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Synthesis and Structure of Cuboctahedral and Anticuboctahedral Cages Containing 12 Quadruply Bonded Dimolybdenum Units

Yanxiong Ke, David J. Collins, and Hong-Cai Zhou*

Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056

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The syntheses and structures of two clusters containing 12 Mo–Mo quadruple bonds, $[Mo_{24}(C_{12}H_{12}O_4)_{24}](C_5H_5N)_{12}$ and $Mo_{24}(C_8H_4O_4)_{24}$, are reported. The 12 paddlewheel building blocks and 24 ligands self-assemble into cuboctahedral and anticuboctahedral polyhedra, respectively, depending on the manner in which the two halves of the cluster are aligned. These clusters contain twice as many dimolybdenum units as any previously reported cluster. Possible assembly mechanisms are also proposed.

In the burgeoning field of supramolecular chemistry, coordination-driven self-assembly has led to highly symmetric nanoscale polyhedral cages. These clusters not only exhibit aesthetically pleasing structures, but might also have roles in molecular recognition, host−guest chemistry, and catalysis. The introduction of metal−metal-bonded units into such assemblies has not only expanded the field but also added electrochemical and spectroscopic probes to the study of such clusters. Recently, Cotton and co-workers reported polyhedral clusters of T_d symmetry containing six Mo−Mo or Rh−Rh bonds, which represent the largest self-assembled discrete molecules containing metal−metal bonds in the literature.[1] To expand this interesting chemistry, herein, we report the synthesis and crystal structure of cuboctahedral and anticuboctahedral cages containing 12 quadruply bonded Mo−Mo units and their implications in the mechanism of self-assembly of clusters and coordination networks.

By carefully selecting the bridging ligand and the metal or metal cluster nodes, the architecture of the final molecule can be designed. As shown previously, the key for producing a finite coordination cluster rather than an infinite network is the use of a bent linking ligand rather than a linear one.[2] The use of a square-planar metal center or a paddlewheel dimetal unit and ditopic 120° bridging ligands results in the assembly of clusters with the symmetry of a cuboctahedron.

To build the clusters containing 12 Mo−Mo units, preformed Mo−Mo paddlewheel building blocks were combined with the 120° ditopic ligands 1,3-benzenedicarboxylate (BDC) and 4-*tert*-butyl-1,3-benzenedicarboxylate (BBDC), the latter being more soluble in solvents of low dielectric constants. In this report, a cuboctahedral cluster, $[Mo_{24}(BBDC)_{24}](py)_{12}$ (**1**), and an anticuboctahedral cluster, $Mo_{24}(BDC)_{24}$ (**2**), are presented. Additionally, a cuboctahedral cluster based on a dicopper paddlewheel building block (formed in situ) and the ligand BBDC, $[Cu_{24}(BBDC)_{24}](py)_{12}(MeOH)_{12}$ (**3**), similar to previously reported Cu−BDC cuboctahedron clusters,[3] is also discussed.

Compounds **1** and **2** were synthesized using solvothermal methods by the reaction of $Mo_2(ac)_4$ (prepared according to literature method),[4] pyridine, and either (**1**) BBDC in 1,2-dichlorobenzene or (**2**) BDC in DMF. Crystals of both **1** and **2** are extremely air-sensitive and lose solvent readily upon removal from the mother liquor. Compound **3** was synthesized using layering of a nitrobenzene solution containing BBDC and pyridine with a methanol solution of copper(II) nitrate.

Compound **1** crystallizes in the tetragonal space group $I4/m$.[5] Each of the dimolybdenum units is coordinated by four BBDC units to form an all-cis paddlewheel (idealized point group C_{4v}, vide infra). Merging of the 12 all-cis dimolybdenum units forms a cuboctahedron (Figure 1). The two crystallographically unique Mo−Mo distances are 2.1109(5) and 2.1101(8) Å, which fit within the typical range of Mo−Mo quadruple bond distances.[6] A pyridine molecule is located at the axial position of each Mo−Mo pair pointing

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* To whom correspondence should be addressed. E-mail: zhouh@muohio.edu.

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(5) Crystallographic data for **1**: $Mo_{24}C_{348}H_{348}N_{12}O_{96}$, fw 8536.94, tetragonal, $I4/m$, $a = b = 28.8679(10)$ Å, $c = 42.999(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 35833(3)$ Å^3, $Z = 2$, $\rho_{calc} = 0.791$ g/cm^3, $\mu = 0.444$, R1 = 0.0642, wR2 = 0.1729.

