

A host–guest complex between a metal–organic cyclotrimeratrylene analog and a polyoxometalate: [Cu₆(4,7-phenanthroline)₈(MeCN)₄]2PM₁₂O₄₀ (M = Mo or W)

Jacqueline M. Knaust, Chad Inman and Steven W. Keller*

Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA.

E-mail: KellerS@missouri.edu; Fax: (573) 882-2754; Tel: (573) 884-6893

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The synthesis and crystal structure of Cu₆(4,7-phenanthroline)₈(MeCN)₄⁶⁺ a novel Cu(I)-molecular hexamer is described in which the metal cations and phenanthroline molecules self-assemble into a dimer of shallow triangular-shaped bowls, within which are located large spherical polyoxometalate anions PM₁₂O₄₀³⁻ (M = Mo or W).

The supramolecular host–guest complexation of cations has been quite extensively studied since the pioneering work on crown ethers by Pedersen¹ and cryptands by Lehn² in the 1960's. The following decade Cram's spherands³ and Atwood's calixarenes further expanded the range of host molecules.⁴

The design of molecular receptors for neutral molecules and anions however, presents more of a challenge due to their large size, various shapes and large enthalpies of solvation.⁵ Therefore fewer examples have been reported. Of note, cyclotrimeratrylene (CTV), a saucer-shaped organic macrocycle has been shown to complex C₆₀, a spherical molecule approximately 7 Å in diameter.⁶ Using metallocene-derivatized CTV hosts, Holman and co-workers prepared host–guest complexes of both neutral and anionic guests including NO₂Me, BF₄⁻, CF₃SO₃⁻ and ⁹⁹TcO₄⁻.⁷ Complexation of the larger Keggin ion, PW₁₂O₄₀³⁻ (ca. 10.5 Å in diameter) requires a larger bowl in which the anion can reside.

Hybrid metal–organic analogues of organic macrocycles are being vigorously pursued and recent successes include some very interesting triangular systems akin to CTV.⁸ In addition to potentially new magnetic systems⁹ and unique reactivity control¹⁰ most of these metallomacrocycles have the advantage in that they are both larger and inherently cationic, and therefore should be better suited for anion complexation. We recently reported an extended chain structure composed of Cu(I)₃phen₃ triangles in which the bowl-shaped cavities formed included phenyl groups from a neighboring chain within their interior, instead of the small BF₄⁻ counter anions.¹¹ Here we report the synthesis and structure of an *isolated* Cu(I)-phenanthroline double bowl-shaped hexamer within which are contained two PM₁₂O₄₀³⁻ units as non-coordinated anions.

Single crystals† of [Cu₆(4,7-phenanthroline)₈(MeCN)₄]2PM₁₂O₄₀ (M = Mo, **1** or W, **2**), are recovered as yellow–orange prisms from vapor diffusion of diethyl ether into a solution of [Cu(MeCN)₄]₃PM₁₂O₄₀ and 4,7-phenanthroline.‡ The asymmetric unit of both contain three unique Cu(I) cations each displaying a different coordination sphere. Cu1 is bonded in a nearly T-shaped fashion to two phenanthroline molecules and one MeCN molecule; the large angle occurs between the phenanthrolines (N_{phen}–Cu–N_{phen} = 152°, N_{MeCN}–Cu–N_{phen} = 101° and 106°). Cu3 also displays a distorted trigonal geometry (not quite as T-shaped or planar as Cu1) consisting of three phenanthroline molecules (N–Cu–N angles of 100°, 101° and 143°). Cu2 is the only four-coordinate metal center, having three phenanthroline molecules (all of the phenanthroline molecules are bridging in this structure) and one terminal MeCN in its distorted tetrahedral coordination sphere.

As shown in Fig. 1, the three unique Cu(I) centers form the corners of a triangle whose sides are three bridging phenanthroline ligands (two from each of the copper cations). The third phenanthroline ligand coordinated to Cu2 and Cu3 link two

triangles together into (depending on your perspective) a molecular hexamer or a dimer of triangles related by a crystallographic inversion center.

