[18] The proton hyperfine couplings have been estimated from Figure 2, based on the observed maximum shift Δv^s, according to the method of Pöppl and Kevan (A. Pöppl, L. Kevan, *J. Phys. Chem. B* **1996**, *100*, 3387). In Figure 2, Δv^s is 0.3 MHz which based on the relationship $T = (2/3)[8\Delta v^s v_I/(2)^{1/2}]^{1/2}$ gives a hyperfine anisotropy for this proton $T = 3.27$ MHz. Using this as starting value, we have calculated the proton isotropic hyperfine coupling based on numerical simulations. The final values are $A_{iso} = 2.2$ MHz, $T = 3.5$ MHz.
[19] A. M. Tyryshkin, S. A. Dikanov, R. G. Evelo, A. J. Hoff, *J. Chem. Phys.* **1992**, *97*, 42.
[20] a) D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. T. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[21] a) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 270; b) W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284; c) P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[22] T. H. Dunning Jr., P. J. Hay *in Modern Theoretical Chemistry, Vol. 3* (Ed.: H. F. Schaefer III), Plenum, New York, **1976**, p. 1.
[23] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

Polyoxomolybdenum(V) Sulfite Complexes: Synthesis, Structural, and Physical Studies[**]

Manolis J. Manos, J. Derek Woollins,
Alexandra M. Z. Slawin,[*] and
Themistoklis A. Kabanos[*]

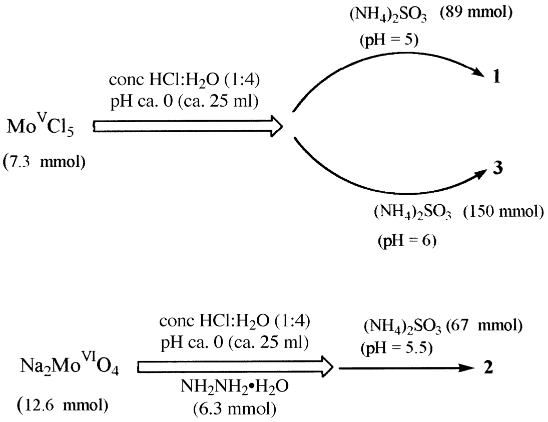
The contemporary interest in polyoxometalates reflects the ubiquitous nature of this family of inorganic networks, which exhibit a diverse compositional range and considerable structural versatility,[1] as well as important magnetic,[2] optical,[1] and catalytic properties.[1] A great deal of attention has been paid to heteropolyanions containing inorganic anionic ligands,[3] mainly tetrahedral phosphate groups, because of the fascinating electronic and structural properties of polyoxomolybdenum and vanadium phosphates.[4] Among these derivatized polyoxoanions, examples incorporating the pyramidal sulfite anion as the inorganic ligand are largely unknown, except for the molybdenum(VI) derivative $[Mo^{VI}_5O_{15}(SO_3)_2]^{4-}$.[5] The lack of such complexes is surprising for two main reasons: first, metal–sulfite chemistry is very attractive in view of its potential for restricting the serious environmental problem of acid rain,[6] and second, exploring the possibility of incorporating the pyramidal sulfite anion into frameworks, rather than the more frequently used tetrahedral phosphate groups, could result in unprecedented structural features and novel properties for these frameworks.[7] Furthermore, molybdenum–sulfite chemistry is of great biological interest, since the enzyme sulfite oxidase, which is associated with the in vivo oxidation of SO_3^{2-} to SO_4^{2-}, contains a molybdenum atom at its active center.[8] Herein, we describe the synthesis, structural, and physicochemical characterization of the first polyoxomolybdenum(V) sulfite complexes **1**–**3**.

$(NH_4)_{20}[(Mo^{V}_2O_4)_6(\mu_2\text{-}SO_3)_{12}(\mu_3\text{-}SO_3)_4]\cdot 4\,H_2O$ **1**

$(NH_4)_{15}\{Na[(Mo^{V}_2O_4)_6(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)]_2\}\cdot 5\,H_2O$ **2**

$(NH_4)_8[(Mo^{V}_2O_4)(SO_3)_4(\mu_2\text{-}SO_3)]\cdot 2\,H_2O$ **3**

Complex **1** was prepared by treating Mo^VCl_5 (7.3 mmol) in concentrated (37 %) $HCl:H_2O$ (1:4 v/v, pH approximately 0) with solid $(NH_4)_2SO_3$ (Scheme 1). Upon addition of $(NH_4)_2SO_3$ (89 mmol) the pH of the solution changed to approximately 5, and thus it is apparent that the SO_3^{2-} ion performs the dual role of raising the pH of the solution, as well as acting as a ligand. However, if the same reaction was performed with a larger quantity of $(NH_4)_2SO_3$ (150 mmol, final pH of the solution was approximately 6), complex **3** was isolated (Scheme 1). Reduction of $Na_2Mo^{VI}O_4$ dissolved in concentrated (37 %) $HCl:H_2O$ (pH approximately 0) with an excess of hydrazine, followed by addition of $(NH_4)_2SO_3$ (final pH of the solution was approximately 5.5) resulted in the formation of **2** (Scheme 1).



