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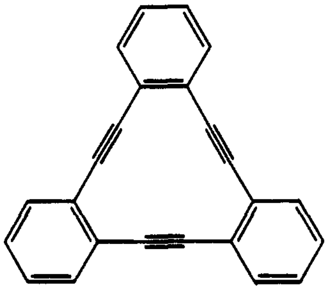
Synthesis and Molecular Structure of a Trinuclear Copper(I) Cofacial Bimacrocycle

Sir:

We recently reported the synthesis and characterization of the two complexes Ni(TBC)[1] and Cu(TBC)(OTf)[2] (OTf$^-$ = $O_3SCF_3^-$ = triflate ligand) showing the novel coordination of a metal atom in the center of the cavity of a macrocyclic trialkyne ligand, TBC (1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne[3]). Copper(I) often forms oligomeric and polymeric aggregates with bridging ligands.[4] Herein we report the synthesis and structural characterization of $Cu_3(OTf)_3(TBC)$ in which the ligand TBC provides three alkyne sites for the binding of three Cu(μ_2-OTf) units.



TBC

The complex $Cu_3(OTf)_3(TBC)$ was initially obtained from an experiment designed to give crystals of Cu(OTf)(TBC). Benzene solutions[5] of $[Cu_2(OTf)_2(C_6H_6)]$[6] and TBC (Cu to TBC ratio = 1:1) were allowed to diffuse into each other through a narrow horizontal tube in an H-tube reaction vessel over a 3-week period. Crystals of $Cu_3(OTf)_3(TBC)\cdot C_6H_6$ suitable for X-ray diffraction formed at the copper-rich end of the horizontal tube. These crystals were also characterized by single-crystal FT-IR spectroscopy. Other products, including Cu(OTf)(TBC), were also formed in the H-tube reaction vessel. The complex $Cu_3(OTf)_3(TBC)\cdot C_6H_6$ can be prepared in much higher yield by the reaction of stoichiometric amounts of $[Cu_2(OTf)_2(C_6H_6)]$ and TBC in methyl ethyl ketone (MEK) followed by precipitation with benzene[7,8] or by prolonged reaction of stoichiometric quantities of Cu(TBC)(OTf) with $[Cu_2(OTf)_2(C_6H_6)]$ in refluxing benzene. The complex $Cu_3(OTf)_3(TBC)$ reacts with water, THF, and MEK (slowly).

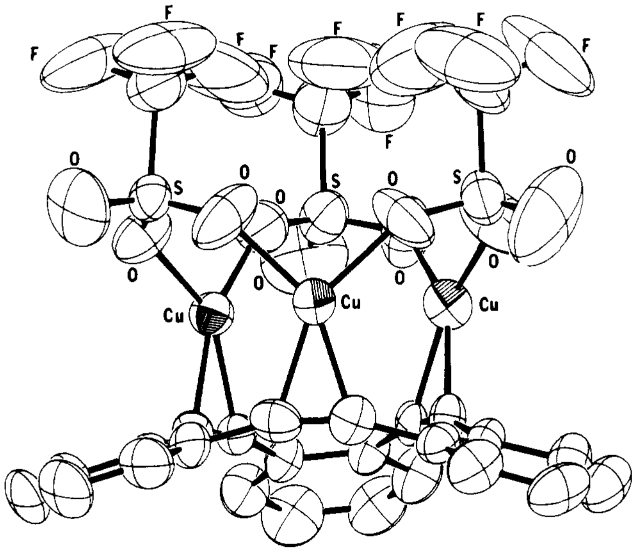


Figure 1. ORTEP diagram of $Cu_3(OTf)_3(TBC)$. Cu, O, S, and F atoms are labeled; C atoms are not. The thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

The IR spectrum[9] of $Cu_3(OTf)_3(TBC)\cdot C_6H_6$ shows a weak band at 2067 cm^{-1} for the C≡C stretch, which is similar to that in Cu(TBC)(OTf) (2085 cm^{-1}).[2] The small shift in frequency (150 cm^{-1}) of the C≡C stretch from that of the free ligand (2217 cm^{-1}) is consistent with two-electron donation from each alkyne to Cu(I) and poor back-donation from Cu(I) to the alkynes.[10] Slightly

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(1) Ferrara, J. D.; Tessier-Youngs, C.; Youngs, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 6719–6721.

