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Cucurbit[*n*]uril−Polyoxoanion Hybrids

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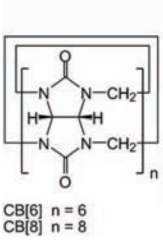
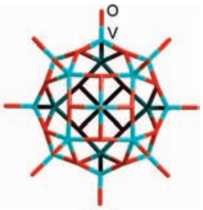
The emerging family of cucurbit[n]urils (CB[n], $n = 5, 6, 7,...$) now has become one of the preeminent synthetic receptors along with other macrocycles, such as crown ethers, cyclodextrins, and calixarenes. With a range of sizable cavities, they display a marked preference toward hosting positively charged guest species, and the related supramolecular chemistry has been extensively studied.[1] Little is known, however, about their interactions with anions, particularly those of sizes too large to act as guests.

Herein we describe the first hybrid complexes based on CB[n] and polyoxometalates (POMs),[2] a wide class of metal-oxide clusters generally characterized by large molecular structures and a wide range of (negative) charges. Hybridization of redox-active inorganic clusters with organic CB macrocycles could represent a versatile route to multifunctional materials that can combine the key merits of both sources, for example, magnetic, catalytic, zeolitic, and recognition properties. Indeed, this approach offers new perspectives in the design of functional porous materials, as will be seen. We will also show that the host−guest chemistry of CBs may be enhanced by the versatile redox behavior characteristic of POMs, providing a means to isolate reactive inclusion complexes that are otherwise difficult to obtain.



CB[6] n = 6
CB[8] n = 8

CB[6]



$\{V_{18}\}$

The POM of focus is a polyoxovanadate archetype, $[H_2O\subset V^{IV}{}_{18}O_{42}]^{12-}$.[3] This fully reduced polyoxoanion itself is capable of the uptake of ionic, as well as neutral guests (H_2O in this case), and derivatives with different V^{IV}:V^{V} ratios (16:2, 10:8) exist as well.[4] Synthesis of a hybrid complex of $\{V_{18}\}$ and CB[6] was accomplished by in situ generation of the polyoxoanion from $VOSO_4$ and hydroxide base in an alkaline solution of CB[6] under argon (Supporting Information). From the reaction mixture (dark red, pH ≈ 14), the potassium salt of anion complex $[CB[6](H_2O\subset V^{IV}{}_{18}O_{42})]^{12-}$ (**1a**) is isolated as brown needles (yield 77%).

The crystal structure of K_{12}**1a**$\cdot 27H_2O$ (**1**) shows striking complementarity between the inorganic and organic entities, as seen in a space-filling model (Figure 1a). Figure 1b illustrates the representative supramolecular interactions between $\{V_{18}\}$ and CB[6]. The CB/POM complexation is driven primarily by ion−dipole attraction, a highly directional force recognized for its role in stabilizing host−guest CB complexes through carbonyl oxygen binding to cationic guests.[1,5] However, this CB−POM hybrid **1** now exploits the very opposite end of the carbonyl dipole, the electron-deficient carbon sites. The close contacts between the two entities are reflected in short $V{=}O\cdots C{=}O$ distances, of only 3.00−3.09 Å, well below the sum of van der Waals radii, 3.25 Å. All relevant $O\cdots C{=}O$ angles tend toward 90°, resembling the orthogonal, polar contacts widely seen in proteins as well as some small organic molecules.[6] In addition, the two components are held together through a network of hydrogen bonding. As exemplified in Figure 1b, one μ_3-bridging oxygen from $\{V_{18}\}$ is hydrogen-bonded to two methine groups on a nearest glycoluril unit ($V{-}O\cdots H{-}C$, $C\cdots O$ distances: 3.23−3.33 Å), while a third, distant methine forms hydrogen bond to a terminal oxygen on $\{V_{18}\}$ ($V{=}O\cdots H{-}C$, $C\cdots O$ distance: 3.31 Å).