The bowls open in opposite directions (with respect to the plane of metal centers) and contain the polyoxometalate (POM) ion as shown in Fig. 2. One notable difference between these metal–organic structures and the CTV macrocycles is the orientation of the “sides” of the bowls. Most often, the all-organic cyclotrimeratrylene species form a bowl with approximate C₃ symmetry. In each metallo-triangle in **1** one of the “flaps” is open; the phenanthroline bridging Cu1 and Cu3 is directed opposite the other two as shown on the right side of Fig. 2. The shallowness of the bowl necessitates the POM protruding out from the cavity (the distance from the plane of the Cu atoms to the phosphorus atom located in the center of the POM is ca. 7.2 Å), but there is significant evidence of host–guest interaction. Although the POM is normally thought of as a sphere the peripheral oxygen atoms create “facets” (see the views in Fig. 2 and 3). Two of these flat planes fit well against the two

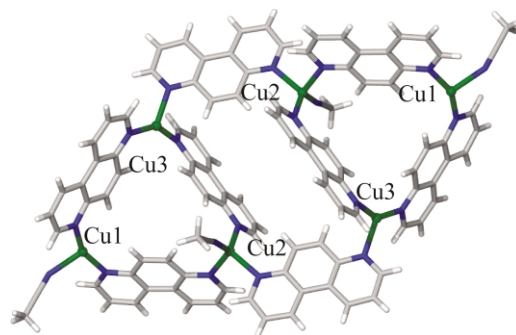


Fig. 1 Stick diagram of **1**. Cu: Green, N: blue, C: gray; H: white.

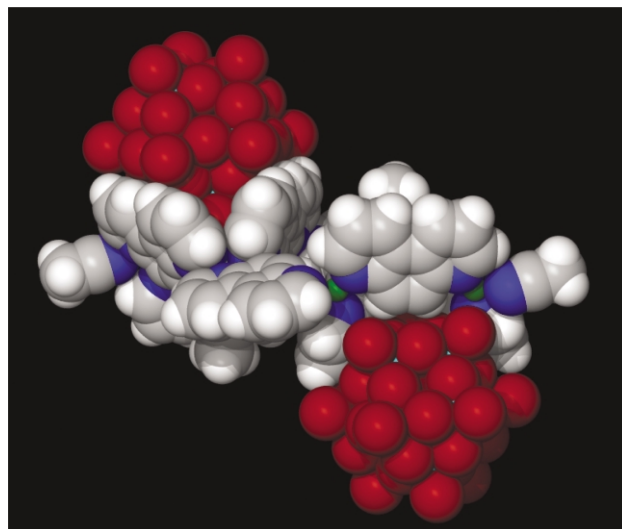


Fig. 2 Space-filling side view of the two polyoxometalate anions sitting in the two bowl-shaped cavities of the hexamer.

