Supramolecular Chemistry

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Fivefold Coordination of a Cu^{II}–Aqua Ion: A Supramolecular Sandwich Consisting of Two Crown Ether Molecules and a Trigonal-Bipyramidal $[Cu(H_2O)_5]^{2+}$ Complex**

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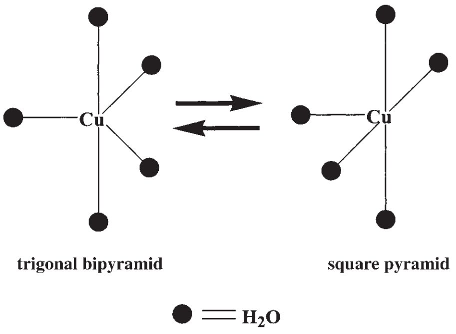
Copper ions play an important role in biological systems; for example, a normal human body contains between 80 and 120 mg of copper as one of the essential elements.[1] The more common oxidation state of copper is +2. However, the simplest aqueous form of the Cu^{II} ion is still not clearly understood. More than 40 years ago, aqueous solution-state divalent copper ions were presumed to have a tetragonal four-coordinate structure.[2,3] It was subsequently considered to be a distorted octahedral hexaqua ion,[4–7] based on ESR experiments and single-crystal spectroscopy of hexaqua copper(II) complexes.[8,9]

It is generally assumed that a Cu^{II} ion in an aqueous solution forms an octahedral $[Cu(H_2O)_6]^{2+}$ complex that undergoes Jahn–Teller distortion with elongated axial bonds because of its d^9 electronic configuration.[10–22] The shorter (equatorial) Cu–O bonds lengths in aqueous solution have been characterized by several experimental techniques including EXAFS (extended X-ray absorption fine structure),[13–16] XANES (X-ray absorption near-edge structure),[15] and isotropic substitution in neutron diffraction.[17–19] These physical studies provide consistent values for the equatorial Cu–O bond lengths in the range from 1.94 to 2.00 Å. The longer axial bond lengths obtained experimentally range from 2.12 to 2.60 Å,[19] because experimental techniques such as EXAFS and XANES require fitting procedures that incorporate some a priori assumptions about the structure.[10–16]

In 2001, Pasquarello and co-workers reported their combined experimental and theoretical investigation on the structure and dynamics of hydrated copper(II) in aqueous solution.[23] They determined the structure by both neutron diffraction and first principles molecular dynamics. The major breakthrough is that, in contrast to the generally accepted picture that assumes the Cu^{II} ion has an octahedral environment of solvent molecules, their experimental and theoretical results favor fivefold coordination around a copper center, $[Cu(H_2O)_5]^{2+}$. The solvated complex, $[Cu(H_2O)_5]^{2+}$, undergoes frequent transformations between square-pyramidal and trigonal-bipyramidal (tbp) configurations by a Berry twist mechanism (Scheme 1).[24] Fivefold coordination of water molecules around a Cu^{2+} ion in a tbp geometry is one of the possible conformations.[23] However, to date there is no crystallographic evidence of a tbp $[Cu(H_2O)_5]^{2+}$ ion to confirm unambiguously its existence. We report herein the crystal structure of a "supramolecular sandwich" consisting of two crown ether molecules ([18]crown-6) that stabilize a tbp $[Cu(H_2O)_5]^{2+}$ cation with a polyoxomolybdate ion, $[Mo_6O_{19}]^{2-}$, in the compound $[Cu(H_2O)_5([18]crown\text{-}6)_2][Mo_6O_{19}]$ (**1**), which was obtained according to Equation (1).



Scheme 1. Interconversion between square-pyramidal and tbp configurations by a Berry twist mechanism.

$$Cu(NO_3)_2\cdot 3\,H_2O + 2\,[18]crown\text{-}6 + (Bu_4N)_2[Mo_6O_{19}] + 2\,H_2O \rightarrow [Cu(H_2O)_5([18]crown\text{-}6)_2][Mo_6O_{19}]\ (\mathbf{1}) + 2\,[Bu_4N]NO_3 \qquad (1)$$

This is the first metal–aqua complex that is perfectly sandwiched by two crown ether molecules through well-defined hydrogen bonds that involve metal-coordinated water molecules and oxygen atoms of the crown ether molecules.