Scheme 1. The synthetic routes leading to the isolation of **1**–**3**.

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[*] Dr. T. A. Kabanos, M. J. Manos
Department of Chemistry
Section of Inorganic and Analytical Chemistry
University of Ioannina, 45110 Ioannina (Greece)
Fax: (+30) 6510-44831
E-mail: tkampano@cc.uoi.gr

Dr. A. M. Z. Slawin, Prof. J. D. Woollins
Department of Chemistry
University of St. Andrews
St. Andrews, Fife KY16 9ST (UK)
Fax: (+44) 1334-463-384
E-mail: jdw3@st-andrews.ac.uk

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The X-ray structure of **1**[9] exhibits a $[(\mathrm{Mo}_2^{\mathrm{V}}O_4)_6(SO_3)_{16}]^{20-}$ cluster **1a** (Figure 1 A), which contains 12 Mo^{V} centers within the main structural unit. Each molybdenum atom has octahedral coordination, and is bonded to a terminal oxo group, two μ_2-O^{2-} ions, and three sulfite (two μ_2- and one μ_3-) oxygen atoms. The twelve Mo^{V} atoms form six binuclear units $[\mathrm{Mo}_2^{\mathrm{V}}O_4]^{2+}$ with a Mo−Mo separation of about 2.56 Å (single bond). The six $[\mathrm{Mo}_2^{\mathrm{V}}O_4]^{2+}$ moieties are connected to each other by twelve sulfite ligands, Twelve of which have a μ_2-(2L,2M) bonding mode, while the remaining four anions have the novel μ_3- (3L,3M) mode of ligation (see below). The μ_2-SO_3^{2-} ions can be considered as "outer" groups, and each of these anions bridges two $\mathrm{Mo}_2^{\mathrm{V}}O_{10}$ units comprised of two edge-sharing $\mathrm{Mo}^{\mathrm{V}}O_6$ octahedra, while the four μ_3-SO_3^{2-} anions are the "inner" groups, and each of these anions are connected to three Mo_2O_{10} dimeric moieties (Figure 1 B).[10] Four ammonium cations are located deep within the $[(\mathrm{Mo}_2^{\mathrm{V}}O_4)_6(SO_3)_{16}]^{20-}$ ion (Figure 1 B), and contribute to its stability. The arrangement of the molybdenum atoms in **1** is similar to an ε-Keggin isomer (Figure 1 C),[1a, 11] except that **1** contains six separated $\{Mo_2O_{10}\}$ moieties (Figure 1 B). This arrangement is in contrast to ε-Keggin derivatives (and other Keggin forms), where the twelve MO_6 octahedra are arranged in four groups of three edge-shared octahedra, M_3O_{13}.

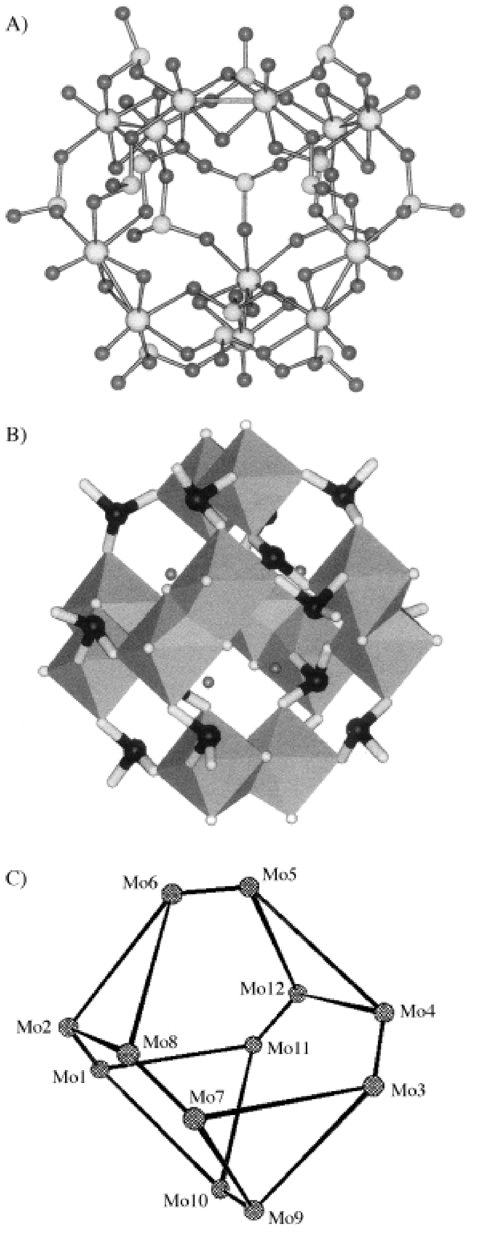


Figure 1. A) Ball-and-stick representation of the $[(Mo_2O_4)_6(SO_3)_{16}]^{20-}$ ion: Mo: gray, S: smaller gray balls, O: dark-gray. Average bond lengths [Å]: Mo=O 1.69(1), Mo-O (μ_2-O^{2-}) 1.944(9), Mo-O (μ_2-SO_3^{2-}) 2.13(1), Mo-O (μ_3-SO_3^{2-}) 2.20(1), Mo-Mo (single bond) 2.561(4), S-O (terminal) 1.49(1), S-O (μ_2-SO_3^{2-}) 1.55(1), S-O (μ_3-SO_3^{2-}) 1.537(9); B) polyhedral representation of the $[(Mo_2O_4)_6(SO_3)_{16}]^{20-}$ ion: S: black, O: white, N: gray; C) the arrangement of the twelve Mo^{V} atoms of the $[(Mo_2O_4)_6(SO_3)_{16}]^{20-}$ ion.