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(3) (a) Staab, H. A.; Graf, F. *Tetrahedron Lett.* **1966**, 751–757. (b) Campbell, I. D.; Eglington, G.; Henderson, W.; Raphael, R. A. *J. Chem. Soc., Chem. Commun.* **1966**, 87–89.

(4) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980, pp 804–811.

(5) The solutions contained 0.1345 mmol of $[Cu_2(OTf)_2(C_6H_6)]$ or 0.2690 mmol of TBC, each dissolved in 10 mL of C_6H_6. Sufficient benzene (10 mL) was carefully added above the two solutions to provide contact between them.

(6) (a) Purchased from Strem Chemical Co. and used without further purification. (b) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889–1897.

(7) Typically 0.524 mmol of $[Cu_2(OTf)_2(C_6H_6)]$ and 0.333 mmol of TBC were each dissolved in 20 mL of MEK. The TBC solution was added to the copper solution, the mixture was stirred for 20 min and filtered, and most of the MEK was removed in vacuo, leaving a clear green viscous solution. Addition of benzene induced precipitation of a yellow powder. Comparison of the FT-IR spectrum of the yellow powder with that of the single crystal from the H-tube synthesis[5] established the identity of the major product as $Cu_3(OTf)_3(TBC)\cdot C_6H_6$ and indicated a small amount of Cu(TBC)(OTf)[2] was present. Yield: 63% based on TBC.

(8) Anal. Calcd: Cu, 18.75; F, 16.82; C, 39.00; H, 1.79. Found: Cu, 18.17; F, 15.44; C, 41.30; H, 1.77. The sample contained a small amount of Cu(TBC)(OTf) impurity.

(9) IR data for $Cu_3(OTf)_3(TBC)$ (Nujol), cm^{-1}: 2067 vw, 1993 vw, 1975 vw, 1956 vw, 1922 vw, 1876 vw, 1842 vw, 1764 vw, 1645 vw, 1588 w, 1475 m, 1309 vs, 1261 m, 1243 m, 1218 vs, 1201 vs, 1175 m, 1158 m, 1039 s, 767 s, 680 w, 637 s, 591 w, 551 w, 518 w, 511 w, 479 w.

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larger shifts (160–179 cm^{-1}) of the $C\equiv C$ stretching frequency upon η^2-complexation of other alkyne ligands to Cu(I) centers have been reported.[11] Infrared bands of the triflate ligand region (1390–1000 cm^{-1}) are consistent with bidentate coordination.[12] An ^1H NMR study of a mixture of Cu(TBC)(OTf) and $Cu_3(OTf)_3(TBC)$ indicates that the two complexes exchange freely in solution at room temperature on the NMR time scale.

The complex $Cu_3(OTf)_3(TBC)$ can be described as a cofacial bimacrocycle as a result of the binding of TBC to a cyclic trimer of copper triflate ligands (Figure 1).[13] The bidentate triflate ligands bridge the three copper atoms via the oxygen atoms and form a 12-membered macrocycle with CuOSO as the repeat unit. Each copper of the macrocycle is bound to an alkyne of the TBC ligand. The coordination geometry about each copper ion is a distorted trigonal plane with an alkyne and two oxygen atoms occupying the three coordination sites. The trifluoromethyl and benzo groups point away from their respective macrocycle. The Cu–Cu distances are 3.399 (2), 3.755 (2), and 3.811 (1) Å, indicating a significant distortion of the $(CuOSO)_3$ ring from 3-fold symmetry. A range of Cu–O bond lengths (1.955 (5)–2.006 (5) Å) and O–Cu–O angles (94.4 (3)–101.5 (3)°) is observed. The Cu–C bond lengths do not vary significantly from the mean of 1.996 (3) Å (range 1.991 (8)–2.001 (7) Å). The $C-C\equiv C$ angles in $Cu_3(OTf)_3(TBC)$ range from 163.0 (8) to 166.0 (8)°. The benzo groups are bent downward from the least-squares plane defined by the three alkynes with a mean angle of 19 (3)°. The bonds between the alkyne and benzo carbons average 1.433 (7) Å, and the aromatic C–C bonds average 1.391 (18) Å. A benzene solvate is present in the lattice but does not interact with $Cu_3(OTf)_3(TBC)$.