Compound **1** was characterized by elemental analysis, thermogravimetric analysis (TGA), single-crystal X-ray structure analysis,[25] and spectroscopic methods (IR, UV/Vis, EPR). In its crystal structure $[Cu(H_2O)_5([18]crown\text{-}6)_2]^{2+}$ and $[Mo_6O_{19}]^{2-}$ ions are present as shown in Figure 1. In the isopolyanion $[Mo^{VI}{}_6O_{19}]^{2-}$ (also known as Lindqvist type polyoxometalate (POM) anion) each Mo atom is surrounded by a distorted octahedron consisting of one central (O_c), one terminal (O_t), and four bridging (O_b) oxygen atoms (Figure 1). The Mo–O bond lengths can be grouped into three sets: Mo–O_t 1.677–1.694, Mo–O_b 1.851–2.021, and Mo–O_c 2.308–2.329 Å. The bond angle of Mo-O_b-Mo is 116.0–117.1°, while that of Mo-O_c-Mo is 179.5–179.7°.

The most exciting feature of the structure is the presence of a hitherto elusive tbp $[Cu(H_2O)_5]^{2+}$ ion that is flawlessly sandwiched by two crown ether molecules through O–H···O hydrogen-bonding interactions (Figure 2). The exactness of

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

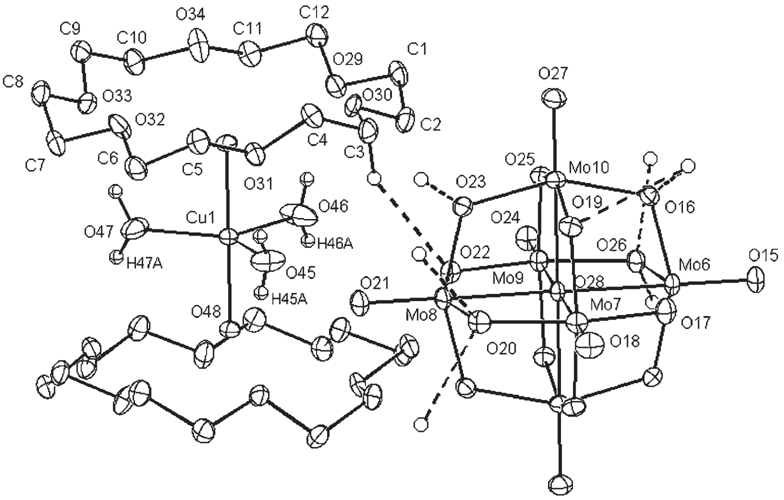

Figure 1. X-ray crystal structure of **1** as a thermal ellipsoidal plot (hydrogen atoms of the crown ether molecules are omitted for clarity). Oxygen atoms O16, O19, O20, O22, and O26 of the isopolyanion $[Mo_6O_{19}]^{2-}$ are involved in C−H⋯O hydrogen-bonding interactions. White circles are hydrogen atoms from surrounding crown ether molecules (see also Figure 3 in the context of molecular clipping).