X-ray structural analysis of **2**[9] revealed the presence of the discrete anion $[Na\{(\mathrm{Mo}_2^{\mathrm{V}}O_4)_3(\mu_2\text{-}O)_3(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)\}_2]^{15-}$ (**2a**; Figure 2 A), with ammonium cations and water of crystallization also present in the lattice. The anion **2a** consists of two identical hexanuclear polyoxomolybdenum sulfite anions $[(\mathrm{Mo}_2^{\mathrm{V}}O_4)_3(\mu_2\text{-}O)_3(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)]^{8-}$ (**2b**; Figure 2 B), linked by a sodium cation. The six molybdenum(v)

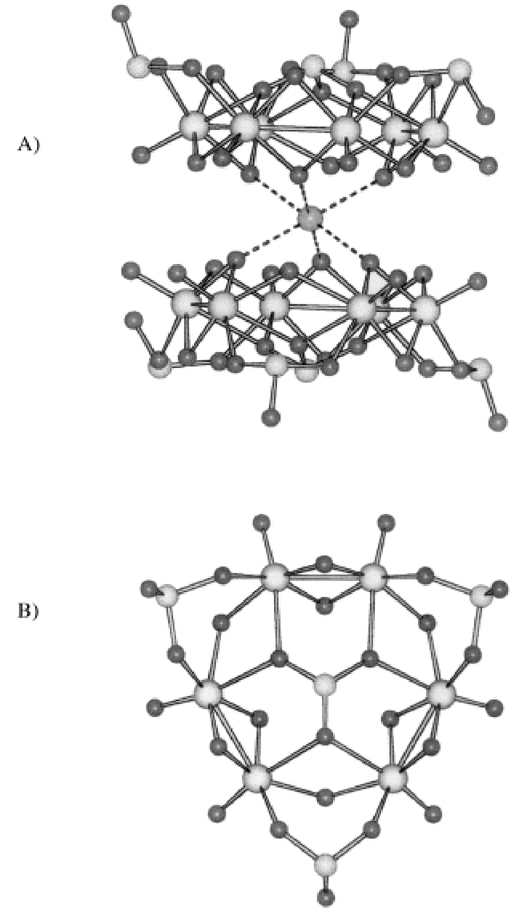


Figure 2. A) Representation of the $[Na\{(Mo_2O_4)_3(O)_3(SO_3)_4\}_2]^{15-}$ dimer: Mo: light-gray, S: smaller light-gray balls, O: dark gray, Na: gray; B) ball-and-stick representation of **2b**: Mo: gray, S: smaller gray balls, O: dark gray. Average bond lengths [Å]: Mo = O 1.673(1), Mo-O (μ_2-O^{2-} of the $\{Mo_2O_4\}$ units) 1.944(8), Mo-O (μ_2-O^{2-} bridging $\{Mo_2O_4\}$ units) 2.11(1), Mo-O (μ_2-SO_3^{2-}) 2.059(3), Mo-O (μ_6-SO_3^{2-}) 2.36(2), Mo-Mo (single bond) 2.597(5), S-O (terminal) 1.48(1), S-O (μ_2-SO_3^{2-}) 1.565(8), S-O (μ_6-SO_3^{2-}) 1.528(2).

atoms are co-planar, and are arranged in a pseudohexagonal arrangement, in which alternating bonding and non-bonding contacts are evident. There are four sulfite groups in **2b**: three of these are on the periphery of the cluster and possess a terminal oxo group, while the unique central sulfite group provides three μ_2-oxygen bridges, so as to join each pair of molybdenum(v) centers. There are three crystallographically independent molybdenum atoms in the asymmetric unit, (Figure 2B). Each atom has severely distorted octahedral geometry (ignoring the Mo^{V}–Mo^{V} bond), being coordinated to three μ_2-O^{2-} ions, two sulfite (one μ_2- and one μ_6-) oxygen atoms, as well as an oxo group. The sulfite groups (3μ_2- and one μ_6-) and the three "*syn*" μ_2-O^{2-} ions are located on one side, with the terminal oxo group and the six "*anti*" μ_2-O^{2-} ions found on the other side, such that the $[(Mo_2{}^{V}O_4)_3(\mu_2\text{-}O)_3(\mu_2\text{-}SO_3)_3(\mu_6\text{-}SO_3)]^{8-}$ cluster takes the shape of an adorned crown. In the dimeric assembly **2a** (Figure 2A) a sodium cation is sandwiched between two identical **2b** anions. The two anions are staggered with respect to one another, so as to effect octahedral coordination of the sodium cation, which interacts with the six *anti*-μ_2-O^{2-} ions of the $[Mo^{V}_{2}O_4]^{2+}$ moieties. The anion **2b** is closely related to several molybdenum(v) oxometalates containing phosphate ligands[4b, 12a–d] as well as sulfate/arsenite[12e] and carbonate groups, for example **4**.[12f]

