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1,3,5-Triazine Templated Self-Assembly of a Hexameric Copper(I) Chloride Triphenyl Phosphite Core

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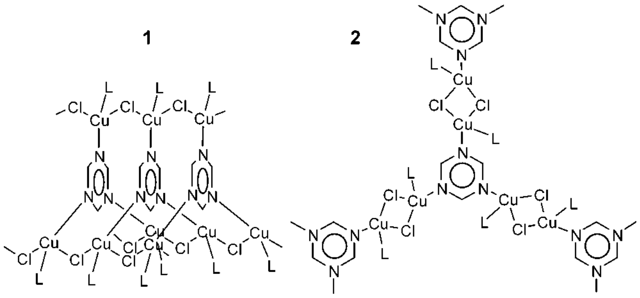
The reaction of CuCl, $P(OPh)_3$, and 1,3,5-triazine (Trz) in $CHCl_3$ produces $[(CuCl)_6(P(OPh)_3)_6(Trz)_2]$ via molecular self-assembly. An X-ray structural study has revealed a D_{3d} symmetry hexamer containing an oblate spheroid core. The core consists of a Cu_6Cl_6 macrocycle, which is capped by two μ_3-Trz ligands. Seven parallel stacked atom planes are present: P_3, Trz, Cu_3, Cl_6, Cu_3, Trz, and P_3. The six copper atoms are not coplanar with the Trz ligands and form a distorted octahedron. Crystal data: triclinic $P\bar{1}$, $a = 14.1489(7)$ Å, $b = 15.7470(8)$ Å, $c = 29.6572(14)$ Å, $\alpha = 76.4330(10)°$, $\beta = 79.5120(10)°$, $\gamma = 72.2260(10)°$, $V = 6088.5(5)$ Å^3, $Z = 2$, 27470 reflections, $R = 0.0359$.

The self-assembly of metal−organic networks is of great current interest, for example, in the formation of materials for guest inclusion or chemical separations. Of particular importance is the expansion of existing quasi-ionic networks, such as metal halides, cyanides, and sulfides with bridging ligands.[1] The resulting nonionic materials may produce robust, porous materials.

Copper(I) halides (CuX = CuCl, CuBr, and CuI) are known to form a variety of self-assembled oligomeric and polymeric arrays based upon $(CuX)_2$ rhomboids or $(CuX)_\infty$ chains.[2,3] Halide ligand μ_3-bridging arrangements produce CuX cubane, stair step, and similar arrays. The reaction of CuX with bidentate ligands, such as pyrazine, 4,4′-bipyridyl, and so forth, usually produces 2D sheets based on $(CuX)_2$ or $(CuX)_\infty$ units. When CuX and bridging ligands are combined in the presence of large monodentate ligands (L = PPh_3, $P(OPh)_3$, etc.), 1D chains composed of linked $(CuX)_2$ dimers are formed.[2] Several copper(I) halide networks incorporating the potentially tridentate 1,3,5-triazine (Trz) ligand are known.[4] However, no ternary compounds of CuX, Trz, and L have yet been reported.

Chart 1. Putative $[(CuCl)_3(P(OPh)_3)_3(Trz)]$ Polymers



When a solution of CuCl and $P(OPh)_3$ (0.089 M each) in $CHCl_3$ was treated with a $CHCl_3$ solution of triazine ($^1/_3$ equiv) under N_2, a pale yellow solution formed. After stirring for 20 min, the solution was concentrated and ether added. The mixture was cooled to −10 °C overnight, causing slow crystallization of an air-stable yellow-orange product. Product formulation as $[(CuCl)_3(P(OPh)_3)_3(Trz)]$ was confirmed by the results of atomic absorption (Cu: 14.5% expt, 14.6% theory), microanalysis (C 50.2% expt, 52.3% theory; H 3.60% expt, 3.70% theory; N 2.99% expt, 3.21% theory) and ^1H NMR integration of $P(OPh)_3$:Trz (15.9:1 expt, 15.0:1 theory). The yield was 73%. Single crystals were grown by slow diffusion of ether into a $CHCl_3$ solution.

Two polymeric networks, shown in Chart 1, were envisioned as possibly representing the product. Putative structure **1** is based on $(CuX)_\infty$ chains and results in a 1D channel arrangement. In contrast, putative structure **2**, based on $(CuX)_2$ units, forms a 2D sheet.