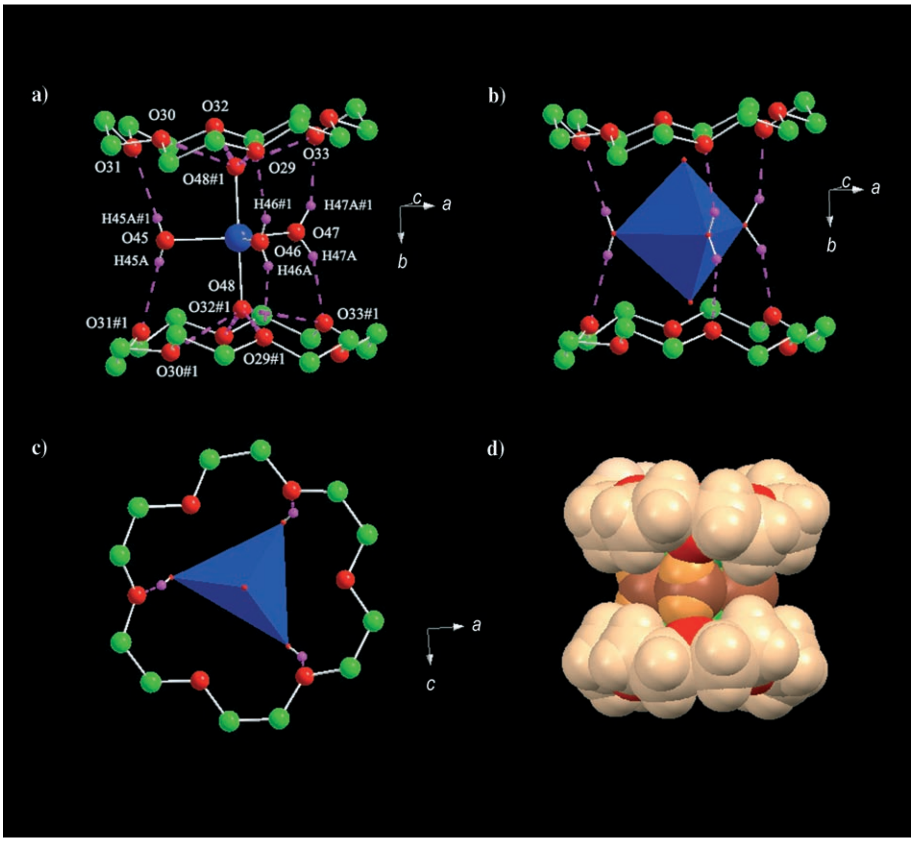

Figure 2. Supramolecular sandwich $[Cu(H_2O)_5([18]crown\text{-}6)_2]^{2+}$ consisting of two crown ether molecules and a tbp pentaaqua copper(II) ion: a) ball-and-stick representation; b) polyhedral representation of the $[Cu(H_2O)_5]^{2+}$ ion; c) view along the crystallographic *b* axis showing the exactness of the sandwich. Cu blue; O red; C green; H purple; hydrogen bonds are shown as purple dashed lines; d) space-filling plot of the sandwich. Hydrogen bonds between axial water and crown ether molecules are shown in Figure 2a but not in Figure 2b)–d) for clarity. Hydrogen-bonding parameters: O45−H45A⋯O31#1: 0.68(3), 2.05(3), 2.714(2), 169(5); O46−H46A⋯O29#1: 0.74(3), 1.99(3), 2.684(2), 157(3); O47−H47A⋯O33#1: 0.83(3), 1.94(3), 2.709(2), 155(3); O48⋯O29#1: 2.975(2); O48⋯O30#1: 2.833(2); O48⋯O32#1: 2.946(3); O48⋯O33#1: 2.976(2).

the sandwich with respect to the crown ether molecules is clearly evident when it is viewed down the crystallographic *b* axis (Figure 2c). The local molecular structure of $[Cu(H_2O)_5]^{2+}$ in the supramolecular sandwich $[Cu(H_2O)_5([18]crown\text{-}6)_2]^{2+}$ involves a five-coordinate $\{CuO_5\}$ chromophore with tbp geometry. The two out-of-plane Cu1−O48 bond lengths (related by a symmetry operation) are identical (1.936 Å) and form an almost perfect line, with O48-Cu1-O48 179.7°. The in-plane Cu−O distances are not significantly different (av = 2.012 Å) and longer than the out-of-plane Cu−O bonds by 0.076 Å.