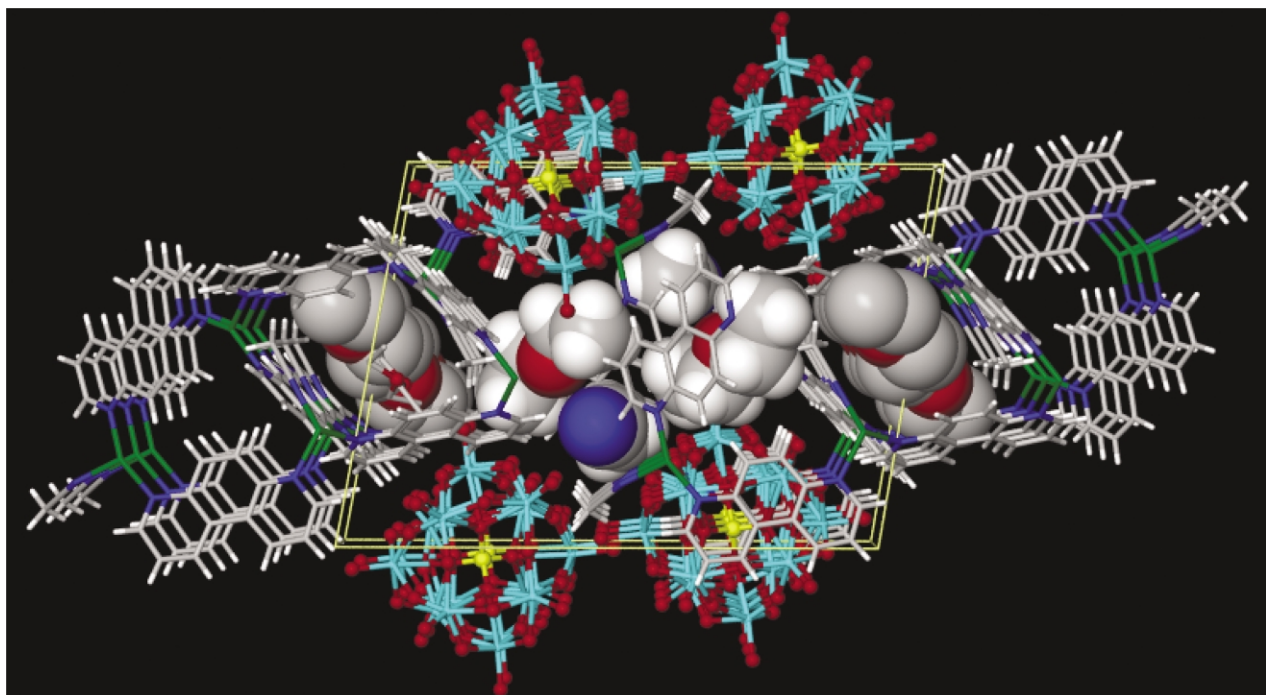


Fig. 3 Packing diagram of **1** viewed down the *a*-axis. The Cu-phen hexamers are shown in stick representation, the anions as balls-and-sticks, and the included solvent molecules (diethyl ether and acetonitrile) as space-filling spheres. The outline of the unit cell is shown in yellow.

phenanthroline sides, while the “open” side allows a closer approach to the three-coordinate Cu1 center; the Cu–O distance is 2.9 Å. When the same POM is crystallized within a Cu(I)-4,4'-bipyridine network, such interactions are not manifested, and the anions reside in larger cavities with much longer contacts to the aromatic rings.¹² Further, the orange color of the crystals indicates some degree of charge-transfer interaction between the d¹⁰-Cu(I) of the host and the d⁰ W(VI) in the guest; all of our previously reported non-POM Cu(I)-phenanthroline networks are yellow. The host-guest complexation is also supported by the fact that the structure formed with the smaller BF₄[−] anion contains *linked* triangles in a *different* orientation (*vide supra*).⁹

Fig. 3 shows how the hexamers and anions pack into columns running parallel to the *a*-axis. In addition, the rectangular space formed from the joining of the two triangles creates channels that house one of the diethyl ether solvent molecules. Also crystallized within the structure is one molecule of MeCN per formula unit. As polyoxometalates are known to catalyze certain selective oxidation reactions,¹³ it is useful to have potential substrates in close proximity. We hope the solvate molecules will play this role, though no photoreactivity studies have been performed. Further investigations to characterize the chemistry and charge-transfer properties of these new hybrid materials including diffuse reflectance spectroscopy and electrochemical measurements are currently underway.

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Notes and references

† Crystal structure determination for **1**: *Crystal data*: Cu₃C₆₈H₅₆N₁₄P-Mo₁₂O₄₀, *M* = 2995.0 g mol^{−1}, triclinic, space group, *P* $\bar{1}$, *a* = 13.025(2), *b* = 16.002(2), *c* = 21.112(3) Å, α = 79.799(2), β = 87.654(2), γ = 72.576(2)°, *V* = 4131.8(9) Å³, *T* = 173(1) K, *Z* = 2, μ (Mo–K α) = 2.627 mm^{−1}, 29964 reflections measured, 17864 unique (*R*_{int} = 0.0507), observed with *I* > 2 σ (*I*) which were used in all refinements. The final *R*(*F*) was 0.0533 for observed data. CCDC for **1** and Cu₃C₆₈H₅₆N₁₄PW₁₂O₄₀, **2**,

are 217094 and 217095 respectively. See <http://www.rsc.org/suppdata/cc/b3/b309255k/> for crystallographic data in .cif or other electronic format.

‡ [Cu(MeCN)₄]₃PM₁₂O₄₀ (*M* = Mo or W) was synthesized as an orange polycrystalline powder via a modification of the method of Kubas.¹⁴ Preparation of [Cu₆(MeCN)₄(phen)₈](PMo₁₂O₄₀)₂·2Et₂O·MeCN, **1**. In a 5 mL vial [Cu(MeCN)₄]₃PMo₁₂O₄₀ (32.1 mg, 0.009 mmol) in 2.5 mL MeCN was added to 4,7-phenanthroline (12.2 mg, 0.068 mmol) in 1.5 mL nitrobenzene. That small vial was placed in a 20 mL screw-top vial containing 5 mL diethyl ether, which was allowed to diffuse into the solution at room temperature. Over the course of several weeks a yellow precipitate formed from which darker, yellow–orange crystals of **1** were harvested.

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