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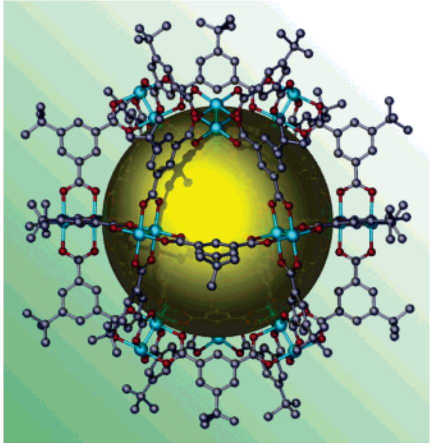

Figure 1. Molecular structure of **1**, $[Mo_{24}(BBDC)_{24}](py)_{12}$. Pyridine groups and all hydrogen atoms are omitted for clarity. The golden sphere represents solvent-accessible space inside the cage.

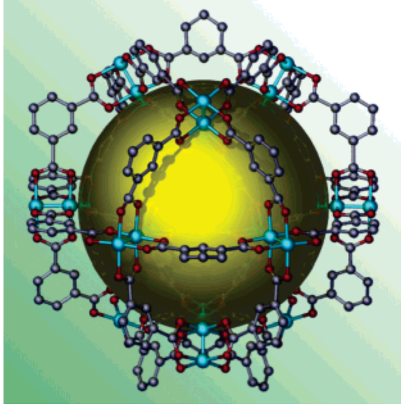

Figure 2. Molecular structure of **2**, $Mo_{24}(BDC)_{24}$. All hydrogen atoms are omitted for clarity. The golden sphere represents solvent-accessible space inside the cage.

away from the center of the cluster. One of the pyridine molecules is disordered in two orientations. No ordered axial ligation was found inside the cluster. The Mo−N distances are 2.514(6) and 2.563(6) Å, typical for axially coordinated pyridine on a Mo−Mo quadruple bond.[6a,7] The ideal symmetry of the cuboctahedron is O_h, but the crystallographically imposed symmetry is reduced to C_{4h}. Idealizing the structure as a sphere, the diameter of **1** is 3.123 nm (the longest distance between the hydrogen atoms on *tert*-butyl groups), and the total volume is estimated at 15.94 nm^3.

Compound **2** crystallizes in the tetragonal space group $I\bar{4}2m$.[8] Again, 12 all-*cis* $Mo_2(BDC)_4$ paddlewheels merge to form the anticuboctahedron of **2** with idealized D_{3h} symmetry (Figure 2). The average Mo−Mo distance is 2.114(4) Å, again consistent with the length for a Mo−Mo quadruple bond.[6] Disordered axial ligands were found but not modeled.

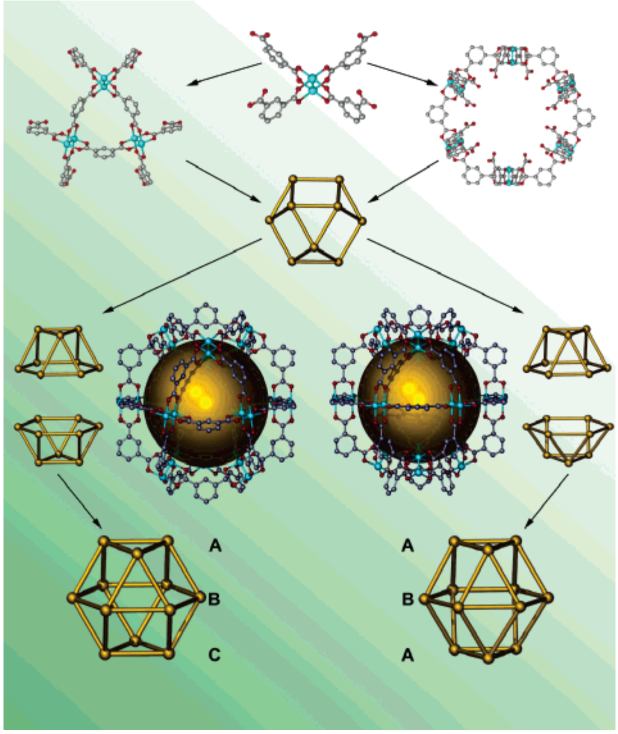

Figure 3. Assembly of the cuboctahedral and anticuboctahedral cages.

In both **1** and **2**, severely disordered solvent molecules inside the cages were found but not modeled.

The synthesis of **3** using BBDC and dicopper building blocks results in a cuboctahedral cluster identical in topology to **1**.

The cuboctahedron is one of the 13 Archimedean solids and, in particular, one of the two convex quasiregular polyhedra (the other being the icosidodecahedron). It is composed of eight equilateral triangles and six squares, all of the same edge length, and exhibits 12 identical vertices and O_h symmetry. The 12 vertices of the cuboctahedron correspond to the 12 nearest neighbors surrounding the central sphere in a cubically close-packed set of spheres.

