A Polyoxothiometalate Tetramer

A Supramolecular Tetra-Dawson Polyoxothiometalate: $[(\alpha\text{-}H_2P_2W_{15}O_{56})_4\{Mo_2O_2S_2(H_2O)_2\}_4\{Mo_4S_4O_4(OH)_2(H_2O)\}_2]^{28-}$

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The control of the aggregation processes in supramolecular inorganic chemistry is one of the keys for the targeted synthesis of mesoscopic materials with a high level of complexity. In this context, the self-assembly of modular inorganic systems into larger structures constitutes a rational

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approach to reach structures on the nanometer scale. Polyoxometalate (POM) chemistry has provided a huge diversity of compounds with a variety of exciting behaviors, such as catalytic, magnetic, and anti(retro)viral properties.[1] For several years, we have been exploring a fundamentally fruitful strategy, namely "the building-block strategy" which consists in the self-assembly of preformed building units.[2] Highly negatively charged polyvacant heteropolytungstates are strong nucleophilic groups which react quickly with the cationic oxothio fragment $[M_2O_2S_2]^{2+}$ (where M = metal center).[3] Several polyoxothioanions have been prepared by this way, the architecture of the resulting oxothio compounds is mainly governed by the stereochemistry of the parent lacunary polyanion.[4]

Herein, we report the structural and multinuclear NMR spectroscopic characterization (^{31}P and ^{183}W) of the first Dawson α-$[P_2W_{15}O_{56}]^{12-}$ thio derivative. The title compound **1** is a unique polyoxothiometalate-based macrocycle, about 30 Å in diameter, which results from direct connections between the complementary cationic fragment $[Mo_2O_2S_2]^{2+}$ and the basic trivacant α-$[P_2W_{15}O_{56}]^{12-}$ ion. In addition, the formation of Mo−OH−Mo bridges contributes to the build up of the tetrameric cluster, and shows that it is possible to generate elaborate architectures based on POM-incorporated cyclic oxothiomolybdates. The tetra-Dawson macrocycle **1** is the first multiunit POM compound to have pairs of hydroxy bridges that ensure the inter $\{Mo_2O_2S_2\}$-building-block connections.

Compound **1** was formed at pH 2 by the reaction of $[I_2Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]^{2-}$ ions[5] with the trivacant Dawson anion α-$[P_2W_{15}O_{56}]^{12-}$ (30 % yield). A recrystallization is necessary to obtain **1** as pure mixed sodium–potassium salt ($Na_{14}K_{14}$-**1**). The various attempts to prepare **1** by a one-pot procedure always produced a mixture of isomers, characterized by the presence of two multicomponent-sets of resonance signals in the ^{31}P NMR spectra. A recrystallization step is required for the preparation of the tetra-Dawson anion as single crystals of $Na_{14}K_{14}$-**1** suitable for X-ray crystallography.[6]

A crystallographically imposed inversion center is located in the center of the cluster. Nevertheless, the tetra-Dawson anion depicted in Figure 1, approaches the maximum possible C_{2h} idealized symmetry, the two α-$\{P_2W_{15}O_{56}\}$ moieties in the asymmetric unit are quasi-equivalent and present no local symmetry.

For clarity, the macrocycle will be described as the association of two formal dimers formed from two trivacant anions α-$[P_2W_{15}O_{56}]^{12-}$ connected to two $\{(H_2O)_2Mo_2O_2S_2\}^{2+}$ ions (hatched octahedra) as represented in Figure 2. One molybdenum atom of the $\{(H_2O)_2Mo_2O_2S_2\}^{2+}$ cation is singly bonded to a Dawson unit by a single Mo-μO-W bridge, while the second molybdenum atom is connected to the other Dawson unit by a double Mo-(μO-W)$_2$ bridge. A crystallographic C_2 axis passes through the center of the dimeric subunit while the two equivalent α-$[P_2W_{15}O_{56}]^{12-}$ moieties have no local symmetry.

