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A New Oxomolybdate Component Extracted from the “Virtual Dynamic Library” Yielding the Macrocyclic Anion $[(Mo^{VI}{}_8O_{28})_4(Mo^{V}{}_2O_2S_2)_4]^{24-}$

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A rare isomer of the $\{Mo_8O_{28}\}^{8-}$ anion has been trapped from an acidified aqueous solution of molybdate by using the $\{Mo_2O_2S_2\}^{2+}$ oxothio cation as the linker and isolated as a part of a unique macrocyclic anion, which consists of four isopolyoxomolybdate fragments $\{Mo_8O_{28}\}$ bridged by four $\{Mo_2O_2S_2\}$ units.

Polyoxometalate (POM) chemistry represents a large growing area in inorganic chemistry,[1] and the ongoing interest is driven mainly by their potential applications in catalysis,[2] medicine and biology,[3] or nanochemistry.[4] The properties of such classes of molecular materials are intimately related to their structural architecture and composition. In this context, the chemistry of polyoxomolybdates is unique because it allows one to select adequate molybdenum oxide based building blocks from a “virtual dynamic library” for the design of new architectures.[5] Condensation processes of the tetraoxomolybdate ion in aqueous solution lead to the formation and isolation of numerous anionic species with different sizes, shapes, and structures,[6] but in the presence of exogeneous species, such as weakly chelating ligands, reducing agent, metallic cations, etc., the formation of unusual building blocks, intrinsically unstable components of a virtual dynamic library, can be engaged within nanosized discrete species. Thereby, the discovery of novel components as topologically suitable building blocks is an important goal in today’s chemical research. One of the nicest examples that illustrate such a concept is probably the striking pentagonal motif $\{Mo_6O_{21}\}^{6-}$ at the origin of numerous spectacular compounds such as molybdenum oxide based nanowheels or ball-shaped Keplerate capsules.[7] Herein, we report on a straightforward synthesis and characterization of a Mo_{40}-membered ring built on connections between four octamolybdate building blocks and four oxothio cationic $\{Mo_2O_2S_2\}$ linkers. The investigation of the $\{Mo_2O_2S_2\}$ chemical system is part of our continuing project on sulfur-containing POMs. In this context, preformed (oxo)thiomolybdic cations, such as $[Mo_2O_2S_2(OH_2)_6]^{2+}$ or $[Mo_3S_4(OH_2)_9]^{4+}$ species, are revealed to be adequate to react with lacunary polyoxotungstate ions to produce modular or saturated sulfur-containing POMs.[8,9] Not only platonic structural building blocks, these components should bring their intrinsic functionalities to the assembly, such as redox properties for the Mo^{VI}-containing building blocks and electrocatalytic sites for the $\{Mo_2O_2S_2\}$ linkers.[10]

The $[(Mo_8O_{28})_4(Mo_2O_2S_2)_4]^{24-}$ macrocyclic anion, denoted as **1**, is synthesized in good yield (38%) by mixing an aqueous acetate solution of ammonium heptamolybdate and a solution of the $[Mo_2O_2S_2(OH_2)_6]^{2+}$ cation acidified by H_2SO_4.[11]

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(11) Synthesis of $K(NH_4)_{23}[(\{Mo_8O_{28}\}\{Mo_2O_2S_2\})_4]\cdot 48\ H_2O$ (**NH_4K-1**): Two solutions (**A** and **B**) were first prepared separately and then mixed. **A**: Ammonium heptamolybdate tetrahydrate (2.0 g, 1.62 mmol) is dissolved in 25 mL of 1.5 $mol\cdot L^{-1}$ aqueous ammonium acetate. **B**: The cyclic precursor $K_2I_2[Mo_{10}O_{10}S_{10}(OH)_{10}(H_2O)_5]\cdot 15H_2O$ (0.650 g, 0.28 mmol) was suspended in 10 mL of water and acidified by 8 mL of 2 $mol\cdot L^{-1}$ H_2SO_4. The solution was heated up to 40 °C for 15 min and then filtered to get a clear red-orange solution. Solution **B** was quickly added to solution **A** under vigorous stirring at 40 °C, provoking a strong color change from orange to dark red, and the resulting pH of the mixture was 4. The solution was stirred for 10 min and then allowed to stand at room temperature for 4−6 h for crystallization. Orange crystalline material suitable for X-ray diffraction analysis was collected by filtration. Yield: 1 g (38% based on Mo^{VI}).