If the cuboctahedron is bisected by one of the four equatorial planes (perpendicular to one of the C_3 axes), both the lower and upper halves form triangular cupolas with three squares and four triangles (Figure 3). Performing a C_6 rotation on one of the halves and rejoining the cupolas forms the triangular bicupola, or anticuboctahedron, with D_{3h} symmetry. The 12 vertices of the anticuboctahedron correspond to the 12 nearest neighbors around the central sphere in a hexagonally close-packed set of spheres.[9]

Taken as a group, the syntheses described herein result in both forms, depending on how the two "halves" of the polyhedron are assembled in solution, as shown in Figure 3.

Only the cuboctahedral structure was observed in Mo−BBDC and Cu−BBDC and the anticuboctahedral structure in Mo−BDC; however, only one crystal was measured for each. The possibility of forming both clusters in one pot cannot be excluded (vide infra).

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(8) Crystallographic data for **2**: $Mo_{24}C_{192}H_{96}O_{96}$, fw 6241.25, tetragonal, $I\bar{4}2m$, $a = b = 46.622(3)$ Å, $c = 43.695(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 94976(13)$ Å^3, $Z = 8$, $\rho_{calc} = 0.873$ g/cm^3, $\mu = 0.652$, R1 = 0.0601, wR2 = 0.1326.

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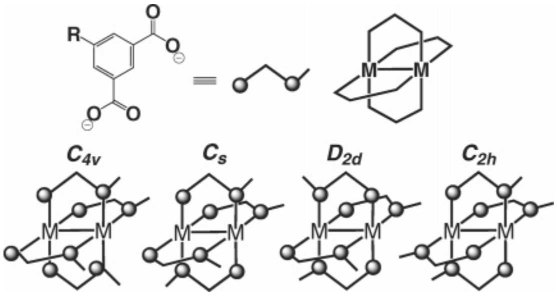

Figure 4. The four possible geometric arrangements of ligands around a paddlewheel dimetal unit.

In contrast to the reported Cu−BDC compounds, compound **1** is only very slightly soluble in solvents such as THF, toluene, and dichlorobenzene, and compounds **2** and **3** are almost insoluble. The absorption spectrum of **1** in THF shows a broad peak at $\lambda_{\max} = 442$ nm, which is ascribed to the $\delta \rightarrow \delta^*$ transition.[6a,10] Unfortunately, because of the very low molar solubility of the cluster, we have been unable at this point to collect a satisfactory cyclic voltammogram.

A fascinating aspect of the syntheses described above is the formation of both cuboctahedral and anticuboctahedral clusters from the same basic synthetic methods and materials. The following is our attempt to understand this unusual assembly behavior:

There are four geometric isomers of a paddlewheel compound containing four BDC ligands and one Mo−Mo unit (Figure 4), namely, the ones with idealized C_{4v}, C_s, D_{2d}, or C_{2h} point group symmetries. Although energetically there is little difference among the four isomers in this case, and thus an equal opportunity to form each of them, only the C_{4v} isomer will lead to the formation of a closed cage; the other isomers will instead result in the formation of coordination polymers. The C_{4v} isomer should be the starting point for cage assembly.

The C_{4v} paddlewheel will then serve as a template for the formation of a cis triangle of three C_{4v} paddlewheels (Figure 3). Again, only the cis triangle will lead to the formation of a closed cage. The trans triangle will generate coordination polymers. The cis triangle, with six carboxylate groups all pointing one direction, templates the formation of a hexagon of six paddlewheels to form a triangular cupola. The cupola, with its six carboxylate groups pointing to one direction, in turn, can serve as a template for the formation of a new triangle to close the cage. If the two triangles above and below the hexagon are aligned, the anticuboctahedron is obtained. Otherwise, the cuboctahedron will be the final product.

The triangular cupola can also be formed starting from the assembly of six C_{4v} paddlewheels by sharing a pair of trans carboxylate groups on each paddlewheel to form a hexagon with six carboxylate groups pointing to one direction and six other carboxylate groups pointing to the opposite direction (Figure 3). The hexagon can then serve as a template for the formation of the triangles above and below.

In both mechanisms, there are equal chances of formation of the cuboctahedral and anticuboctahedral cages. This is analogous to close-packing of spheres if one sphere is added at the center of a cage. The cuboctahedral cage corresponds to cubic close-packing (abcabc...), and the anticuboctahedron corresponds to hexagonal close-packing (abab...). Energetically there is no preference for the formation of one over the other.

The reason for the low yields (<36%) for the assembly reactions is evidently the precipitation of various coordination polymers. To increase the yield of cages, one needs to find ways to keep the starting material in solution before the precipitation of the cage product. Changing the ligand to a more soluble one, using starting materials such as $Mo_2(TFA)_4$ (TFA = trifluoroacetate), and running the reaction at elevated temperature are all possible means to improve the assembly procedure. Research along these lines is currently underway in our laboratory.

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Supporting Information Available: Synthetic details, absorption spectra, crystallographic data, and bond lengths and angles for **1**−**3** are available free of charge via the Internet at http://pubs.acs.org.

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