The out-of-plane angle of exactly 90° (Figures 1 and 2) is rarely observed, as previously reported tbp copper complexes showed out-of-plane angular distortions of (90 ± 10)°.[26] However, the in-plane angles show very significant deviations from the 120° necessary for ideal tbp geometry: O45-Cu1-O46 113.43(16)°; O46-Cu1-O47 112.86(18)°; O45-Cu1-O47 133.72(16)° (Figure 1). This deviation, which is not significantly reflected in the in-plane Cu−O bond lengths, may be due to the fact that each axial water molecule, having two hydrogen atoms, cannot interact in a highly symmetrical fashion with the crown ether molecules (see Figure 2a). The sense of this deviation can also be rationalized in terms of the pathway of the Berry twist mechanism (Scheme 1), which describes the interconversion of a complex of regular tbp geometry to that of regular square-pyramidal geometry through bonding modes of vibration of a $\{CuO_5\}$ chromophore of C_{2v} symmetry. This interconversion occurs because the tbp and square-planar forms are energetically comparable.[27]

In the present study, the tbp coordination geometry around the Cu center in the $[Cu(H_2O)_5]^{2+}$ ion is governed by the participation of the ion in forming a supramolecular sandwich with two crown ether molecules that involves hydrogen-bonding interactions of copper-coordinated water molecules and oxygen atoms of the crown ether molecules (Figure 2). The formation of the sandwich can be explained by the fact that each of the equatorial water molecules of the tbp $[Cu(H_2O)_5]^{2+}$ ion forms hydrogen bonds with both upper and lower crown ether molecules, thus bringing the crown ether molecules closer together. This interaction accounts for the significant deviations of H-O-H angles (111.6, 119, and 121.4°) in the copper-coordinated equatorial water molecules from the ideal (≈109°). The relevant hydrogen-bonding parameters are provided as Supporting Information.

The Lindqvist type anion $[Mo_6O_{19}]^{2-}$ plays an important role in arranging the crown ether molecules in the crystal of **1** and therefore may be called a sandwich "clipper" (Figure 3). In the crystal, each sandwich is anchored—through C–H···O hydrogen bonds—by four surrounding isopolyanions and, similarly, each isopolyanion is hydrogen-bonded to four surrounding sandwich complexes. It is remarkable that each polyanion extends its four pairs of C–H···O hydrogen-bonding "hands" towards four sandwich complexes in such a way that each pair of hands uses one hand to attach the upper and the other hand to fasten the lower crown ether molecule of the sandwich (the relevant C–H···O hydrogen-bonding parameters are described in the Supporting Information). This situation is equivalent to each sandwich being clipped by four surrounding isopolyanions. The clipping of the sandwich by surrounding isopolyanions is presented in Figure 3.

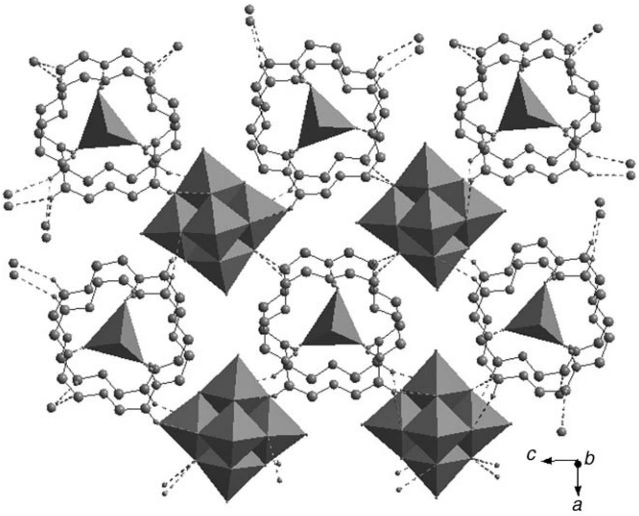

Figure 3. Representation of the clipping of the sandwich by the isopolyanions $[Mo_6O_{19}]^{2-}$. Isopolyanions and copper–aqua ions are shown in polyhedral representation.

