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Inclusion of a Cu^{2+} Ion by a Large-Cavity Crown Ether Dibenzo-24-Crown-8 through Supramolecular Interactions[†]

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A supramolecular copper–aqua–crown ether complex, $[Cu^{II}(H_2O)_4$(dibenzo-24-crown-8)$]^{2+}$ (**1c**) is stabilized with a Lindqvist-type polyoxometalate anion, $[Mo^{VI}_6O_{19}]^{2-}$ (**1a**), in an ion-pair compound $[Cu^{II}(H_2O)_4$(dibenzo-24-crown-8)$][Mo^{VI}_6O_{19}] \equiv$ [**1c**][**1a**] $\equiv$ **1**. In the crystal, **1c** and **1a** assemble to a chainlike structure in which each polyoxoanion **1a** is sandwiched by two **1c** cations. **1c** is a structurally characterized dibenzo-24-crown-8 (a larger-cavity crown ether) supramolecular complex that shows encapsulation of a small cation at the center of its internal cavity, and compound **1** represents a unique example of a first-row transition metal–crown ether inclusion complex that interacts with a polyoxometalate anion.

Crown ethers have been extensively used in supramolecular chemistry because they have potential applications in molecular recognition, transportation, and catalysis.[1] The most striking characteristics of crown ethers is their selective complexation ability with the cationic species.[2] These macrocyclic polyethers (crown ethers), which have “hard” donor atoms, do not readily form complexes with first-row transition metals in their low oxidation states because such metal ions provide only “soft” coordination (acceptor) sites. Only a small number of first-row transition metal−crown ether complexes had been structurally characterized, in which the direct bond formation between the transition metal and the crown ether oxygens became possible (in complexes with the smaller ring crown ethers, e.g., 15-crown-5 and 12-crown-4 ethers).[3] In the case of (comparatively) larger ring crown ethers, the linkage between the metal center and the crown ether is usually provided by one or more water molecules that are directly coordinated to the metal ion and hydrogen-bonded to the oxygens of the crown ether. In such cases, the crown ethers act as second-sphere ligands.[4] The macrocyclic polyether dibenzo-24-crown-8, originally synthesized by Pedersen,[2a] has been shown to form complexes with alkaline and alkaline-earth metal ions[4f] and a $ScCl_2^+$ ion (as a first-row transition-metal complex ion).[4a] Most of these dibenzo-24-crown-8 complexes include both direct linkage and second-sphere complex formation via hydrogen-bonding interactions. Because dibenzo-24-crown-8 is a relatively larger cavity crown ether, it accommodates more than one K^+ in its cavity using direct covalent bonds[5] and it hosts one Ba^{2+} ion[6] (a bigger cation) or one $ScCl_2^+$ ion through both direct coordination and second-sphere complexation but in an “off-center” position.[4a,6] The encapsulation of any cation at the center of the cavity of dibenzo-24-crown-8 has not yet been achieved probably because of its larger cavity size and flexible nature. We report here the inclusion of a Cu^{2+} ion (a cation, smaller than a Na^+ ion) by introducing a polyoxomolybdate anion $[Mo_6O_{19}]^{2-}$ that stabilizes the Cu^{2+} ion at the center of the “large-cavity crown ether” dibenzo-24-crown-8 via supramolecular hydrogen-bonding interactions. The coexistence of polyoxoanion and crown ether has attracted special attention and opened a new field in the area of polyoxometalate (POM) chemistry.[7] The crown ethers, supported by polyoxoanions, can be used to separate specific metal ions (depending on the cavity size of the crown ether) from aqueous solutions by precipitation methods.[8] To date, the reported crown ether−POM compounds contain mostly alkali and alkaline-earth metals[7a−i] and sometimes lanthanides[7j] and hydronium ions[7g] as cations.

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[†] Dedicated to Professor Animesh Chakravorty on the occasion of his 70th birthday.