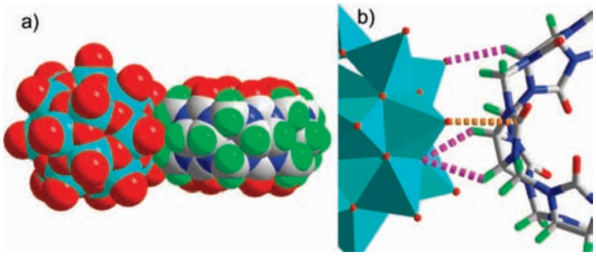


Figure 1. (a) Neighboring $\{V_{18}\}$ and CB[6] units of **1** in space-filling mode: V, cyan; O, red; C, gray; N, blue; H, green. (b) An enlarged view showing the supramolecular contacts (dotted lines): ion−dipole interaction in orange; hydrogen bonding in purple.

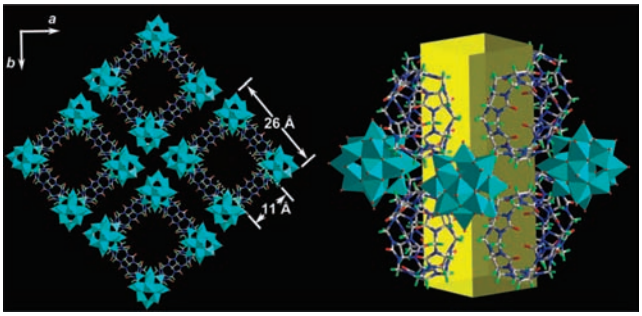


Figure 2. Extended structures of **1**. (left) Packing along *c*-axis (countercations and solvent molecules omitted for clarity); (right) the side view of a 1D square channel (highlighted in yellow).

The supramolecular assembly of **1** adopts a (4,4) packing motif in the solid state. Given this arrangement, each CB[6] or $\{V_{18}\}$ is involved in a total of 4 ion−dipole interactions and 12 hydrogen bonds with its neighbors (Supporting Information, Figure S1).

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Figure 2 shows how these supramolecular interactions collectively help to construct large infinite 1D square channels along the crystallographic *c*-axis that are lined with carbonyl functional groups. The square channels in the extended structure are built up from CB[6] "walls" with spherical $\{V_{18}\}$ anions indented at its four corners. The exterior of the channels spans over 26 Å and enclosed square openings are about 11 Å wide, close to the size of a Keggin ion. Some of the K^+ counterions are intercalated between the channels, further supporting the porous architecture via electrostatic attractions (with polyanions) and ion-dipole interactions ($K^+\cdots O{=}C$) that have been commonly observed.

When it comes to larger CB homologues, such as CB[8], their poor solubility poses a big challenge in hybrid syntheses. We eventually resorted to the inclusion complex of CB[8] with the methyl viologen dication (*N*,*N′*-dimethyl-4,4′-bipyridinium, MV^{2+}) because the cationic guest can remain protonated at high pH (>13), hence the resultant complex remains well soluble under such conditions. We found that, from this soluble CB[8] complex, a deep-violet CB[8]−$\{V_{18}\}$ hybrid (**2**) can be prepared in an analogous manner as **1** in nearly quantitative yields.

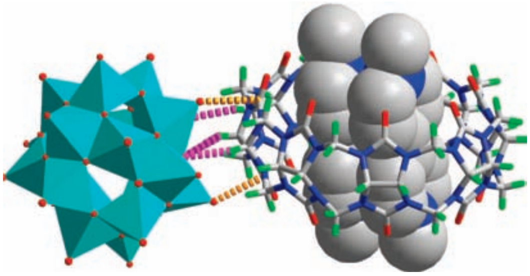

Figure 3. Neighboring CB[8] and $\{V_{18}\}$ of Na_{12}**2a**$\cdot 34H_2O$ (**2**); the dimeric (stacked) methyl viologen guests are shown in space-filling mode.