$(NH_4)_5[(Mo^{V}_{2}O_4)_3(\mu_6\text{-}CO_3)(\mu\text{-}CO_3)_3(\mu\text{-}OH)_3]$ **4**

All of these complexes, which are reminiscent of the "Anderson" species,[1a] possess a Mo$_6$-planar core with a central μ_6 and three peripheral μ_2 ligands as well as three additional hydroxy (in most cases) or oxo groups bridging the three $[Mo^{V}_{2}O_4]^{2+}$ moieties. In **2b**, these ligands are pyramidal SO$_3^{2-}$ ions, whereas in the "Anderson"-like molybdenum(v) hexametalates so far reported, the equivalent ligands are generally tetrahedral (phosphates), or less frequently trigonal-planar anions (carbonates) or mixed tetrahedral-pyramidal building blocks (sulfate – arsenite anions).

A comparison of **1a**, **2b** and the ion $[(Mo^{V}_{2}O_4)_3(OH)_3(CO_3)_4]^{5-}$)[12f] (**4a**) reveals that the same structural unit $[(Mo^{V}_{2}O_4)(\mu_2\text{-}XO_3)]$ (X = S, C) exists in all cases, where short Mo^{V}–Mo^{V} separations (Mo^{V}–Mo^{V} single bonds; **1a**: 2.561(4), **2b**: 2.597(5), **4a**: 2.5884(6) Å) alternating with longer Mo···Mo contacts (**1a**: 5.70(3), **2b**: 3.593(4), **4a**: 3.548(6) Å). This observation proves that the 4d electrons must be regarded as being localized in all $\{Mo^{V}_{2}\}$ pairs, a fact which corresponds to the diamagnetism and the red color of the cluster complexes **1**, **2**, and **4**.[13]

As shown in Figure 3, the anion of **3** is a centrosymmetric dimer.[9] Each molybdenum(v) atom is coordinated in a distorted octahedral geometry (ignoring the Mo^{V}–Mo^{V} interaction) by two μ_2-O^{2-} ions, three sulfite (two terminal and one μ_2-) oxygen atoms, and an oxo group. A comparison of **3**, which contains the *syn*-Mo^{V}(O)(μ_2-O)$_2$Mo^{V}(O) core, with $[(SO_4)Mo^{V}(O)(\mu_2\text{-}S)_2Mo^{V}(O)(SO_4)]^{2-}$,[14] which contains the *syn*-Mo^{V}(O)(μ_2-S)$_2$Mo^{V}(O) unit, reveals that the Mo^{V}–Mo^{V} bond is approximately 2.60 Å for **3**, compared with 2.80 Å for the latter complex. In addition, the Mo-O$_b$(S$_b$)-Mo (b = bridging) bond angles are approximately 83.5 and 74.5°, respectively, while the O$_b$(S$_b$)-Mo-O$_b$(S$_b$) bond angles are approximately 95° for **3** and 105° for the latter.

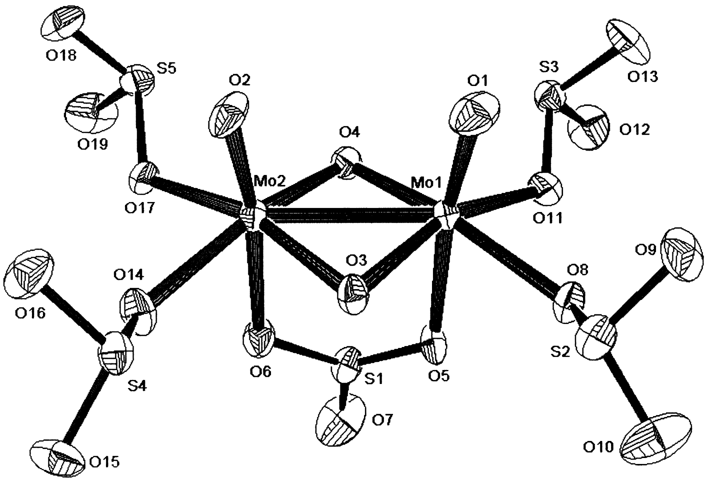
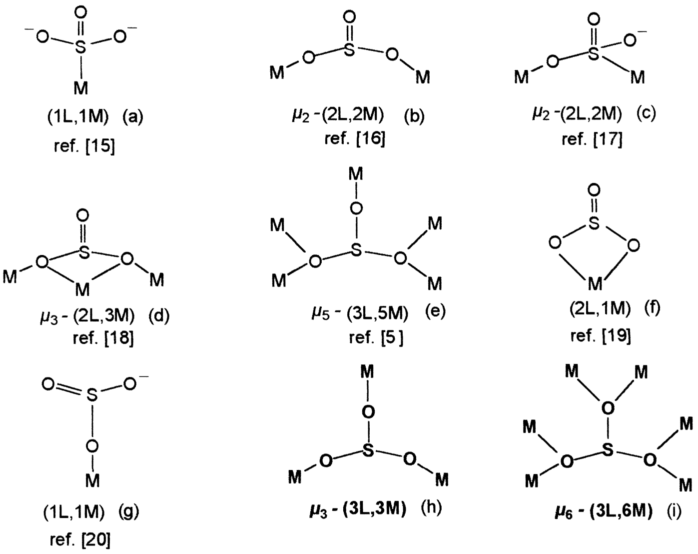