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To our knowledge, no first-row d-block transition metal–crown ether inclusion complex that interacts with a POM anion has yet been reported. Such systems would be important and valuable additions in the area of POM chemistry because of their interesting physical properties and thereby their applications in interdisciplinary areas. We describe here a copper–aqua–crown ether inclusion complex, $[Cu^{II}(H_2O)_4(\text{dibenzo-24-crown-8})]^{2+}$ (**1c**), that sandwiches a Lindqvist-type POM anion, $[Mo^{VI}_6O_{19}]^{2-}$ (**1a**), forming a chainlike arrangement in the title compound $[Cu^{II}(H_2O)_4(\text{dibenzo-24-crown-8})][Mo^{VI}_6O_{19}] \equiv$ [**1c**][**1a**] $\equiv$ **1**.

Compound **1** was prepared[9] as brown rectangular-shaped blocks from an acetonitrile solution dissolving dibenzo-24-crown-8 ($C_{24}H_{32}O_8$), $[Bu_4N]_2[Mo_6O_{19}]$, and $Cu(NO_3)_2 \cdot 3H_2O$. The crystals of **1** were characterized by IR, elemental analysis,[10] visible, and ESR spectroscopy and unambiguously by a single-crystal X-ray diffraction technique.[11]

The crystal structure of **1** consists of **1c** as a cation and **1a** as an anion. The crystal structure of **1** is shown in Figure 1.

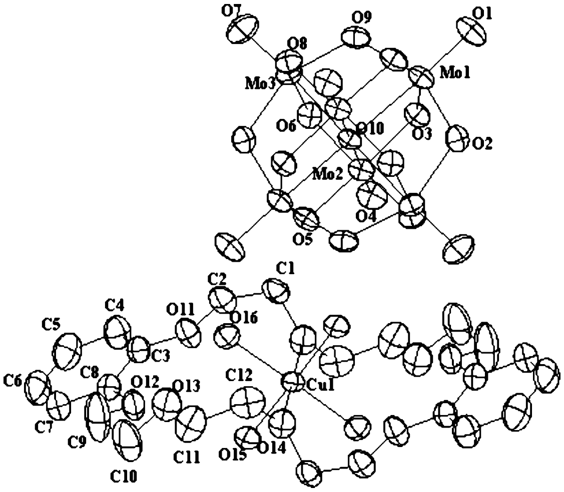

Figure 1. Thermal ellipsoid plot of **1c** (bottom) and **1a** (top) in **1**. Hydrogen atoms of the crown ether and water molecules have been omitted for clarity.

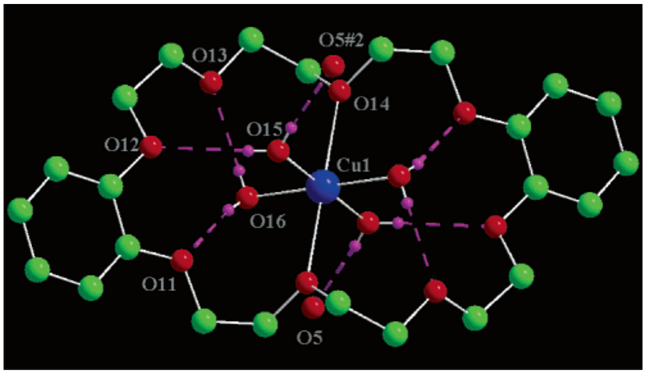

Figure 2. View of **1c** showing direct Cu–crown ether bonding and the interactivity hydrogen bonding as second-sphere complexation. Color code: Cu, blue; O, red; C, green; H, purple. Hydrogen bonds are shown as dashed purple lines. Hydrogen-bonding parameters: O15–H15Y···O5#2, 0.69(4), 2.07(4), and 2.751(3) Å, 173(4)°; O15–H15X···O12, 0.66(3), 2.23(3), and 2.883(3) Å, 165(4)°; O16–H16Y···O13, 0.65(4), 2.06(4), and 2.688(3) Å, 165(4)°; O16–H16X···O11, 0.62(3), 2.18(3), and 2.789(3) Å, 166(4)°.