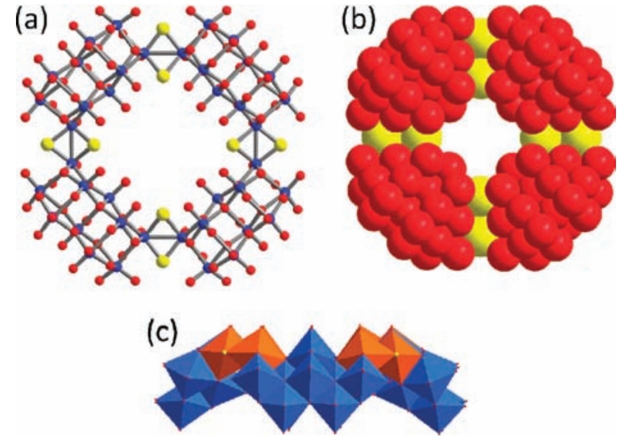

Figure 1. "Ball-and-stick" (a) and space-filling (b) representations of the ring-shaped **1** (color code: red, O; blue, Mo; yellow, S). (c) Side view of **1** in a polyhedral representation ($\{Mo_8O_{28}\}^{8-}$ in blue and $\{Mo_2O_2S_2\}^{2+}$ in orange).

Compound **1** is isolated as single crystals of a mixed ammonium−potassium salt from a solution with a resulting pH of 4 and characterized by single-crystal X-ray structural analysis,[12] elemental analysis,[13] thermogravimetric analysis (TGA; Figure S1 in the Supporting Information, SI), and FT-IR and UV−vis spectral analysis (Figures S4−S6 in the SI).

The structure of $K(NH_4)_{23}[(Mo_8O_{28})_4(Mo_2O_2S_2)_4]\cdot 48H_2O$ (**NH$_4$K-1**) consists of a 40-molybdenum-membered, ring-shaped anion, $[(Mo_8O_{28})_4(Mo_2O_2S_2)_4]^{24-}$ (Figure 1), which delimits an open cavity of about 5 Å in diameter. The cyclic assembly is built of two connected components consisting of an octamolybdenum oxo cluster $\{Mo_8O_{28}\}^{8-}$ and the oxothio cation $\{Mo_2O_2S_2\}^{2+}$. In the crystal structure of **NH$_4$K-1**, a mirror plane intersects the polyanion (C_s symmetry), but an idealized C_{4v} symmetry could be properly used to describe the isolated anion **1**, in agreement with analysis of the geometrical parameters and local symmetry within the four building blocks. The $\{Mo_8\}$ oxo building blocks, as shown in Figure 2a, retain a C_s local symmetry and correspond to two $\{Mo_3O_{13}\}$ triads fused through two corner-shared octahedra. The resulting $\{Mo_6O_{24}\}^{12-}$ core coordinates an additional $\{Mo_2O_4\}^{4+}$ group disposed along the symmetry plane to give the resulting building block $\{Mo_8O_{28}\}^{8-}$, where all of the Mo^{VI} ions display an octahedral geometry with one, two, or three terminal metal−oxo bonds in their coordination sphere. $\{Mo_8O_{28}\}^{8-}$ can be alternatively described as two staggered layers of three and five zigzag edge-sharing molybdenum octahedra. The 28 O atoms of the isolated $\{Mo_8O_{28}\}^{8-}$ polyoxoanion are divided into 15 terminal O atoms and nine μ_2-O, one μ_3-O, and three μ_4-O bridging atoms. All of the Mo^{VI}−O bond distances fall within the usual range. As expected, the shorter bonds correspond to Mo═O bonds with distances ranging between 1.69(2) and 1.74(2) Å, while longer distances are found between Mo atoms and bridging O atoms in the trans position with respect to the Mo═O bonds [2.21(2)−2.48(2) Å]. Nevertheless, the longest Mo−O bonds correspond to those ensuring the contact between the layers of three Mo and five Mo atoms [2.42(2)−2.48(2) Å]. The bond valence sum (BVS) analysis carried out on $\{Mo_8O_{28}\}^{8-}$ building blocks reveals that no protonation occurs on the surface of the $\{Mo_8O_{28}\}$ moieties and confirms the +VI oxidation states of the eight Mo atoms (Figure S2 in the SI).[14] The distribution of the Mo−O−Mo angles within the $\{Mo_8\}$ cluster spreads from 95(5)° to 148(8)°. Each μ_4-O atom is involved in two closed [95(5)−97(5)°] and two open [143.1(7)−148.8(7)°] junctions. The single μ_3-O atom gives two closed Mo−O−Mo bridges [104.1(7)−104.8(7)°] and a larger one [146.0(6)°], whereas the Mo−μ_2-O−Mo angles fall in a narrower range [110.5(5)−117.7(7)°]. Each of the two peripheral Mo atoms contains three terminal O atoms in the isolated $\{Mo_8\}$ units. However, in the ring-shaped anion **1**, one of these O atoms and two neighboring μ_2-O atoms constitute two symmetric coordination sites available for the two $\{Mo_2O_2S_2\}$ linkers. Thus, all Mo^{V} atoms are equivalent, and each one is triply coordinated to the $\{Mo_8\}$ oxo cluster to fulfill the requirements for octahedral coordination. The bond distances and angles within the $\{Mo_2O_2S_2\}$ linkers have the usual values [Mo^{V}−Mo^{V} = 2.80(1)−2.84(1) Å; Mo^{V}−S = 2.29(1)−2.32(1) Å; Mo═O = 1.66(2)−1.72(2) Å]. The Mo^{V}−O bonds within the Mo^{V}−O−Mo^{VI} junctions are shorter when the involved O atoms are located within the equatorial coordination sites [2.11(2)−2.16(2) Å] and longer when they are axially directed in a trans disposition along the Mo^{V}═O bonds [2.28(2)−2.37(2) Å]. The constitutive $\{Mo_8O_{28}\}^{8-}$ building blocks represent one of the most intriguing structural aspects of **1** because, until now, such a cluster had never been described in the literature and therefore can be viewed as a new component extracted from the Mo^{VI}−oxo dynamic library. However, structural relationships can be found with another structural type that retains the discrete formula $[Mo_8O_{26}X_2]^{6-}$ where X = OH^{-}.[15] Such an arrangement was