Two independent $[Mo_6O_{19}]^{2-}$ isopolyanions and two independent sandwich complexes appear in the crystal structure of **1**. The oxygen atoms of one of the polyanions involved in molecular clipping through the C–H···O hydrogen bonds include O16, O19, O20, O22, and O26 (Figure 1). A similar pictorial representation of the other isopolyanion in the crystal of **1**, which shows four oxygen atoms (O2, O5, O9, and O12) interacting with surrounding crown ether molecules through C–H···O hydrogen bonds, is presented in the Supporting Information. The tbp $[Cu(H_2O)_5]^{2+}$ ion sandwiched by two crown ether molecules shows a tetragonal compression (see above) instead of a tetragonal elongation toward the apical positions. The fact that the tbp $[Cu(H_2O)_5]^{2+}$ ion is sandwiched by two crown ether molecules, which in turn are supported by surrounding polyoxometalate anions, is seemingly the driving force for the formation of a compressed tbp $[Cu(H_2O)_5]^{2+}$ complex cation.

ESR spectra of the complex also indicate the presence of an axially compressed trigonal geometry, as characterized by a d_{z^2} electronic ground state. Both room-temperature and liquid-nitrogen-temperature powder ESR spectra of compound **1** exhibit an inverse $g_\perp > g_\parallel > g_e$ pattern (g_e: g factor of the free electron (=2.0023)) (Figure 4; $g_\perp = 2.235$, $g_\parallel = 2.04$). The solid-state electronic reflectance spectrum of **1** shows a broad peak centered at about 820 nm (see the Supporting Information). This spectrum is comparable with the visible/near-IR spectrum of an aqueous solution of Cu^{II} ions, which exhibits a broad band at around 820 nm. Is this result consistent with fivefold coordination of a Cu center? Pasquarello and co-workers calculated the joint density between the relevant filled and empty d states. For comparison, they also calculated such a density of states for a $[Cu(H_2O)_6]^{2+}$ ion and found that the two calculated spectra were essentially indistinguishable, which suggests that the transition energies are not substantially affected by the different bonding hybridizations in the five- and six-coordinated Cu^{II} complexes. Their calculated spectra showed a fair agreement with the experimental absorption spectrum.[23]

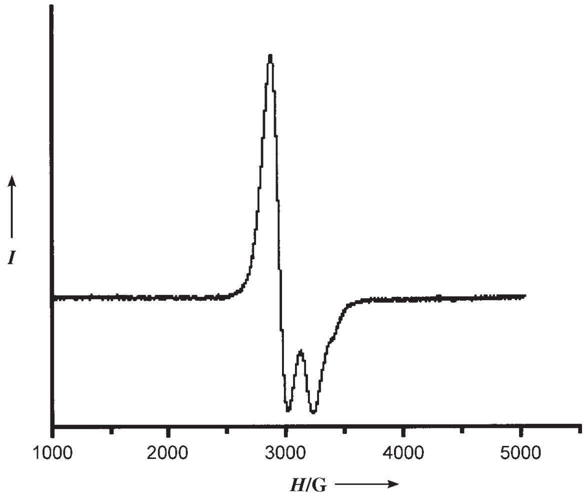

Figure 4. ESR spectrum of a powdered sample of **1** at liquid-nitrogen temperature.

TGA performed on **1** showed a weight loss (3.42 %) at around 100 °C that corresponds to the loss of three water molecules (calcd 3.46 %). We argue that these three water molecules are the equatorially coordinated of the tbp $[Cu(H_2O)_5]^{2+}$ ion. The other two water molecules (axially coordinated) are lost along with two crown ether molecules at around 200 °C. This is reflected in the second loss of the TGA curve (weight loss = 35.70 %; calcd weight loss 36.17 %; see the Supporting Information).