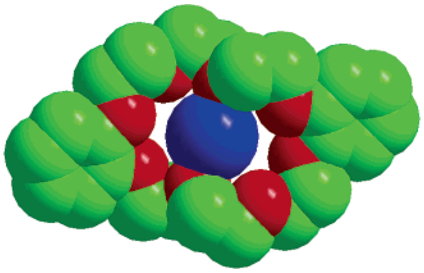

Figure 3. Space-filling plot of the crown ether dibenzo-24-crown-8 that encapsulates the Cu^{2+} ion at the center of the cavity. Copper-coordinated water molecules and relevant hydrogen bonds are not shown. Color code: Cu, blue; O, red; C, green.

The structure of cation **1c** is separately shown in Figures 2 and 3. The Cu^{2+} ion sits exactly at the center (that is, the crystallographic inversion center) of the octagon consisting of polyether oxygen atoms. In **1c**, the copper center is coordinated by two trans ethereal oxygen atoms (O14) of the crown ether and four water molecules (two O15 and two O16 atoms) to give a distorted octahedral geometry around copper. The average equatorial $Cu-OH_2$ distance of 1.957(2) Å is considerably smaller than those in other related copper–aqua complexes.[12] This is probably the result of exclusive hydrogen-bonding interactions (vide infra). The coordination of crown ether–oxygen atoms at the apical sites of the copper ion (average axial Cu–O = 2.383(2) Å) is the geometrical constraint for a large-cavity crown ether dibenzo-24-crown-8. Upon complex formation, the 24-membered ring of the free ligand dibenzo-24-crown-8, which takes a planar

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(9) Dibenzo-24-crown-8 (0.2 g, 0.044 mmol) was dissolved in 35 mL of acetonitrile. After it was dissolved completely, $[Bu_4N]_2[Mo_6O_{19}]$ (0.2 g, 0.14 mmol) was added to the above reaction mixture under stirring conditions, followed by the addition of copper nitrate (1.0 g, 4.13 mmol), resulting in a green color solution. This reaction mixture was further stirred for 14 h under open conditions at room temperature. It was then filtered, and the filtrate was kept in an open flask for 4 days. The brown crystals that precipitated during this time were filtered, washed with 100 mL of water, and dried at room temperature. Yield: 0.03 g (54% based on crown ether).

(10) Anal. Calcd for $C_{24}H_{40}CuMo_6O_{31}$ (1463.74): C, 19.69; H, 2.75. Found: C, 19.46; H, 2.81.

(11) Crystal data of **1**: $C_{24}H_{40}CuMo_6O_{31}$, $M = 1463.74$ g mol^{-1}, triclinic, space group $P\bar{1}$, $a = 9.3293(6)$ Å, $b = 10.8783(7)$ Å, $c = 12.2488(7)$ Å, $\alpha = 101.6260(10)°$, $\beta = 107.7010(10)°$, $\gamma = 111.9120(10)°$, $U = 1026.55(11)$ Å^3, $Z = 1$, $D_C = 2.368$ g cm^{-3}, $\mu = 2.386$ mm^{-1}, $F(000) = 713$, crystal size = 0.30 × 0.18 × 0.12 mm^3. 11930 reflections were measured with 4762 unique reflections ($R_{int} = 0.0388$), of which 4316 ($I > 2\sigma(I)$) were used for the structure solution. Final R1 (wR2) = 0.0241 (0.0613), 299 parameters. The final Fourier difference synthesis showed minimum and maximum peaks of −0.496 and +0.567 e Å^{-3}.

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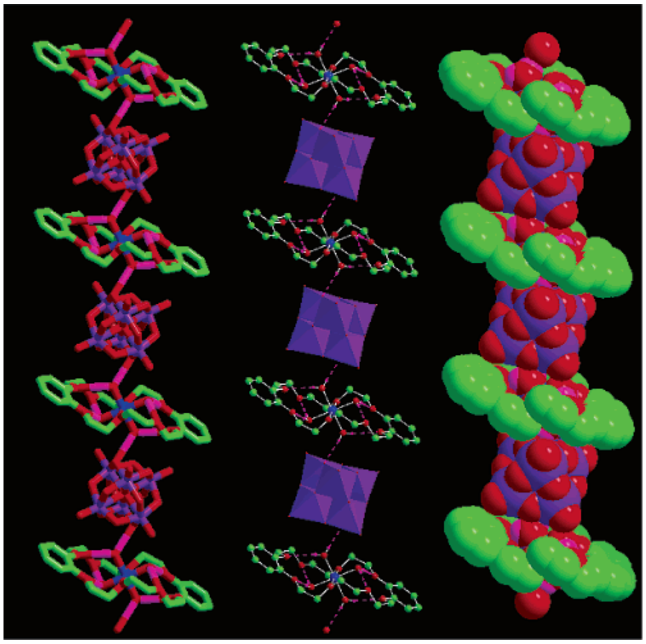