X-ray crystallographic analysis of the new ternary complex revealed the remarkable structure shown in Figure 1.[5] Selected bond lengths and angles are provided in Table 1. The asymmetric unit contained two independent, chemically identical half molecules of the copper complex and two molecules of chloroform.

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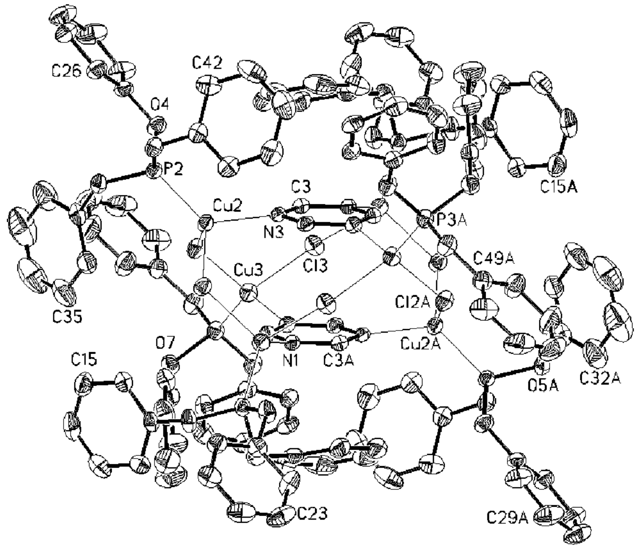

Figure 1. Molecular unit of [$(CuCl)_6(P(OPh)_3)_6(Trz)_2$] (molecule 1) shown with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths and Angles for [$(CuCl)_6(P(OPh)_3)_6(Trz)_2$]

bond or angle	occurrences[a]	range (Å or deg)
Cu−N	6	2.0583(18)−2.1058(18)
Cu−P	6	2.1544(6)−2.1629(7)
Cu−Cl	12	2.3215(6)−2.4297(6)
C−N	16	1.327(3)−1.342(3)
N−Cu−P	6	121.97(5)−126.42(5)
N−Cu−Cl	12	94.07(5)−98.75(5)
P−Cu−Cl	12	108.31(2)−121.53(2)
Cl−Cu−Cl	6	110.41(2)−113.97(2)
Cu−Cl−Cu	6	127.81(3)−133.58(3)
C−N−C	6	115.32(19)−116.21(18)
N−C−N	6	123.7(2)−124.9(2)

[a] Total number of nonredundant bond or angle occurrences in the two independent molecules.

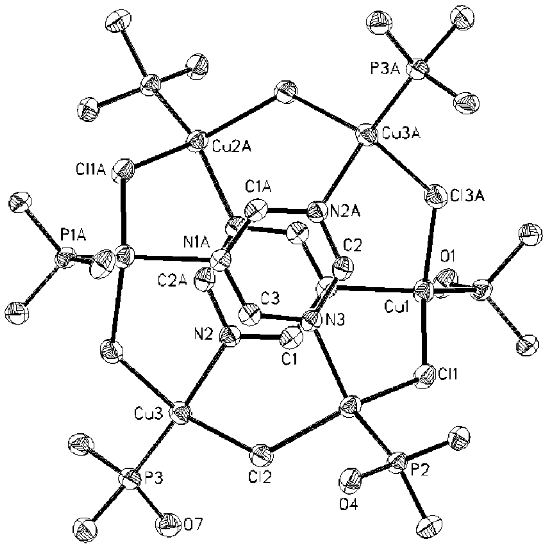

Figure 2. View of the core structure (molecule 1) illustrating 3-fold proper rotational and 6-fold improper rotational symmetry. Thermal ellipsoids are at 50%, and phenyl groups and hydrogens are removed for clarity.

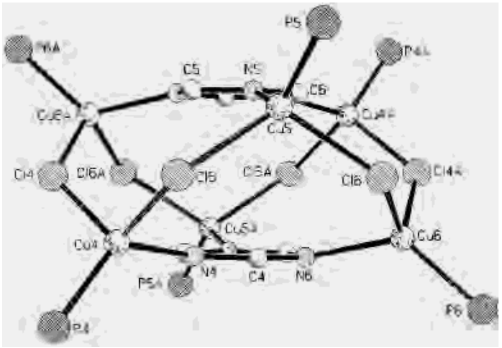

Figure 3. Ball and stick view of the core structure (molecule 2) illustrating atom planes. Phenoxy groups and hydrogens are removed for clarity.

