	116.4	38.4	41.9	17.6	6
$(\text{TEA})_2[\text{Cu}(\text{TIM})](\text{CuCl}_4)_2$	2.867	118.7	50.4	30.3	20.7	6
$(\text{TMA})_2[\text{Cu}(\text{TIM})](\text{CuBr}_4)_2$	2.974	113.6	47.0	35.0	3.3	6
$(\text{TMA})_2[\text{Cu}(\text{TIM})](\text{CuCl}_4)_2$	2.856	115.2	44.2	37.8	6.9	6
$\text{Cu}(\text{TIM})\text{CuCl}_4$	2.676	115.8	41.3	57.3	13.3	7
	3.164	122.0	94.5	14.8	-2.6	

^a TEA = tetraethylammonium, TMA = tetramethylammonium, TIM = 2,3,9,10-tetramethyl-1,3,8,10-tetraenecyclo-1,4,8,11-tetraazatetradecane.

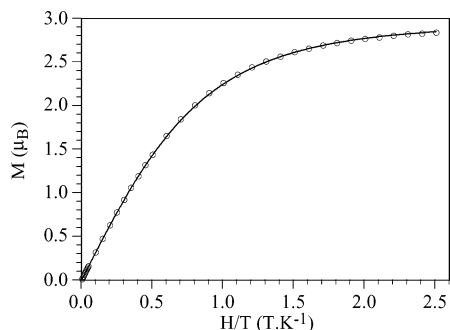


Figure 4. Magnetization of $(\text{TAEA})_2\text{Cu}_3\text{Cl}_{14}$ at 2.0 K with the calculated Brillouin function for $S = 3/2$.

reported in which ferromagnetic interactions are present. In $(\text{LCuCl})_2\text{CuCl}_4$, where L = 2,6-(diacetylpyridinedioxime)-chlorocopper(II), the square planar LCuCl^{+1} cations sandwich the flattened tetrahedral CuCl_4^{2-} anions. The copper atoms in the cations are linked to the central CuCl_4^{2-} anion via $\text{Cu}\cdots\text{Cl}$ bonds to yield ferromagnetically coupled magnetic trimers.¹⁴ A series of ferromagnetically coupled magnetic trimers $(\text{R}_4\text{N})_2[\text{Cu}(\text{TIM})](\text{CuX}_4)_2$ (R = Me or Et, TIM = 2,3,9,10-tetramethyl-1,3,8,10-tetraenecyclo-1,4,8,11-tetraazatetradecane and X = Cl or Br) has also been studied in which the central $\text{Cu}(\text{TIM})^{2+}$ macrocycle complex is coordinated by two CuX_4^{2-} anions via semicoordinate $\text{Cu}\cdots\text{X}$ linkages.¹⁵

The ferromagnetic intratrimer coupling in all of these systems can be rationalized on the basis of the conformation of the bridging $\text{Cu}_a\cdots\text{X}-\text{Cu}_b$ linkages, where Cu_a denotes the copper ion in the square planar copper complex and Cu_b denotes the copper ion in the distorted tetrahedral CuX_4^{2-} anion. The unpaired electron in both the central square planar

ion and the terminal distorted tetrahedral ion will lie in molecular orbitals that show significant delocalization of the unpaired electron density into halide σ orbitals. In all of these cases, the plane of the bridging $\text{Cu}_a\cdots\text{X}-\text{Cu}_b$ linkages nearly bisect one of the cis $\text{L}-\text{Cu}_a-\text{L}$ angles in the square planar complex. This can be seen in Figure 1 for the title compound and is documented in Table 1, where τ and τ' denote the angle between the plane of the $\text{Cu}_a\cdots\text{X}-\text{Cu}_b$ linkage and the two Cu_a-L vectors, respectively. Thus, the overlap integral will be nearly zero between the magnetic σ orbital on the CuX_4^{2-} anion with the $d_{x^2-y^2}$ based SOMO on the square planar complex. This implies that the exchange coupling should be ferromagnetic, as is observed experimentally. It should be noted that this argument also explains the alternating ferromagnetic/antiferromagnetic exchange coupling in the linear chain system in the compound $\text{Cu}(\text{TIM})-\text{CuCl}_4$.¹⁶ Here, in one case, the $\text{Cu}_a\cdots\text{X}-\text{Cu}_b$ linkage again nearly bisects one of the cis $\text{L}-\text{Cu}_a-\text{L}$ angles, giving a ferromagnetic coupling. However, in the other case, the $\text{Cu}_a\cdots\text{X}-\text{Cu}_b$ linkage is nearly coplanar with one of the Cu_a-L bonds, so that the overlap integral of the two magnetic orbitals will be nonzero, giving rise to antiferromagnetic coupling.

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Supporting Information Available: Crystal data for both compounds in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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