Figure 4. View illustrating intermolecular O−H···O hydrogen-bonded interactions between **1c** and **1a** that lead to the formation of a supramolecular sandwich-type chainlike arrangement. From left to right: polyhedral (**1a**) representation, wire frame, and space-filling plot. Color code: Cu, blue; Mo, violet; O, red; C, green; H, purple.

conformation,[13] changes to a chairlike structure. This is consistent with the differences in torsion angles in the rings of free dibenzo-24-crown-8 and in complex **1c** (see the Supporting Information). Six hydrogen atoms of four copper-coordinated water molecules get hydrogen-bonded to the crown ether via ethereal oxygen atoms, making **1c** a unique supramolecular entity. The other two hydrogen atoms of the copper-coordinated waters are hydrogen-bonded to two bridging oxygen atoms (O5) of two neighboring POM anions $[Mo^{VI}_6O_{19}]^{2-}$.

This results in the formation of a supramolecular chainlike arrangement, along which the isopolyanion **1a** is sandwiched by two copper−aqua−crown ether complex cations (**1c**) and so on, as shown in Figure 4. We believe that the isopolyanion **1a** plays an important role in the encapsulation of the copper ion at the center of the cavity of the larger ring crown ether dibenzo-24-crown-8 by stabilizing a tetra-aqua−Cu(II) complex $[Cu(H_2O)_4]^{2+}$ and forming a sandwichlike arrangement that consists of **1c** and **1a**. Indeed, the O−H···O hydrogen bonds involving isopolyanion **1a** are stronger among all eight hydrogen bonds as far as the ∠OHO angle is concerned (see the caption of Figure 2). In the polyanion **1a**, each Mo atom is surrounded by a distorted octahedron consisting of one central O_c, one terminal O_t, and four bridging O_b atoms (Figure 1). This anion has approximate O_h symmetry. Compound **1** is a paradigm of direct encapsulation of a first-row transition-metal ion by this large-cavity crown ether that exists with a POM anion. Remarkably, the complex cation **1c** is unique in the sense that, besides the inclusion of a Cu^{2+} ion at the center of its cavity, all eight water hydrogens and crown ether oxygens are exclusively involved in supramolecular interactions (Figure 2).

In the IR spectrum of compound **1**, the copper-coordinated water molecules appear as well-resolved peaks at 3308 and 3076 cm^{-1}, supporting the theory that all hydrogen atoms in **1** are involved in hydrogen-bonding interactions. ESR spectra measured at liquid-nitrogen temperature and room temperature showed the g anisotropy with axial symmetry ($g_{\|} > g_{\perp}$). The electronic reflectance spectrum consists of a broad band with a maximum at 800 nm, which can be assigned to d−d transition for a Cu^{2+} (d^9) system (see the Supporting Information for IR, ESR, and electronic spectral figures and related discussions).

In summary, complex **1c** is a novel example in which a large-cavity crown ether dibenzo-24-crown-8 includes a considerably smaller cation Cu^{2+} ion at the center of its internal cavity. We have described a unique system **1** that comprises a first-row transition-metal-encapsulated crown ether supramolecular complex interacting with a POM anion. Compound **1** represents a rare example of a first-row transition metal−tetra-aqua supramolecular complex in inorganic crown ether chemistry and a new sandwich-type organic−inorganic hybrid material in POM chemistry.

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Supporting Information Available: Text and figures depicting IR, ESR, and electronic spectral studies, figures related to the crystal structure of **1**, tables of torsion angles and hydrogen-bonding parameters, and X-ray crystallographic data for **1** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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