Although the stoichiometry of the new complex conformed to that of **1** or **2**, the actual structure proved to be hexameric, rather than polymeric. Its construction is based on $(CuX)_6$ units, rather than $(CuX)_\infty$ chains (**1**) or $(CuX)_2$ dimers (**2**). In addition, the triazine ligands form links within hexamer units, producing discrete molecules rather than an extended network. Each hexamer molecule has an oblate spheroid core. Two views of these cores are shown in Figures 2 and 3. The core consists of a puckered 12-membered Cu_6Cl_6 ring, which is capped on either face with a μ_3-triazine ligand. The complex also features six $Cu_3Cl_2N_2C$ rings, three of which are fused to each of the triazine rings.

Both independent molecules within the unit cell are located on a crystallographic inversion center. The molecules possess inversion symmetry, as well as a coincident 3-fold proper rotation axis and 6-fold improper rotation axis. Three 2-fold axes and mirror planes complete the molecular point group symmetry of D_{3d}.

As is evident in Figure 3, the copper atoms are not coplanar with the triazine ligands. The angles between Cu−N bonds and the ring planes are 9.6°−16.9°. Other heteroaromatic copper complexes show out-of-plane metal displacements of only a few degrees.[2] The six chlorine atoms in each hexamer form a plane to within 0.0825, 0.0278 Å (data pairs correspond to the two independent molecules, respectively). Above and below the Cl_6 plane are Cu_3 planes, and above and below these copper planes are the triazine planes, and finally, P_3 planes. The seven alternating triangular and hexagonal planes P_3−Trz−Cu_3−Cl_6−Cu_3−Trz−P_3 are parallel to one another to within about 1.6°, 2.6°. The spacings between the planes are P_3−Cu_3 1.512, 1.471 Å; Cu_3−Trz 0.398, 0.401 Å; Cu_3−Cl_6 1.327, 1.305 Å. Because the Cu_3 planes are rotated by 60° with respect to one another, the six copper atoms form a trigonally distorted octahedron. Similar arrangements can be recognized for the six nitrogen and the six phosphorus atoms, respectively. The "top" and "bottom" Cu_3 planes are separated by only 2.654, 2.610 Å;

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(5) Crystal data: $M = 2856.64$, $C_{116}H_{98}N_6O_{18}P_6Cl_{12}Cu_6$, crystal dimensions $0.40 \times 0.30 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.1489(7)$ Å, $b = 15.7470(8)$ Å, $c = 29.6572(14)$ Å, $\alpha = 76.4330(10)°$, $\beta = 79.5120(10)°$, $\gamma = 72.2260(10)°$, $Z = 2$, $\rho_{calcd} = 1.558$ g/cm^3, $2\theta_{max} = 28.28°$, Mo Kα = radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K. Data were collected using Bruker AXS equipment with Apex CCD system, and the structure was solved via direct methods. Full matrix refinement on F using SHELXTL-97 converged with final $R = 0.0359$ and $R_w = 0.0832$ for 27470 independent reflections with $I > 2\sigma(I)$ and 1497 parameters. One of the $CHCl_3$ molecules showed some disorder, which was modeled.

other pairings of Cu_3 planes lie about 4.63 Å apart. A space filling projection of the hexamer reveals a void at its center, which is roughly 7.3 Å across by 3.0 Å high.

The formation of the hexamer molecules probably results from a combination of two geometric factors. First, the bulk of triphenyl phosphite ligands results in their favoring orientation in peripheral positions around the core. Second, the "templating" effect of the triazine molecules must be considered. In contrast to the ready formation of copper(I) halide clusters,[6] macrocycle assembly is very rare, apparently requiring direction by a templating agent.[7,8] These template molecules are found occupying central positions with respect to the macrocycle, either capping the ring or lying at its center. In addition to the capping triazine ligands reported herein, other known templates are capping [(triphos)Co(P_3)][7] and centering $[MoS_4]^{2-}$ or $[WS_4]^{2-}$.[8] The self-assembly of such templated molecular knots within extended networks could prove useful in the design of porous supramolecular systems.

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Supporting Information Available: Crystallographic data in CIF format and tables of atomic coordinates and equivalent isotropic displacement coefficients, bond lengths and angles, and anisotropic displacement coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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