The two pseudodimers are connected each others by two symmetric tetranuclear $\{Mo_4S_4O_4(OH)_4(H_2O)\}^{2+}$ moieties. This tetranuclear core can be viewed as a fragment of a cyclic molecular ring consisting of two $\{Mo_2O_2S_2\}$ fragment mutually linked by a double hydroxy bridge.[5] A water molecule completes the coordination sphere of each of the two central molybdenum atoms, ensuring a face-shared connection.

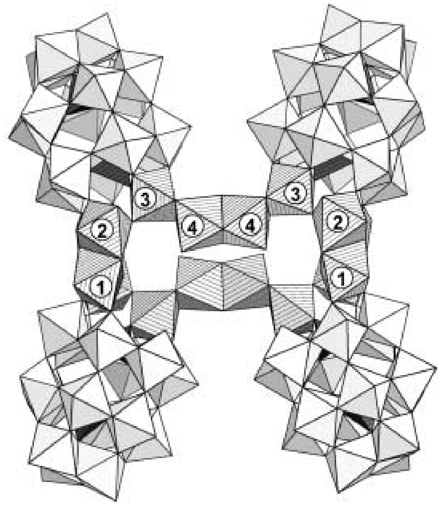

Figure 1. Polyhedral representation of **1**: the four α-$[P_2W_{15}O_{56}]^{12-}$ subunits (assemblies of nonhatched octahedra) are anchored to two $\{Mo_8S_8O_8(OH)_2(H_2O)_5\}^{6+}$ ribbons (hatched numbered octahedra) in which the $\{MoO_4S_2\}$ octahedra are connected through S-edge shared junctions (①–② and ③–④), by O-corner shared junctions (②–③), and by face-shared junctions (④–④). Gray WO_6 octahedra; dark gray PO_4 tetrahedra; hatched $\{MoO_4S_2\}$ octahedra.

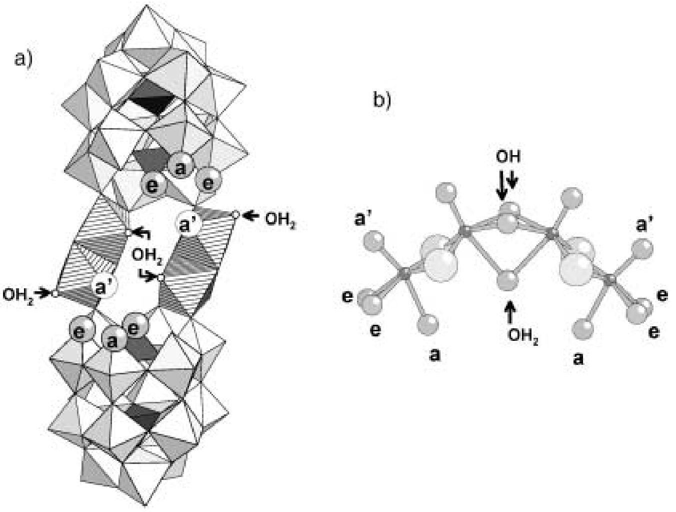

Figure 2. a) Pseudodimer in **1**: The two α-$[P_2W_{15}O_{56}]^{12-}$ subunits are directly connected by two $\{Mo_2O_2S_2(H_2O)_2\}^{2+}$ fragments (hatched octahedra). b) The $\{Mo_4S_4O_4(OH)_2(H_2O)\}^{2+}$ bridging core is linked to the two dimers by axial and equatorial junctions (labeled *a*, *a′*, and *e*). O Medium gray sphere; S big light-gray spheres; Mo little dark-gray sphere.

