opinion, these strategies will play a significant role in the development of catalysts and absorbents through the use of highly specialized and dedicated multifunctional units for sample preparation and identification/characterization, and through operation with a minimum of manual intervention.

Experimental Section

Routine X-ray diffraction analysis was carried out on small sample quantities (1–10 mg) with steps of 0.05° (2θ) and counting times of 0.5 s. For selected diffractograms, the quality was enhanced greatly by using maximum likelihood noise filtration strategies.

Mixing procedures: For the Na_2O-Al_2O_3-SiO_2 system, the composition of the reaction mixtures was defined according to relation (1) (molar ratios) in which $a/(a+x+y+z) = 0.95$.

$$x\,Na_2O{:}y\,Al_2O_3{:}z\,SiO_2{:}a\,[H_2O] \quad (1)$$

For the TMA_2O-Cs_2O-Li_2O-Na_2O-Al_2O_3-SiO_2-H_2O system, the composition of the reaction mixtures were defined according to relation (2) in which $0 \leq r,\ s,\ t \leq 12.15$; $1.45 \leq x \leq 13.6$; $r+s+t+x = 13.6$; $a/(a+r+s+t+x+y+z) = 0.93$; $z/y = 17.3$; $0 \leq r/x \leq 8.8$.

$$r\,TMA_2O{:}s\,Cs_2O{:}t\,Li_2O{:}x\,Na_2O{:}y\,Al_2O_3{:}z\,SiO_2{:}a\,[H_2O] \quad (2)$$

The mixtures were prepared by using the following sequence of aqueous solutions 1) NaOH; 2) LiOH; 3) CsOH; 4) TMAOH; 5) Ludox LS 30 % silica sol; 6) $NaAlO_2$ + NaOH. The water contents were corrected for by adding distilled water, giving a total volume of 0.5 mL. The sequence of mixing was elaborated in separate experiments before it was applied to all 100 syntheses. Homogenization of the mixtures was performed in a number of ways; for the prototype presented here, we chose to stir the autoclave contents consecutively, after the addition of all reagents, by using a simple stirring device. The gel mixtures were aged for 24 h at room temperature and the autoclave subsequently placed in an oven for one and six days at 100 °C, for the above-mentioned mixtures, respectively. Washing and isolation of the products was done in situ in the autoclave block by removing both top and bottom seals (Figure 1), and the products were flushed onto a single plate/sheet of adsorbent material with water. Once the products were thoroughly washed, they were transferred to sample holders ready for X-ray analysis and dried at room temperature.

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[1] *Acc. Chem. Res.* **1996**, 29, 112–170 (Special issue, Eds.: A. W. Czarnik, J. A. Ellmann).

[2] X. D. Xiang, X. Sun, G. Briceño, Y. Lou, K. A. Wang, H. Chang, W. G. Wallace-Freedman, S. W. Chen, P. G. Schultz, *Science* **1995**, 268, 1738–1740.

[3] D. E. Akporiaye, I. M. Dahl, A. Karlsson, R. Wendelbo, Norwegian patent application number 97.0788.

[4] D. W. Breck, *Structure, Chemistry and Use of Zeolite Molecular Sieves*, Wiley, New York, **1974**.

[5] P. D. Hopkins, *ACS Symp. Ser.* **1989,** 398, 153–160.

[6] C. Colella, M. de Gennaro, *ACS Symp. Ser.* **1989**, 398, 196–208.

$[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$: A Cyclic Molecular Cluster Based on the $[Mo_2S_2O_2]^{2+}$ Building Block

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Dedicated to Professor Achim Müller
on the occasion of his 60th birthday

Polyoxoanions of tungsten, molybdenum, and vanadium have been the subject of interest since their wide variety of compositions, structures, and properties gave rise to numerous important applications.[1] Polyoxometalates are regarded as models for MO_3 oxide surfaces, and they are very strong acids and active oxidation catalysts. For example, the superacid $H_3[PW_{12}O_{40}]$ promotes esterification reactions and activates C_6 alkanes,[2] while salts of $[PMo_{12}O_{40}]^{3-}$ catalyze the mild oxidation of isobutyric acid to methacrylic acid.[3]

Conversely, alumina-supported molybdenum and tungsten sulfides are hydrogenation catalysts with applications in the hydrodesulfuration of crude oil and the activation of dihydrogen.[4] If these compounds are regarded as functional analogues of the active surface of MoS_2, then binary compounds with discrete M–S units could serve as models for studying the reactivity of the corresponding solids.[5] However, thiometalates are far less common than oxometalates.[6] In addition to their remarkable structural diversity, polyoxometalates can contain a large number of metal centers. In contrast, only low-nuclearity thiometalates have been obtained so far by sulfurization of oxo precursors.[7] Therefore, the synthesis of high-nuclearity sulfur-containing species by combining polyoxometalate and thiometalate chemistry represents a stimulating challenge.