Figure 3. ORTEP plot of **3**. Displacement ellipsoids are plotted at the 50% probability level. Average bond lengths [Å]: Mo=O 1.686(5), Mo-O (μ_2-O^{2-}) 1.940(9), Mo-O (terminal-SO$_3^{2-}$) 2.10(1), Mo-O (μ_2-SO$_3^{2-}$) 2.27(1), Mo-Mo (single bond) 2.5872(18), S-O (terminal) 1.46(10), S-O (terminal-SO$_3^{2-}$) 1.57(2), S-O (μ_2-SO$_3^{2-}$) 1.53(1).

It is worth noting that the sulfite anion exhibits the bonding modes a – g, (Scheme 2) in the known metal complexes[15–20] and the only polyoxometal sulfite complex.[5] The two new bonding modes h and i, observed in complexes **1** and **2**, are also shown in Scheme 2. Characteristic IR bands, solid- and solution-state UV/Vis spectra, as well as thermogravimetric analysis data for complexes **1**–**3** are reported in the Experimental Section.



Scheme 2. The bonding modes (a – g) of SO$_3^{2-}$ ions observed in metal complexes and the only polyoxometal sulfite complex, and the two new bonding modes (h and i) present in complexes **1** and **3**, respectively.

In conclusion, the first polyoxomolybdenum(v) sulfite complexes **1**–**3** have been synthesized and structurally and physicochemically characterized. The modification of the oxide microstructure by the incorporation of SO_3^{2-} groups is apparent in the structure of the dodecamer **1**, which exhibits a unique structural motif among polyoxomolybdenum(v) dodecamers (and polyoxometalates in general). Thus, the insertion of pyramidal SO_3^{2-} ions into polyoxometalate units can be effective for the assembly of frameworks with novel structural characteristics (and possibly new properties), as compared to established metal oxides containing tetrahedral phosphate ligands. Furthermore, the novel μ_3-(3L,3M) and μ_6-(3L,6M) coordination modes of the sulfite anion observed in **1** and **2**, respectively, reveal the great versatility of the sulfite group. Therefore, this seemingly pedestrian anion can be an excellent ligand not only in polyoxometalates, but in coordination complexes in general.

Experimental Section

1: Solid $(NH_4)_2SO_3$ (12.00 g, 89 mmol) was added in one portion to a light-red solution of $MoCl_5$ (2.00 g, 7.3 mmol, pH ~ 0) in concentrated (37 %) HCl:H_2O (1:4 v/v, 25 mL). After stirring the mixture for 5 min, the initially formed orange solid had redissolved, and a dark red (pH ~ 5) solution was obtained. The solution was kept in an open beaker for one day and then the precipitated red needles were filtered and dried in the air. Yield: 1.44 g (73 % based on Mo). IR: $\tilde{\nu} = 1637$ [$\delta(H_2O)$], 1401 [$\delta(NH_4^+)$], 1051 [$\nu(SO_3^{2-})$], 988 [$\nu(Mo{=}O)$], 969 [$\nu(Mo{=}O)$], 895 [$\nu(SO_3^{2-})$], 837 [$\nu(SO_3^{2-})$], 677 [$\nu(SO_3^{2-})$], 479 cm^{-1} [$\nu(SO_3^{2-})$]; UV/Vis (solid-state reflectance spectrum): $\lambda = 553$, 329 nm; UV/Vis (H_2O): λ/nm (ε/$dm^3 mol^{-1} cm^{-1}$) = 314 (30200); TGA: percentage weight loss (temperature (°C)) = 5.17 (28.2), 32.53 (135.1), 9.52 (254.8), 4.66 (396); elemental analysis calcd (%) for $H_{88}Mo_{12}N_{20}O_{76}S_{16}$ (3249.14): H 2.73, N 8.62, S 15.79, Mo 35.43; found: H 2.85, N 8.50, S 15.90, Mo 35.65.