The structure of $Cu_3(OTf)_3(TBC)$ is unusual in several respects. The binding of the three Cu(I) centers to the face of TBC is a new type of TBC–metal coordination.[1,2] The TBC ligand is far more distorted from planarity in $Cu_3(OTf)_3(TBC)$ than in the cavity complexes Ni(TBC) or Cu(TBC)(OTf) ($C-C\equiv C >$ 173°).[1,2] The Cu(I) alkyne complexes $[(\eta^2\text{-}PhC\equiv CPh)(\mu\text{-}O_2CPh)Cu]_2$[11b] and $[(\eta^2\text{-}HC\equiv CH)(HN(2\text{-}py)_2)Cu]BF_4$[14] have trigonal-planar geometries similar to $Cu_3(OTf)_3(TBC)$. The distortions from linearity of the alkyne ligands in these two complexes are similar to those of $Cu_3(OTf)_3(TBC)$ and are smaller than those observed in most other metal alkyne complexes.[15] The Cu–C bond lengths in $Cu_3(OTf)_3(TBC)$ are longer than those in the trigonal-planar Cu(I) complexes (1.953 (9)[11b] and 1.971 (4) Å,[14] respectively) but shorter than those in the trigonal-pyramidal complex Cu(TBC)(OTf) (2.060 (4) Å).[2] The triflate ligand in $Cu_3(OTf)_3(TBC)$ differs from all other structurally characterized coordinated triflate ligands[12a,16] and appears to be the first example of a fully coordinating bidentate triflate ligand (the Cu–O bonds are all within the normal range for Cu(I)–O bonds of 1.83–2.23 Å[11b,17]). Other structurally characterized triflate ligands in Cu(I) complexes are monodentate in Cu(TBC)(OTf)[2], tridentate in $[Cu_2(OTf)_2(C_6H_6)]$,[18] and mixed bi- and tridentate in $Cu(OTf)(C_6H_{10})$.[19] The steric requirements of bridging ligands appear to determine the Cu–Cu separation in Cu(I) aggregates.[4,20] In $Cu_3(OTf)_3(TBC)$ the distance between the Cu(I) centers appears to be controlled by two opposing forces: the alkynes, whose centers are separated by 3.45 (2) Å in free TBC[21] and 3.46 (3) Å in $Cu_3(OTf)_3(TBC)$, and the steric congestion of the bidentate triflate ligands. The change in aggregation of the Cu(OTf) unit from polymeric[18] (solid state) in the starting material $[Cu_2(\mu_3\text{-}OTf)_2(C_6H_6)]$ to trimeric in $Cu_3(\mu_2\text{-}OTf)_3(TBC)$ suggests that the TBC ligand is acting as a template. Few examples of trimeric Cu(I) aggregates are known.[4,22]

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Registry No. TBC, 5385-26-2; $Cu_3(OTf)_3(TBC)$, 114422-78-5; $Cu_3(OTf)_3(TBC)\cdot C_6H_6$, 114422-79-6; $l[Cu_2(OTf)_2(C_6H_6)]$, 37234-97-2; Cu(TBC)(OTf), 106568-05-2.

Supplementary Material Available: Tables of crystal data, data collection and reduction, and refinement details, atomic positional and thermal parameters, rigid-body parameters, bond lengths and angles, and least-squares planes (11 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106-2699

Joseph D. Ferrara
Claire Tessier-Youngs
Wiley J. Youngs*

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(13) (a) The air-sensitive yellow crystals were mounted in capillary tubes under an argon atmosphere. Crystallographic data: space group, $P\bar{1}$, $a = 9.666$ (2) Å, $b = 13.720$ (3) Å, $c = 17.066$ (4) Å, $\alpha = 98.48$ (2)°, $\beta = 103.86$ (2)°, $\gamma = 113.80$ (1)°, $Z = 2$, $\rho_{calcd} = 1.746$ (1) g cm^{-3}, fw 1016.32. The intensity data were collected from $3.5 \leq 2\theta \leq 50.0°$. Refinement to convergence on the 3382 unique reflections, $I \geq 3\sigma(I)$, resulted in the final agreement factors $R(F) = 0.054$ and $R_w(F) = 0.055$ and on the 6093 unique reflections, $I \geq 0$, resulted in $R(F) = 0.108$ and $R_w(F) = 0.067$. All structural results are based on the 6093 reflections. Each asymmetric unit contained one benzene molecule, which was modeled as a rigid body.[13b] (b) UCLA Crystallographic Computing Package, Dec 2, 1985.

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