The first method for introducing sulfur into a Keggin-type polyoxoanion was illustrated by the synthesis of α-$[PW_{11}NbSO_{39}]^{4-}$, by selective substitution of the terminal oxygen atom of an Nb=O group by a sulfur atom, and its subsequent characterization.[8] The second technique was the stereospecific addition of an $[Mo_2S_2O_2]^{2+}$ fragment to the cavity-containing polyanion γ-$[SiW_{10}O_{36}]^{8-}$.[9] These strategies are convenient for preparing thio complexes that are derived from well-defined structural types, but are unsuitable for the synthesis of new structures or frameworks with higher sulfur contents.

Here we present a new method for increasing the sulfur content; it is based on the one-step self-condensation of sulfur-containing building blocks. The $[Mo_2S_2O_2]^{2+}$ unit was first prepared by selective oxidation of the terminal S_2 ligands of $[(S_2)MoO(\mu_2\text{-}S)_2MoO(S_2)]^{2-}$ with iodine.[10, 11] The self-condensation reaction was performed by controlled addition of potassium hydroxide to an aqueous solution of the building

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block. The title compound was isolated as pale orange crystals and fully characterized by X-ray structure analysis.[12] The IR spectrum exhibited intense bands at 969 and 535 cm^{-1}, attributed to ν(Mo=O) and ν(Mo-OH-Mo) vibrations, respectively, and less intense absorptions at 493 (ν(Mo-S-Mo)), 413, and 346 cm^{-1}.

The formula of the cluster is $[Mo_{12}S_{12}O_{12}(OH)_{12}(H_2O)_6]$. A noteworthy feature of the structure is the cyclic arrangement of the neutral Mo_{12} cluster, which creates a central cavity (Figure 1, top). Six $\{Mo_2O_2S_2\}$ units are connected to each other by hydroxo double bridges; the coordination spheres of the Mo centers are completed by a terminal oxygen atom and a water molecule that is coordinated to two neighboring molybdenum atoms. Two types of Mo–Mo bonds are present in the cluster: short Mo–Mo distances within the building blocks (2.798(1)–2.814(1) Å), and long Mo–Mo distances between the building blocks (3.289(1)–3.317(1) Å). The short Mo–Mo distances in the $\{Mo_2O_2S_2\}$ units are similar to those in related polychalcogenide compounds and in the precursor, suggesting that the original single Mo^V–Mo^V single bond is retained during the self-condensation process. The title compound can be described as a ring of alternately edge- and face-sharing octahedra (Figure 1, bottom). An S–S edge links the two octahedra of the same building block, and the building blocks are linked through common faces consisting of two OH ligands and one water molecule. The overall cyclic architecture constructed from the $\{Mo_2O_2S_2\}$ building blocks has a cavity of about 11 Å in diameter filled with six water molecules, each of which is bound to two adjacent metal centers.

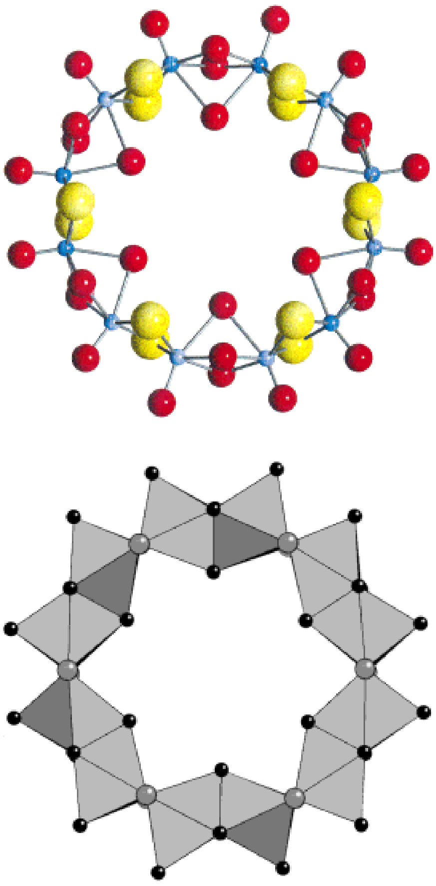

Figure 1. Views of the Mo_{12} cluster. Top: ball-and-stick model showing the Mo_{12} ring with the inner cavity (blue: Mo, red: O, yellow: S). Bottom: polyhedral representation showing the connectivity of the building blocks. Oxygen (black) and sulfur atoms (grey) are emphasized.