The P=O groups located near the vacancy of the α-$[P_2W_{15}O_{56}]^{12-}$ precursor (the O atoms of the P=O groups are noted *e* in Figure 2) are pointing towards the center of the six crown terminal oxygen. This orientation prevents the formation of the typical sandwichlike structure previously reported for the Keggin α-$[(PW_9O_{34})_2\{Mo_2O_2S_2(H_2O)_2\}_3]^{12-}$ cluster. In the pseudodimer, each oxygen atom (noted *e* and *a* Figure 2) of the terminal P=O and W=O bonds of the trivacant Dawson anion is directly bonded to the corresponding equatorial (*e*) and axial (*a*) site of the $\{Mo_4S_4\}^{2+}$ fragment (Figure 2). In addition, the hatched $\{Mo_2O_2S_2(H_2O)_2\}^{2+}$ bridging fragment and the $\{Mo_4S_4O_4(OH)_2(H_2O)\}^{2+}$ central core are connected through a corner junction involving the molybdenum octahedra ② and ③ (Figure 1): the vacant axial site (ⓐ') in the $\{Mo_2O_2S_2(H_2O)_2\}^{2+}$ bridging groups (Figure 2a) is occupied by a terminal oxygen atom *a'* of the $\{Mo_4S_4O_4(OH)_2(H_2O)\}^{2+}$ linking group (Figure 2b) giving a long Mo···O separation (2.315(6)–2.301(8) Å). The two resulting symmetric cationic $\{Mo_8\}^{6+}$ octamers (formed by the eight numbered octahedra in Figure 1) resembles a ribbon decorated by four pendant Dawson units. This tetra-Dawson complex belongs to a series of planar compounds of high nuclearity exemplified by the macrocyclic cryptate $[As_4W_{40}O_{140}]^{28-}$.[7] Finally, the charge balance is ensured by eight protons which combine with oxygen units to form a coordinated H_2O molecule in each of the four α-$[P_2W_{15}O_{56}]^{12-}$ subunits. According to the valence-bond calculations, two protons are firmly trapped on the unshared oxygen atom of the six crown oxygen atoms surrounding the central P=O group (W–OH_2 separation of 2.146(7) and 2.180(6) Å). The other W–O bonds, involved in a W–O–Mo bridge are significantly shorter and are thus assumed to be unprotonated (1.764(6)–1.799(6) Å). The presence of the water ligand in the coordination sphere provokes the displacement of the W^{6+} ion concerned, away from the coordinated H_2O molecule, thus provoking the shortening of the *trans* W–O bond (1.789(6)–1.836(8) Å).

The solid-state structure of **1** (Figure 1) remains intact in aqueous solution. The ^{31}P NMR spectra of $Na_{14}K_{14}$-**1** in solution (Figure 3a) exhibit two sharp resonance signals of 1:1 relative integration at $\delta = -2.70$ and -13.05 ppm, as expected for four equivalent α-$[P_2W_{15}O_{56}]^{12-}$ subunits. Based on literature values, the $\delta = -2.70$ ppm signal is assigned to the $\{PO_4\}$ group near the vacancies while the $\delta = -13.05$ ppm resonance is attributed to the fully encapsulated phosphato group of the $\{PW_9\}$ Dawson anion.[8] The ^{183}W NMR spectrum consists of fifteen lines of equal integration (Figure 3b), which confirms the lack of symmetry of the four Dawson units. The ^{183}W chemical shift values of the fifteen lines are in the $\delta = -100$ to -300 ppm range, values usually observed for polyvacant or pseudovacant heteropolytungstates.[9]

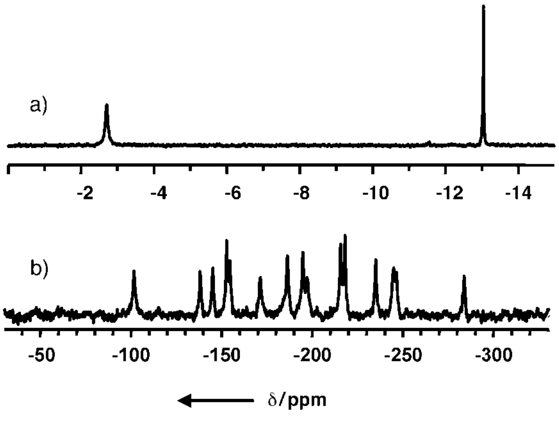

Figure 3. a) ^{31}P NMR spectrum of $Na_{14}K_{14}$-**1** (0.01 molL^{-1} in D_2O) and b) ^{183}W NMR spectrum of **1** as the lithium salt (0.07 molL^{-1} in D_2O).