As shown in Figure 3, X-ray analysis of the crystalline product **2** reveals a very intriguing feature—a stacked viologen dimer (interplane distance, ca. 3.3 Å) is encapsulated in the macrocylic host, forming a ternary complex that has long been sought in CB chemistry. It was early recognized that CB[8] exclusively forms a 1:1 inclusion complex with MV^{2+} despite that its internal cavity is large enough to host two viologen molecules.[7] The $1e^-$-reduced form ($MV^{+\bullet}$), on the other hand, tends to dimerize in solution. Kim et al. have demonstrated that inclusion of the cation radical dimer in CB[8] can be achieved by electrochemical control[8] or addition of reductants,[9] as was confirmed by in situ spectroscopic methods. But the 2:1 ternary complex is not stable enough to be isolated and structurally characterized.

In **2**, the redox-active $\{V_{18}\}$ anion is believed to act as an electron donor and promote the transformation of $2MV^{2+} \rightarrow (MV^{+\bullet})_2$, making it possible for the first time to isolate the elusive inclusion species, $(MV^{+\bullet})_2\subset$CB[8], as an organic−inorganic hybrid compound. In the ^{1}H NMR spectrum, two additional peaks of similar intensity appear at 5.12 and 4.26 ppm (Figure S4) besides the distinctive CB[8] signals, which are considerably broadened because of contact with the paramagnetic $\{V_{18}\}$ cluster. They are attributed to bipyridinium units of $MV^{+\bullet}$ and both undergo significant upfield shifts compared to the 1:1 CB[8]/MV^{2+}complex.[7] The methyl signal, however, is likely concealed by the massive water peak contributed largely from crystal water in **2** (∼34 H_2O per molecule).

Therefore, the hybrid anion can be formulated as $[\{(MV^{+\bullet})_2\subset CB[8]\}(H_2O\subset V^{IV}{}_{16}V^{V}{}_2O_{42})]^{12-}$ (**2a**), where a mixed-valence $\{V_{18}\}$ polyoxoanion[10] results from the transfer of two e^- onto the viologen guests. Partial oxidation of the $\{V_{18}\}$ anion is evident from IR and magnetic susceptibility measurements. The characteristic $\nu(V{=}O_{terminal})$ band shifts from 951 cm^{-1} for **1** to 973 cm^{-1} for **2** (Figure S5). Compound **2** also gives a lower room-temperature $\chi_M T$ value, 2.1 emu K mol^{-1}, compared to 2.8 emu K mol^{-1} for **1**. The data both are in good agreement with those reported previously for $\{V^{IV}{}_{16}V^{V}{}_2\}$ species.[4]

Hybrid **2** displays very similar supramolecular interactions (Figure 3) as seen in **1**, but with two short ion-dipole attractions ($V{=}O\cdots C{=}O$ distances, 2.99−3.01 Å) on each CB[8]/$\{V_{18}\}$ contact. Although still assuming the (4,4) packing mode in the solid state (Figure S2), it does not form the porous channel architecture as anticipated. Instead of packing face-to-face, the CB[8] macrocycles in **2** are all oriented with an offset toward each other (Figure S3). We attribute this to the presence of viologen guest molecules, which would generate considerable steric repulsion for a direct face-to-face packing mode. But the common features in CB−POM contacts and crystal packing mode in **1** and **2** suggest that deliberate control of such hybrid assemblies is possible with the right choices of polyoxoanion, CB and its guest(s), considering their size, shape, and solubility issues.[11]

Work is in progress to further define the physical properties and redox behaviors of these and other hybrids between CB[*n*] and POMs. Given the scope of both areas and the current interest in them, there should be extensive chemistry and physics to be discovered in this uncharted territory.

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Supporting Information Available: Experimental details, additional figures, IR, NMR, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The $\{V^{IV}{}_{18}O_{42}\}$ cluster can be partially oxidized to virtually isostructural derivatives, in which the V(3d) electrons are highly delocalized over the entire shell, resulting in structurally equivalent sites. See ref 4a.

(11) The composition, structure and properties of polyoxometalates can be extensively modified. In this context, it should be noted that the archetypal $\{V_{18}O_{42}\}$ cluster can, for example, adopt two different configurations in which the cluster's 24 μ_3-O sites span either a rhombicuboctahedron (T_d) or a pseudorhombicuboctahedron (D_{4d}), and the cluster can encapsulate different anionic guests to give rise to tunable surface properties. See ref. 4a and: Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328.

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