2: Hydrazine monohydrate (0.320 g, 6.3 mmol) was added to a stirred solution of $Na_2Mo^{VI}O_4 \cdot 2H_2O$ (3.00 g, 12.6 mmol, pH ~ 0) in concentrated (37 %) HCl:H_2O (1:4 v/v, 25 mL). The light-yellow color of the solution changed to dark-blue. Solid $(NH_4)_2SO_3$ (9.00 g, 67 mmol) was then added to the solution in one portion. Upon addition of $(NH_4)_2SO_3$ the dark-blue color of the solution became olive-green, and its pH value was ca. 5.5. The solution was kept in an open beaker for 2–3 days, after which time the precipitated red block-shaped crystals were filtered and dried in the air. Yield: 2.17 g (78 % based on Mo). IR: $\tilde{\nu} = 1637$ [$\delta(H_2O)$], 1408 [$\delta(NH_4^+)$], 1088 [$\nu(SO_3^{2-})$], 981 [$\nu(Mo{=}O)$], 963 [$\nu(Mo{=}O)$], 889 [$\nu(SO_3^{2-})$], 865 [$\nu(SO_3^{2-})$], 809 [$\nu(SO_3^{2-})$], 546 [$\nu(SO_3^{2-})$], 487 cm^{-1} [$\nu(SO_3^{2-})$]; UV/Vis (solid-state reflectance spectrum): $\lambda = 495$, 324, 251 nm; UV/Vis (H_2O) λ/nm (ε/$dm^3 mol^{-1} cm^{-1}$) = 470(sh) (310), 306 (16500), 208 (32200); TGA: percentage weight loss (temperature (°C)) = 3.43 (69.4), 4.02 (128.2), 21.87 (236.4), 1.37 (374.3), 0.84 (397.0), 0.11 (579.1); elemental analysis calcd (%) for $H_{70}Mo_{12}N_{15}NaO_{59}S_8$ (2655.46): H 2.66, N 7.91, S 9.66, Mo 43.36; found: H 2.75, N 8.20, S 9.40, Mo 43.15.

3: This was synthesized in a similar fashion to **1**, except that the amount of $(NH_4)_2SO_3$ added to the $MoCl_5$ (2.00 g, 7.3 mmol) solution was 20.00 g (150 mmol) and the pH value of the resulting dark-red solution was ca. 6. The solution was filtered and red orthogonal crystals of **3** were formed by vapor diffusion of MeOH into the filtrate for one week. The crystals were filtered and dried in air. Yield: 1.20 g (39 % based on Mo). IR: $\tilde{\nu} = 1403$ [$\delta(NH_4^+)$], 993 [$\nu(SO_3^{2-})$], 965 [$\nu(Mo{=}O)$], 903 [$\nu(SO_3^{2-})$], 821 [$\nu(SO_3^{2-})$], 662 [$\nu(SO_3^{2-})$], 527 [$\nu(SO_3^{2-})$], 468 cm^{-1} [$\nu(SO_3^{2-})$]; UV/Vis (solid-state reflectance spectrum): $\lambda = 553$, 325 nm; UV/Vis (H_2O) λ/nm (ε/$dm^3 mol^{-1} cm^{-1}$) = 312 (4000); TGA: percentage weight loss (temperature (°C)) = 67 (160), 1.36 (395.4); elemental analysis calcd (%) for $H_{36}Mo_2N_8O_{21}S_5$ (836.55): H 4.33, N 13.39, S 19.16, Mo 22.94; found: H 4.17, N 13.13, S 19.25, Mo 23.2.

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[1] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, New York, **1983**; b) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34; c) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer Academic Publishers, Dordrecht, **1994**; d) *Chem. Rev.* **1998**, *98*, 8 (guest editor: C. L. Hill).

[2] J. M. Clemente-Juan, E. Coronado, *Coord. Chem. Rev.* **1999**, *193*, 361, and references therein.

[3] A. Müller, F. Peters, M. T. Pope, D. Gatteschi, *Chem. Rev.* **1998**, *98*, 239, and references therein.

[4] a) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268, and references therein; b) R. C. Haushalter, L. A. Mundi, *Chem. Mater.* **1992**, *4*, 31; c) C. du Peloux, A. Dolbecq, P. Mialane, J. Marrot, E. Riviere, F. Secheresse, *Angew. Chem.* **2001**, *113*, 2521; *Angew. Chem. Int. Ed.* **2001**, *40*, 2455.

[5] K. Y. Matsumoto, M. Kato, Y. Sasaki, *Bull. Chem. Soc. Jpn.* **1976**, *49*, 106.

[6] C. Brandt, R. van Eldik, *Chem. Rev.* **1995**, *95*, 119.

[7] a) W. T. A. Harrison, M. L. F. Phillips, J. Stanchfield, T. M. Nenoff, *Angew. Chem.* **2000**, *112*, 3966; *Angew. Chem. Int. Ed.* **2000**, *39*, 3808; b) M. Shich, K. J. Martin, P. J. Squattrito, A. Clearfield, *Inorg. Chem.* **1990**, *29*, 958.

[8] a) R. Hille, *Chem. Rev.* **1996**, *96*, 2757; b) J. L. Johnson in *Molybdenum and Molybdenum Containing Enzymes* (Ed.: M. P. Coughlan), Pergamon, Oxford, **1980**.