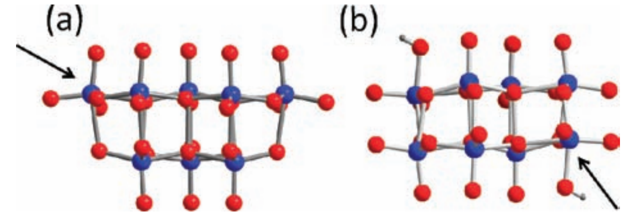

Figure 2. "Ball-and-stick" representations of the $\{Mo_8O_{28}\}^{8-}$ building block within **1** showing the stacking of the two constitutive layers of three and five Mo atoms (a) and its well-known derivative as diprotonated discrete species (b). The structural relationships between both isomeric moieties are highlighted by arrows pointing out the $\{MoO_3\}$ group formally displaced by bond breaking/bond forming processes from one layer to the other.

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[12] Crystal data: $H_{188}K_1Mo_{40}N_{23}O_{168}S_8$; 7332.8 g·mol^{-1}; orthorhombic; *Pnma*; a = 18.658(2) Å, b = 23.714(3) Å, c = 40.864(5) Å; V = 18080(4) Å^3; Z = 4. The diffraction data were collected on a Smart CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. A total of 16353 reflections (1.2−25.0°) were collected, of which 9399 [R(int) = 0.148] independent reflections were used. An empirical absorption correction was performed with the program *SADABS*. The coordinates of the Mo atoms were determined by direct methods, and the remaining non-H atoms were located and refined by the usual procedure of a combination of the difference Fourier synthesis and least-squares technique. The structure was solved using the *SHELX-TL* package and refined to R1 = 0.096 and wR2 = 0.283 [$I > 2\sigma(I)$] for 9399 reflections with max/min residual electron density +1.78 and −2.05 e·Å^{-3}. The countercation (ammonium and potassium) and crystallization water appear severely disordered within the structure and thereby could not be distinguished from the observed electron densities; therefore, all of these positions were refined as O atoms and considered as crystallization water. The data set was corrected with the program *SQUEEZE* (*PLATON* package of crystallographic software) used to remove the disordered solvent or counterion contribution to the overall intensity data.

[13] Anal. Calcd for $H_{188}K_1Mo_{40}N_{23}O_{168}S_8$: K, 0.53; N, 4.39; H, 2.58; Mo, 52.33; S, 3.49. Found: K, 0.57; N, 4.19; H, 2.23; Mo, 52.72; S, 3.70. Elemental analyses were carried out by the Laboratoire Central d'Analyse du CNRS, Solaize, France.

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first published by Yamase[15] and corresponds to a discrete diprotonated centrosymmetric species where the metal oxide framework can be roughly described as two staggered layers of four edge-sharing molybdenum octahedra disposed in zigzag chains (Figure 2b). The relationship between both $\{Mo_8\}$ isomers lies in the location of one peripheral $\{MoO_3\}$ group, which is moved from one layer to the opposite side of another layer to give the {3Mo−5Mo} stacking. The main difference between both arrangements is manifested in the coordination properties of the $\{Mo_8O_{28}\}^{8-}$ building blocks. The centrosymmetric $[Mo_8O_{26}X_2]^{6-}$ building block presents two opposite (in the trans position) coordination sites, leading to either discrete mixed-metal coordination compounds ($M_2\{Mo_8\}$) or infinite one-dimensional chains ($[M\{Mo_8\}])_\infty$ with M = transition metal. Furthermore, numerous derivatized species with such a configuration have been reported because the two hydroxo groups can be replaced by various exogeneous ligands.[16] Finally, the packing analysis reveals that the Mo_{40} wheels stack on top of each other, thus forming pseudochannels, as depicted in Figure S3 in the SI.

The IR spectrum of **NH_4K-1** (Figure S4 in the SI) consists of several characteristic vibrations in the 1000−400 cm^{-1} range. The strong band at 947 cm^{-1} is assigned $\nu_{as}(Mo{=}O)$, while the series of absorptions within the 900−600 cm^{-1} range corresponds to the bridging mode $\nu_{as}(Mo{-}O{-}Mo)$ and reflects the large spread of the Mo−O−Mo angles from 95 to 148°. The electronic spectrum of **1** exhibits two shoulders in the visible domain at 410 ($\varepsilon \sim 7200\ mol \cdot L^{-1} \cdot cm^{-1}$) and 350 nm ($\varepsilon \sim 23\,000\ mol \cdot L^{-1} \cdot cm^{-1}$), attributable to ligand-to-metal charge transfer involving the $\{Mo_2O_2S_2\}$ chromophores (Figure S4 in the SI).[17] The behavior of **1** in solution has been monitored by UV−vis spectroscopy in dilute aqueous solutions in the presence of various electrolytes. Whatever the nature or concentration of the electrolyte (Na_2SO_4, NH_4CH_3COO, and MCl with M = Li, Na, or K), **1** is unstable in dilute solutions ($<10^{-3}\ mol \cdot L^{-1}$) and rapidly decomposes into several polyoxomolybdate species, especially the cyclic ion $[Mo_9S_8O_{12}(OH)_8(OH_2)_2]^{2-}$.[18] Conversely, **1** appears to be fairly stable at concentrations up to $10^{-2}\ mol \cdot L^{-1}$.

In summary, a new ring-shaped polyoxothiomolybdate ion has been successfully obtained during the first investigation of the chemical system based on polyoxomolybdate anions and the $\{Mo_2O_2S_2\}$ building block. More than to report of a novel compound, these results demonstrate that such a chemical system supported by a rational methodology behaves singularly well to trap new isopolyoxomolybdate fragments, the behavior of which herein is nicely exemplified by characterization of the unique $\{Mo_8O_{28}\}$ derivative. This work should bring relevant outcomes in the relationship with the peculiar properties of the molybdenum oxo clusters, such as photocatalysis,[19] thermochromism,[20] or bioactivity.[3,21] Furthermore, some striking analogies exist between this system and the molybdenum oxo system under reductive conditions, which has been nicely explored by Müller[22] or others[23] for giving spectacularly nanosized molybdenum oxide based anions built on the $\{Mo_2O_4\}^{2+}$ cation, which is structurally very close to the $\{Mo_2O_2S_2\}^{2+}$ species employed in the present work. This preliminary result corresponds to the starting point of undergoing work “en route toward sulphurated Keplerates”.

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Supporting Information Available: X-ray crystallographic data in CIF format, experimental details, a TGA curve, BVS calculations, packing views of **1**, and FT-IR and UV−visible spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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