To conclude, the structure of a hydrated Cu^{II} complex was determined recently by both neutron diffraction (experimental) and first-principles molecular dynamics (theoretical) and these results favor fivefold coordination of water molecules around the Cu^{II} ion. This conclusion is in contrast with the generally accepted picture of an octahedrally solvated Cu^{II} ion. We have described here unambiguous crystallographic evidence of fivefold coordination of a aqua–Cu^{II} ion with tbp geometry, which is sandwiched by two crown ether molecules. We have named this a supramolecular sandwich. The polyoxometalate anion $[Mo_6O_{19}]^{2-}$ plays an important role in stabilizing the unique supramolecular ion $[Cu(H_2O)_5([18]crown\text{-}6)_2]^{2+}$.

Experimental Section

[18]Crown-6 ($C_{12}H_{24}O_6$; 0.06 g, 0.227 mmol) was dissolved in glacial acetic acid (10 mL), then acetonitrile was added (50 mL). To this reaction mixture, $(Bu_4N)_2[(Mo_6O_{19}]$ (0.03 g, 0.022 mmol) was added to give a light yellow solution to which $Cu(NO_3)_2{\cdot}3H_2O$ (0.125 g, 0.51 mmol) was added, and the resulting reaction mixture was stirred at room temperature for 24 h in an open reaction vessel. The resulting bluish-green solution was filtered and left to stand. Light green crystals were rendered by the solution; these crystals were isolated by filtration and washed with water (100 mL). Yield: 0.03 g (87 % based on the quantity of molybdenum cluster used).

C,H analysis calcd (%) for $C_{24}H_{58}CuMo_6O_{36}$ (**1**): C 18.45, H 3.74; found: C 18.61, H 3.65. IR (KBr pellet): $\tilde{\nu} = 794$ (s), 954 (vs), 1107 (s), 1253 (m), 1288 (m), 1352 (s), 1469 (s), 1612 (w), 2874 (m), 2910 (m), 3252 cm^{-1} (br).

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[25] Crystal data for **1**: $C_{24}H_{58}CuMo_6O_{36}$, $M = 1561.88\ g\,mol^{-1}$, orthorhombic, space group *Pnma*, $a = 22.5866(11)$, $b = 18.1787(9)$, $c = 22.5402(11)$ Å, $V = 9254.9(8)$ Å^3, $Z = 8$, $\rho = 2.242\ Mg\,m^{-3}$, $\mu = 2.132\ mm^{-1}$, $F(000) = 6168$, crystal size $= 0.34 \times 0.32 \times 0.13\ mm^3$. Crystals of **1** were removed from mother liquor and washed with distilled water cooled to 183(2) K on a Bruker SMART APEX CCD area detector system [$\lambda(Mo_{K\alpha}) = 0.71073$ Å], graphite monochromator, 1315 frames were recorded with an ω scan width of 0.3°, each for 10 s, crystal–detector distance 60 mm, collimator 0.5 mm. A total of 57892 reflections ($1.44 < \theta < 28.28°$) were collected of which 11495 reflections were unique ($R_{int} = 0.0848$). An empirical absorption correction using equivalent reflections was performed with the program SADABS.[28] The structure was solved with the program SHELXS-97[29] and refined using SHELXL-97[30] to $R = 0.0325$ for 9901 reflections with $I > 2\sigma(I)$, $R = 0.0383$ for all reflections; max/min residual electron density 1.160 and $-1.968\ e\,Å^{-3}$. Two independent $[Mo_6O_{19}]^{2-}$ clusters and two independent $[Cu(H_2O)_5(C_{12}H_{24}O_6)_2]^{2+}$ ions appear in the crystal structure of **1**. All equatorial water-hydrogen atoms were located in one tbp $[Cu(H_2O)_5]^{2+}$ ion; in the other tbp $[Cu(H_2O)_5]^{2+}$ ion, two equatorial water-hydrogen atoms could be located. The hydrogen atoms of the axial water ligands could not be located in both cases. The located hydrogen atoms were picked up from differential Fourier maps and their positions were refined using isotropic thermal parameters. CCDC-282495 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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