[9] Crystal data for **1**: $(NH_4)_{20}[(Mo^{V}_2O_4)_6(SO_3)_{16}] \cdot 4H_2O$: $H_{88}Mo_{12}N_{20}O_{76}S_{16}$, $M_r = 3249.14$, monoclinic , space group $C2/c$, $a = 57.0591(3)$, $b = 15.6701(3)$, $c = 27.4303(5)$ Å, $\beta = 116.7510(10)$, $V = 21901.0(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.971$ g cm^{-3}, $T = 293(2)$ K. $R1$(final) = 0.0490, $wR2$ = 0.1260. *Crystal data* for **2**: $(NH_4)_{15}[Na\{(Mo^{V}_2O_4)_3(O)_2(SO_3)_4\}_2] \cdot 5H_2O$: $H_{70}Mo_{12}N_{15}NaO_{59}S_8$, $M_r = 2655.46$, monoclinic, space group $C2/m$, $a = 18.2657(8)$, $b = 14.5326(4)$, $c = 14.6891(7)$ Å, $\beta = 117.600(2)$°, $V = 3455.5(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.552$ Mg cm^{-3}, $T = 293(2)$ K, $R1$(final) = 0.0372, $wR2$ = 0.0946. The crystal was of poor quality. Crystal data for **3**: $(NH_4)_8[(Mo^{V}_2O_4)(SO_3)_5] \cdot 2H_2O$: $H_{36}Mo_2N_8O_{21}S_5$, $M_r = 836.55$, triclinic , space group $P\bar{1}$, $a = 8.8652(4)$, $b = 17.7368(8)$, $c = 19.2683(7)$ Å, $\alpha = 66.9160(10)$, $\beta = 88.167(2)$, $\gamma = 77.4370(10)$°, $V = 2715.6(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.046$ g cm^{-3}, $T = 293(2)$ K, $R1$(final) = 0.0372, $wR2$ = 0.0946. 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 numbers CSD-412299, CSD-412300, and CSD-412301.

[10] Two examples of polyoxometalates that have inner and outer XO_3 groups are reported in the following papers: a) T. Ozeki, H. Ichida, Y. Sasaki, *Acta Crystallogr. Sect. C* **1987**, *43*, 1662; b) M. Leyrie, A. Teze, G. Herve, *Inorg. Chem.* **1985**, *24*, 1275–1277.

[11] a) H. K. Chae, W. G. Klemperer, D. E. Páez Loyo, *Inorg. Chem.* **1992**, *31*, 3187; b) I. Khan, A. Müller, S. Dillinger, H. Bögge, Q. Chen, J. Zubieta, *Angew. Chem.* **1993**, *105*, 1811; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1780; c) H. Ichida, K. Nagai, Y. Sasaki, M. T. Pope, *J. Am. Chem. Soc.* **1989**, *111*, 586; d) A. Müller, C. Beughalt, P. Kögerler, H. Bögge, S. Bud'ko, M. Luban, *Inorg. Chem.* **2000**, *39*, 5186.

[12] a) G. Cao, R. C. Haushalter, K. G. Strohmaier, *Inorg. Chem.* **1993**, *32*, 127; b) L. M. Mundi, R. C. Haushalter, *Inorg. Chem.* **1992**, *31*, 3050; c) E. Cadot, A. Dolbecq, B. Salignac, F. Secheresse, *Chem. Eur. J.* **1999**, *5*, 2396; d) R. C. Haushalter, F. W. Lai, *Angew. Chem.* **1989**, *101*, 802; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 743; e) C. Livage, E. Dumas, C. Marchal-Roch, G. Herve, *C. R. Acad. Sci. Ser. IIc* **2000**, *3*, 95; f) M. J. Manos, A. D. Keramidas, J. D. Woolins, A. M. Z. Slawin, T. A. Kabanos, *J. Chem. Soc. Dalton Trans.* **2001**, 3419.

[13] A. Müller, S. Dillinger, E. Krickemeyer, H. Bögge, W. Plass, A. Stammler, R. C. Haushalter, *Z. Naturforsch. B* **1997**, *52*, 1301.

[14] C. G. Kim, D. Coucouvanis, *Inorg. Chem.* **1993**, *32*, 2232.

[15] a) S. C. Gibney, G. Ferraud, M. Shang, *Inorg. Chem.* **1999**, *38*, 2898; b) V. C. Kinn, P. F. Kelly, C. Papadimitriou, A. M. Z. Slawin, D. J. Williams, J. D. Woolins, *J. Chem. Soc. Dalton Trans.* **1993**, 1805; c) S. Schmidt, F. W. Heineman, A. Grohmann, *Eur. J. Inorg. Chem.* **2000**, 1657.

[16] a) P. T. Maragh, T. P. Dasgupta, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1995**, 1805; b) K. Wierhardt, S. Drueke, P. Chaudhuri, U. Florke, H.-J. Haupt, B. Nuber, J. Weiss, *Z. Naturforsch. B* **1989**, *44*, 1093.

[17] C. Fukahara, E. Asato, T. Shimoji, K. Katsura, M. Mori, K. Matsumoto, S. Ooi, *J. Chem. Soc. Dalton Trans.* **1987**, 1305.

[18] M. Harvey, S. Baggio, R. Baggio, H. Pardo, *Acta Crystallogr. Sect. C* **1999**, *55*, 1278.

[19] a) C. G. Kim, D. Coucouvanis, *Inorg. Chem.* **1993**, *32*, 1881; b) F. Cessoni, C. A. Chilardi, S. Middolini, S. Moneti, A. Orlandini, *J. Organomet. Chem.* **1987**, *323*, 5.

[20] L. O. Larson, L. Niinisto, *Acta Chem. Scand.* **1973**, *27*, 859.

"Molecular Symmetry Breakers" Generating Metal-Oxide-Based Nanoobject Fragments as Synthons for Complex Structures: $[\{Mo_{128}Eu_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$, a Giant-Cluster Dimer**

Leroy Cronin, Christian Beugholt, Erich Krickemeyer, Mark Schmidtmann, Hartmut Bögge, Paul Kögerler, T. Kim K. Luong, and Achim Müller*

Dedicated to Professor Karl Wieghardt
on the occasion of his 60th birthday

The synthesis and manipulation of a huge variety of nanoscaled species of similar chemical nature under one-pot reaction conditions requires access to a potential "dynamic library" of appropriate building blocks.[1a] For instance, by exploiting a detailed knowledge of polyoxometalate chemistry, a variety of discrete clusters (see ref. [1b–g]) and related extended structures[2] can be formed by the linking of well-defined metal–oxygen building blocks. These types of compounds have been shown to exhibit unusual topological as well as electronic properties and, furthermore, are interesting for materials science.[3–5] A couple of years ago, we reported wheel-shaped mixed-valence molybdenum clusters of the type $\{Mo_{154}\}$, $\{Mo_{176}\}$,[1b, 6, 7] and $\{Mo_{248}\}$;[1f] of these, the first two parent species—exhibiting nanometer-sized cavities and therefore presenting fascinating perspectives for a new type of host–guest chemistry—can now be obtained in high yields in facile syntheses.[8] Herein, we describe for the first time a dimer of two giant clusters, that is, of structurally well-defined covalently linked nanoobjects with a rather high degree of complexity. The dimer contains two elliptical molybdenum oxide based units, linked together by two Eu-O-Mo bonds, each unit incorporates 128 $Mo^{VI/V}$ and 4 Eu^{III} centers and includes large fragments of the above-mentioned parent clusters. The interpretation would be that these dimers are formed by Eu^{III} centers acting as symmetry breakers which prevent the corresponding highly symmetrical parent-ring closure.[1b, 6] *Of general importance is that in systems showing growth, potential (abundant) agents, such as* Eu^{III} *centers, can act as "symmetry breakers" which results in the generation of structural complexity.* In any case, it is important to realize that large nanoobject fragments can, in principle, be used as synthons. The ability to connect or assemble clusters in a predefined manner may allow the design of nanoscopic devices using the "bottom up" method (that is, generating large objects from small units).

While the "classical" reduction of an acidified aqueous molybdate solution leads to the blue, wheel-shaped tetra- and hexadecameric parent-cluster anions mentioned above,[6] the generation of smaller species requires the presence of electrophiles, such as Pr^{III} ions which increase the curvature by replacing the larger electrophilic $\{Mo_2\}^{2+}$-type building units (see below). In the presence of smaller Eu^{III} ions, even ring closure to the parent clusters does not take place, which allows the isolation of compound **1** containing a novel cluster collective. Compound **1** was characterized by single-crystal X-ray structure analysis[9] (including bond valence sum (BVS) calculation to aid in the determination of the (formal) number of Mo^V centers and protonation sites),[10] elemental analyses ((K), Eu, Mo; see details in ref. [12]), thermogravimetric analysis, redox titration (to aid in the determination of the (formal) number of Mo^V centers), IR, and EXAFS spectroscopy (Eu-L_{III} edge,[11] with the option to distinguish in principle between the different Eu centers in the lattice and cluster sites) as well as magnetic susceptibility measurements with a SQUID magnetometer.

$Eu_6X_2\mathbf{1a}\cdot \text{ca. } 600\,H_2O$ **1**[12]

$[\{Mo^{VI/V}_{128}Eu_4O_{388}H_{10}(H_2O)_{81}\}_2]^{20-}$ **1a**[12]

The crystal structure of **1** shows the dimeric unit **1a**, which comprises two linked nanosized clusters with 1202 non-hydrogen (including 264 metal) positions, of rather high structural complexity—regarding the versatility of different building blocks and protonation types—packed in a configuration that gives rise to channels incorporating Eu^{III} ions on the inner side of the cavities (Figure 1; see also ref. [12]). Compound **1a** can be geometrically related to fragments of the ring-shaped $\{Mo_{154}\} \equiv [Mo_{154}O_{462}H_{14}(H_2O)_{70}]^{14-}$ (**2a**) parent-cluster archetype. The two cluster units of **1a** are elliptical with an outer and inner ring diameter of about 38

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[*] