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- [20] Abbreviations: Fmoc = 9-fluorenylmethoxycarbonyl, Boc = *tert*-butoxycarbonyl, Trt = trityl.
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A Cluster Rearrangement of an Open Cubane (Cu_4Br_4) to a Prismane (Cu_6Br_6) in a Copper(I)–Olefin Network**

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The rational design and self-assembly of copper(I)–olefin coordination polymers possessing high thermal stability has been the focus of intense interest in recent times.^[1] While these materials possess many of the general features normally associated with coordination polymers, the inclusion of bridging ligands that are capable of π bonding offers the possibility of unusual and novel properties. The Cu^{I} –olefin complexes examined so far have demonstrated an ability to act as fluorescent sensors,^[1] and have potential applications in areas such as olefin separation^[2] and enantioseparation.^[3]

To the best of our knowledge, the presence of clusters, such as cubanes, within Cu–olefin coordination polymers is unknown, however there are a number of metal–organic frame-

works with clusters acting as connecting units. Such materials have demonstrated gas-storage capabilities as well as exhibiting magnetic and catalytic properties.^[4–6] The successful generation of networks incorporating olefin coordination to a copper cluster represents an exciting challenge in modern supramolecular and organometallic chemistry. With this in mind, we have studied the reactions of triallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (TTT) with CuBr at different temperatures. Herein we report the synthesis, solid-state structures, and some electrochemical properties of two materials generated from such reactions.

The reaction between TTT and CuBr in methanol at 50–60 °C in a sealed tube yielded a product with the formula $[\text{Cu}_4\text{Br}_4(\text{TTT})_2]_n$ (**1**), which was examined by single-crystal X-ray diffraction.^[7] In this complex, Cu_4Br_4 clusters are linked by TTT ligands to form a polymeric chain (Figure 1). The Cu

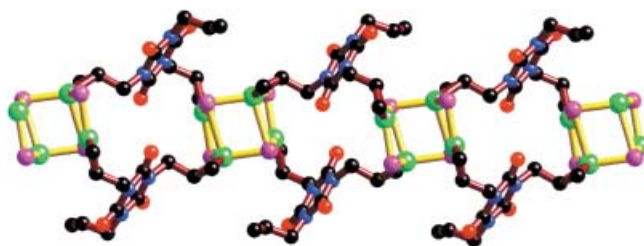


Figure 1. The chain structure of **1** which extends in the *c* direction (Cu green, Br pink, O red, N blue, C black). The open-cubane unit is highlighted with yellow bonds. H atoms have been omitted for clarity. Typical bond lengths [Å]: Cu–Br 2.422–2.395, Cu–C 2.063–2.106, coordinated olefin C=C 1.347–1.402.

and Br atoms occupy corners of a distorted cube, however as is apparent in Figure 1, there are only 10 Cu–Br bonds in each cluster resulting in an open-cubane arrangement (a closed-cubane arrangement would have a bond along each edge). The open-cubane unit has two unique Cu^{I} atoms each being coordinated by an olefin moiety and two bromide ions in an approximate plane with the metal center. One of the unique Cu atoms is coordinated to an extra bromide ion located within the cubane unit. This third Cu–Br bond is almost perpendicular to the plane of the other donor atoms, and with a length of 2.95 Å it is considerably longer than the other Cu–Br bonds.

Only two of the three arms of the TTT ligand are involved in coordination to the cubane units. The terminal carbon atom of the third arm is disordered over two sites. As is apparent in Figure 1, small cavities within the chain exist with approximate dimensions of 5×7.5 Å. These are formed by double-ligand bridges linking neighboring cubane units (a pseudo-3D network representation of **1** can be seen in the Supporting Information).

There are many examples of cubane clusters serving as the connecting node^[8] in metal–organic coordination polymers, however, to the best of our knowledge, **1** is only the second example of olefin-based ligands linking cubane-type units in coordination polymers.^[8c]

The complex $[\text{Cu}_6\text{Br}_6(\text{TTT})_2]_n$ (**2**), was formed in the reaction between CuBr and TTT in ethanol at approximately 90 °C. The solid-state structure of **2**^[7] (Figure 2a) indicates the

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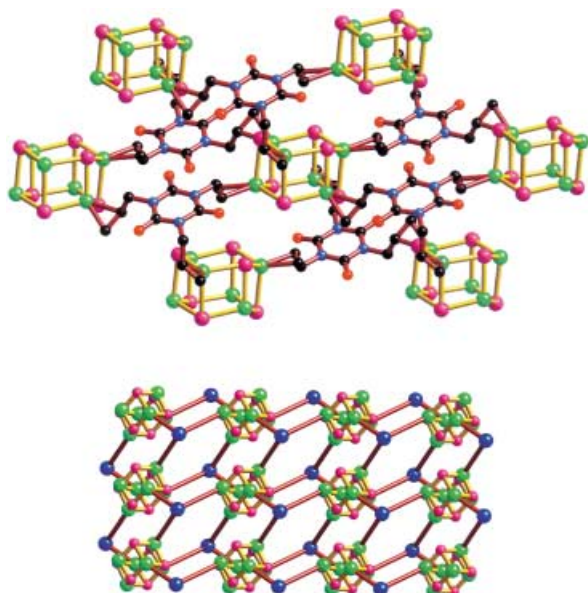
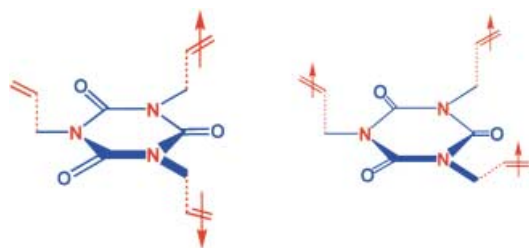