A noteworthy chemical property of this cluster is the reversibility of the self-condensation reaction. Acidification of the title compound results in the starting material $[Mo_2O_2S_2]^{2+}$, which can be recondensed by addition of hydroxide.

Experimental Section

Iodine (9 g, 35.4 mmol) and KI (16 g, 96.3 mmol) were dissolved in hydrochloric acid (70 mL, 1 M). $(NMe_4)_2[Mo_2O_2S_6]$[13] (10 g, 17.7 mmol) was suspended in an aqueous solution of KI (60 mL, 0.7 M), and the iodine solution was slowly added to the suspension with vigorous stirring. The resulting solution was heated to 50 °C for 10 min. The insoluble material formed (mainly solid sulfur and tetramethylammonium iodide) was removed by filtration. The red filtrate was cooled to 0 °C to complete the precipitation of the remaining tetramethylammonium iodide, and after filtration an aqueous solution of potassium hydroxide (4 M) was slowly added until the pH stabilized at about 1.5. A yellow microcrystalline solid precipitated. After cooling to 0 °C, the solid was collected by filtration, washed with cold ethanol, and dried with ether (yield 6 g). Pale orange crystals were obtained by dissolving 0.2 g of the yellow microcrystalline powder in 20 mL of distilled water and allowing the solution to stand for several hours at room temperature.

Crystal data for $H_{64}O_{50}S_{12}Mo_{12}$: $M_r = 2400.46$, monoclinic, $P2_1/c$, $a = 17.972(5)$, $b = 19.835(4)$, $c = 19.461(6)$ Å, $\beta = 99.9(2)^\circ$, $V = 6842(3)$ Å^3, $Z = 4$, $T = 20$ °C, $\rho_{calcd} = 2.33$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å), $\mu = 25.1$ cm^{-1}. Data were collected on a Nonius CAD4 diffractometer. The structure was solved by direct methods and refined on F_o^2 by full-matrix least-squares methods with the program Crystals. All non-hydrogen atoms were refined anisotropically. $R_1 = 0.064$ and $wR_2 = 0.074$ for 8745 unique reflections with $I > 3\sigma(I)$ and 669 parameters. The figures were prepared with the program CrystalMaker (Interactive Crystallography for the Apple Macintosh, CrystalMaker Software, Lynxvale Ltd, 20 Trumpington Street, Cambridge, CB2 1QA, England). Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407925.

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[1] *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds: M. T. Pope, A. Müller), Kluwer, Dordrecht, **1994**.
[2] Y. Yzumi, K. Urabe, *Chem. Lett.* **1981**, 663.
[3] M. Misono, *Catal. Rev.-Sci. Eng.* **1987**, *29*, 269.
[4] O. Weisser, S. Landa, *Sulfide Catalysts, Their Properties and Applications*, Pergamon, New York, **1973**; M. Rakowski DuBois, *Chem. Rev.* **1989**, *89*, 1.
[5] W. Eltzner, M. Breysse, M. Lacroix, M. Vrinat, *Polyhedron* **1986**, *5*, 203.
[6] M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 422.
[7] A. Müller, E. Diemann, *Adv. Inorg. Chem. Radiochem.* **1987**, *31*, 89.
[8] a) E. Cadot, V. Béreau, F. Sécheresse, *Inorg. Chim. Acta* **1995**, *29*, 39; b) E. Radkov, Y. J. Lu, R. H. Beer, *Inorg. Chem.* **1996**, *35*, 552.
[9] E. Cadot, V. Béreau, B. Marg, S. Halut, F. Sécheresse, *Inorg. Chem.* **1996**, *25*, 3099.
[10] K. F. Miller, A. E. Bruce, J. L. Corbin, E. I. Stiefel, *J. Amer. Chem. Soc.* **1980**, *102*, 5102.
[11] D. Coucouvanis, A. Toupadakis, A. Hadjikriacou, *Inorg. Chem.* **1988**, *27*, 3273.
[12] T. Shibahara, *Coord. Chem. Rev.* **1992**, *123*, 73.
[13] A. Müller, E. Krickemeyer, U. Reinsch, *Z. Anorg. Allg. Chem.* **1980**, *470*, 35.

Mesoporous Silica from Lyotropic Liquid Crystal Polymer Templates

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Mesoporous nanostructures are regularly structured solids with pore sizes between 20 and 500 Å and a narrow pore size distribution. They are a welcome supplement to classical zeolites, the application of which was previously restricted because of their limited highest pore diameter of 13 Å.[1,2] Mesoporous ceramic oxides have large specific surface areas and are potential candidates for chemical and physical processes, such as chromatography and catalysis.[3–5] Since the discovery of M41S in 1992,[6] many research groups have focused their interests on mesoporous materials.[7] M41S is formed by a surfactant-assisted reaction pathway as a result of the attractive electrostatic interaction between a ceramic precursor and an ionic amphiphile (sometimes counterion-mediated), upon which a surfactant-rich gel phase precipitates from solution.[8-11] The structure of M41S-type materials depends sensitively on the preparation conditions, as a delicate balance between charge density and volume has to be maintained. Since M41S is obtained as a fine, porous precipitate from a heterogeneous reaction mixture, these nanostructured ceramic oxides have extraordinarily large specific surface areas.[12]

An alternative approach to mesoporous molecular sieves is the exploitation of nonionic surfactants (primary amines) at low concentration,[13] which affords similar materials to M41S. Mesoporous ceramic oxides obtained in the presence of oligoethylene oxide surfactants[14] are less regular than M41S (as determined by X-ray diffraction, which usually reveals just one diffraction peak), but still exhibit high specific surface areas and narrow pore size distributions. Pinnavaia et al. attributed the templating effect to the presence of wormlike surfactant micelles.[14,15] Their results clearly show that there is a displacement mechanism caused by nonionic micellar aggregates.

An alternative route towards ordered mesoporous ceramic nanostructures is the utilization of lyotropic liquid crystal phases as structure-directing media.[16,17] Here, the sol–gel synthesis of the inorganic nanostructure takes place in the ordered environment of a bulk surfactant mesophase: the polycondensation of a water-soluble monomer (e.g., silicic acid) is confined within the aqueous domains of a microphase-separated medium, which acts as a template for the nanostructure. The bulk liquid crystal approach has many advantages over previous routes towards inorganic nanostructures. The resulting ceramic oxide is a direct cast of the liquid crystalline phase, which indicates a high degree of control over the structure. Further, mesoporous ceramic oxides prepared in liquid crystalline phases can be obtained as monoliths (large, crack-free objects, which usually are not macroscopically aligned), because the product is generated by solidifying a homogeneous bulk liquid crystal as opposed to being precipitated from a heterogeneous mixture in the case of M41S. (A certain particle size, if required, can always be achieved after synthesis by grinding and subsequent sifting, and a large particle size of heterogeneous catalysts also facilitates catalyst recovery.)

Using the lyotropic phases of classical nonionic surfactants (low molecular weight amphiphiles) as templates typically affords particles sizes from 300 mm to several millimeters. This big particle size of silica has the effect that the surface area is to a large extent determined by the internal nanostructure and not by the particle surface, an important aspect with respect to size-exclusion processes.[12]

In this paper we describe the preparation of mesoporous silica from lyotropic liquid crystalline polymer templates. Amphiphilic block copolymers (ABCs), like low molecular weight surfactants, can form micelles when mixed with water or other suitable solvents.[18] Accordingly, more complex aggregate structures, namely, lyotropic liquid crystalline phases, are formed at higher polymer concentrations.

ABC templates are expected to show a number of advantages. Firstly, the compatibility of a polymeric amphiphile can be chemically adjusted to the desired product by established procedures of polymer chemistry. Thus, a significant extension of the chemical toolbox for the preparation of mesoporous materials is provided. Secondly, the higher molecular weight slows down exchange and structural relaxation kinetics of the aggregation structures, which makes these lyotropic liquid crystals kinetically less sensitive to phase changes. At the same time, a larger size of the templating lyotropic aggregate is achieved, which directly determines the pore diameter as well as the wall thickness of the mesoporous materials. In addition, such templates should facilitate the preparation and handling of large monoliths, because the resulting hybrid materials are expected to show an improved elasticity and ductility.

In our experiments we employed amphiphilic block copolymers consisting of an apolar polystyrene block (S) and a polar polyethylene oxide block (E) of equal molecular weight (the SE tensides) as polymer templates.[19] The average molecular weight was 1000 $\mathrm{g\,mol^{-1}}$ per block for SE 10/10 and 3000 $\mathrm{g\,mol^{-1}}$ per block for SE 30/30. The polyethylenoxide block's distribution was narrow, whereas the polystyrene block exhibited the Schulz–Flory distribution as a result of a radical polymerization mechanism.

The lyotropic phases of the polymeric SE surfactants investigated are extraordinarily stable. SE 10/10 is characterized by birefringent fluid phases between 45 and 80% (w/w) above 45°C, although the diffuse textures do not allow any

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