Experimental Section

$K_{14}Na_{14}[(\alpha\text{-}H_2P_2W_{15}O_{56})_4\{Mo_2O_2S_2(H_2O)_2\}_4\{Mo_4S_4O_4(OH)_2(H_2O)\}_2]\cdot{\approx}165\,H_2O$ ($K_{14}Na_{14}$–**1**·≈165H_2O). Solid α-$[Na_{12}P_2W_{15}O_{56}]\cdot 23\,H_2O$ (10 g; 2.25 mmol) was added to a stirred solution of $K_2(N(CH_3)_4)_{0.75}I_{2.75}[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]\cdot 15\,H_2O$ (2.1 g; 0.9 mmol) dissolved in aqueous HCl (50 mL of 0.2 molL^{-1}). The resulting red-brown solution was heated at 35 °C for 30 min and the pH value adjusted to 2.0 with about 3 mL of 2 molL^{-1} aqueous HCl before addition of potassium chloride (7.5 g; 100 mmol. After 30 min at 25 °C, the brown precipitate was collected by filtration, washed with ethanol, and dried with diethyl ether, yield: 9.8 g of crude product. The solid was dissolved in aqueous 0.5 molL^{-1} NaCl solution (65 mL). The resulting solution was allowed to stand for one week at 25 °C. About 3 g of well-formed red-brown crystals of $K_{14}Na_{14}$-**1**·≈165H_2O were collected (yield of crystals: about 30 % based on α-$[Na_{12}P_2W_{15}O_{56}]\cdot 23H_2O$). FTIR (KBr pellet): $\tilde{\nu} = 1091$(m), 1048(w), 1031(w), 957(m), 923(m), 815(sh), 771(s), 705(sh), 596(vw), 557(vw), 519(w), 473(w), 427(vw), 365(sh), 322 cm^{-1}(m). ^{31}P NMR (121.496 MHz, 0.01 molL^{-1} in D_2O; H_3PO_4): $\delta = -2.70$ (1P), -13.04 ppm (1P); elemental analysis (%) calcd for $Na_{14}K_{14}H_{32}P_8W_{60}Mo_{16}S_{16}O_{254}\cdot 165H_2O$: Na 1.54, K 2.61, P 1.18, W 52.7, Mo 7.34, S 2.45; found: Na 1.50, K 2.50, P 1.31, W 52.5, Mo 7.39, S 2.63. The water content was determined by thermogravimetric analysis.

Li_{28} salt for ^{183}W NMR spectroscopy: cationic exchange of $K_{14}Na_{14}$-**1** through a Dowex 50W-X2 resin (Li^+ saturated). ^{183}W NMR (12.5 MHz, 0.07 molL^{-1} in D_2O; secondary standard: $H_4SiW_{12}O_{40}$ at $\delta = -103.8$ ppm): $\delta(1W) = -101.75$, -138.12, -145.16, -152.76, -154.63, -171.44, -186.30, -194.86, -197.13, -215.70, -218.09, -235.04, -244.84, -246.38, -283.85 ppm.

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Keywords: molybdenum · polyoxometalates · self-assembly · supramolecular chemistry · tungsten

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[6] Crystal data for $Na_{14}K_{14}$-**1**·165H_2O: Siemens Smart CCD diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å. Red-brown paralepipedic crystal, dimensions $0.04 \times 0.02 \times 0.02$ mm^3, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.4731(1)$, $b = 24.6433(1)$, $c = 29.5413(2)$ Å, $\alpha = 76.384(1)$, $\beta = 79.339(1)°$, $\gamma = 87.211(1)°$, $V = 10063.3(2)$ Å, $Z = 1$, $\rho_{calcd} = 3.351$ $g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 17.932$ mm^{-1}, $F(000) = 8964$, $T = 296(2)$ K. A total of 27541

independent reflections, 20000 observed with $F_0 > 4\sigma(F_0)$, R(int) = 0.0644, $R_1 = 0.0579$, $wR_2 = 0.1181$, 1993 parameters. The structure was solved by direct methods, and refined by full-matrix-block least-squares procedure (SHELX-TL package); disorder in sodium–potassium cations and water molecules was found and partial occupancy factors were applied. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412791.

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