Figure 2. Top: The 2D structure of **2** which extends along the *a-b* plane (Cu green, Br pink, O red, N blue, C black). For clarity only ligands attached to the central prismatic unit are shown. The prismatic units are highlighted with yellow bonds. H atoms have been omitted for clarity. Typical bond lengths [Å]: Cu–Br 2.417–2.741, Cu–C 2.103–2.172, coordinated olefin C=C 1.336–1.350; bottom: an idealized representation of **2** showing the connectivity between prismatic units. The blue spheres represent the tridentate TTT ligands.

presence of Cu_6Br_6 prismatic clusters. Each Cu atom of the cluster is coordinated to three Br atoms and an olefin moiety, which gives rise to a slightly distorted tetrahedral coordination environment around each metal center. Each cluster is attached to six TTT ligands, each of which is attached to three prismatic clusters. The resulting coordination polymer is a 2D-network (a 2D layered representation of **2** is supplied in the Supporting Information).

The tridentate bonding motif adopted by the TTT ligand in **2** contrasts with the bidentate form found in **1**. Another notable difference relates to the position of the olefin moieties relative to the triazine plane of the ligand. In **1** the olefin binding groups are on opposite sides of the triazine plane in an arrangement that may be described as *trans*. In **2**, however, all binding units are on the same side of the plane in what may be regarded as a *cis* arrangement (Scheme 1).

The incorporation of a prismatic cluster into a supramolecular structure such as this is unprecedented. However, Hartl and co-workers reported a compound in which Cu_6I_6 prismatic building blocks were linked intramolecularly to



Scheme 1. Illustration of the *trans*-coordinating mode in **1** (left) and the *cis*-coordinating mode in **2** (right).

form chains in which instead of C=C coordination, the Cu center is coordinated to $n\text{-}\sigma$ bound ligands.^[9] The ability of the prismatic unit to link to six bridging ligands (with metal connecting centers lying at the vertices of a slightly distorted octahedron) makes this an appealing structural motif that may be useful in forming a variety of novel network structures.

Thermogravimetric analysis (TGA) of the crystalline complexes **1** and **2** showed no weight loss below approximately 200 and 265 °C, respectively, which indicates good thermal stability for these compounds, while beyond these temperatures both complexes decompose and lose their crystallinity. Interestingly, **1** can be converted into **2** in high yield by the reaction of **1** with CuBr on heating in ethanol. The conversion reaction may be a consequence of the open-cubane structure possessing a lower thermal stability than the prismatic structure, which is suggested by TGA.

Electrochemical measurements at platinum and glassy carbon working electrodes gave similar results for both complexes. As seen from Figure 3, the cyclic voltammograms of both **1** and **2** displayed one redox couple with similar behaviors, indicative of a closely related structure. The anodic and cathodic peak potentials of **1** were –146 and –530 mV at 150 mV s^{-1} , respectively, while the peaks of **2** occurred at –166 and –530 mV. No peaks were observed in a solution of the ligand, which suggests that these peaks were attributed to the oxidation and reduction of the Cu^{I} centers in the complexes.

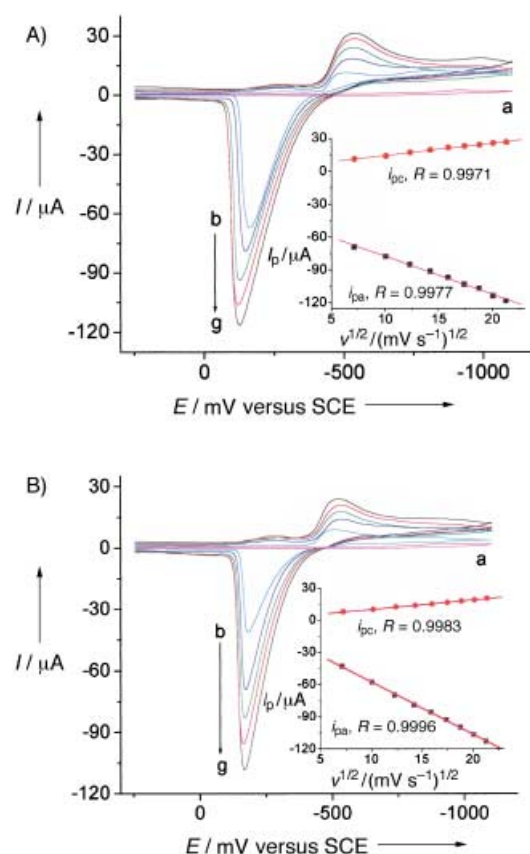


Figure 3. Cyclic voltammograms of 1.0 mM TTT in 0.1M Bu_4NClO_4 solution (CH_3CN) at 150 mV s^{-1} of 1.0 mM of **1** (A) and 0.5 mM of **2** (B) in 0.1M Bu_4NClO_4 solution (CH_3CN) at 50, 150, 250, 350, and 450 mV s^{-1} (from b to g) at a platinum disc working electrode. Insert: plots of anodic and cathodic peak currents versus $v^{1/2}$.

The single oxidation peak for both complexes indicated that all of the Cu^I centers were in the same local coordination environment.^[10] The linear relation between peak currents and the square root of the scan rate, the large difference between anodic and cathodic peak currents, and the large peak-to-peak separations all indicated that both electrode reactions were irreversible processes. The larger peak current of **1**, compared with **2**, was caused by a higher solution concentration of **1** in acetonitrile. A smaller peak-to-peak separation of **2**, compared with **1**, and the larger ratio of peak current to amount of Cu^I centers in solution indicate a more rapid electron-transfer rate in **2**, as a result of its prismane-based structure. However, the exact nature of the species in solution is unclear.

In conclusion, with a precise knowledge of their solid-state structures and facile tunability of their building blocks, the present work definitely holds great promise in the development of novel Cu–olefin supramolecular motifs containing clusters as connecting nodes.

Experimental Section

1: CuBr (2.0 mmol) and TTT (1.0 mmol) were heated in MeOH (1.5 mL) for 3 days at 50–60 °C in a sealed tube to yield colorless platelike crystals of **1** (approximately 0.4 mmol, 40 % yield). IR (KBr): $\tilde{\nu}$ = 3427(brw), 1686(s), 1457(s), 1315(w), 930(w), 764(w), 701(w), 669(w), 605(w), 544 cm^{−1}(w). Complex **1** is slightly soluble in CH₃CN.

2: CuBr (3.0 mmol) and TTT (1 mmol) were heated in EtOH (1.5 mL) for 3 days at 80–90 °C in a sealed tube to yield colorless platelike crystals of **2** (approximately 0.5 mmol, 50 % yield). IR (KBr): $\tilde{\nu}$ = 3426(brw), 2961(w), 1759(w), 1681(s), 1561(w), 1456(s), 1496(m), 1398(m), 1335(w), 1319(w), 1305(w), 1266(w), 977(w), 949(m), 930(w), 778(m), 746(w), 736(w), 695(w), 528(w), 428(w) cm^{−1}. Complex **2** is also slightly soluble in CH₃CN.

Conversion of **1** into **2**: Treatment of powdered **1** (1.0 mmol) with CuBr (1.0 mmol) in EtOH (1.5 mL) for 2 days at 80–90 °C in a sealed tube affords colorless platelike crystals of **2** (approximately 0.5 mmol, 90 % yield).

EPR spectra of the complexes are all silent, thus confirming that the oxidation state of Cu ions in both **1** and **2** is +1.

Electrochemical measurements of **1** and **2** were performed with a BAS 100 B electrochemical analyzer (Bioanalytical Systems Inc., USA) by using a standard three-electrode system comprising a saturated calomel electrode (SCE) as reference, a platinum wire as auxiliary electrode and a platinum disc (1.0 mm diameter) or glassy carbon disc (3.0 mm diameter) as working electrode. The working electrodes were polished to a mirrorlike surface with 0.3 and 0.05- μ m alumina slurries on microcloth pads (Buehler), then rinsed with water and ethanol, and sonicated in twice-distilled water. After the electrodes had been dried in heated air, they were used for electrochemical experiments in deaerated CH₃CN solutions after purging with pure nitrogen for 15 min.

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- [7] Crystal data for **1**: C₂₄H₃₀Br₄N₆O₆Cu₄, M_r = 1072.34, monoclinic, space group C2/c, a = 21.710(19), b = 8.079(7), c = 19.000(16) Å, β = 90.000(17)°, V = 3333(5) Å³, Z = 4, ρ_{calcd} = 2.137 Mg m^{−3}, R_1 = 0.0708, wR_2 = 0.1649, μ = 7.361 mm^{−1}, S = 0.845. Crystal data for **2**: C₁₂H₁₅Br₃N₃O₃Cu₃, M_r = 679.62, monoclinic, space group P2₁/c, a = 10.7562(15), b = 7.9594(11), c = 20.662(3) Å, β = 96.588(2)°, V = 1757.3(4) Å³, Z = 4, ρ_{calcd} = 2.569 Mg m^{−3}, R_1 = 0.0337, wR_2 = 0.0570, μ = 10.432 mm^{−1}, S = 0.726. The structures were solved by direct methods using the SHELXTL program (Sheldrick, 1997).^[11] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically (except for atom C3 which was found to be disordered over two sites) with SHELXTL using the full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. CCDC-179241 (**1**) and CCDC-179242 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).
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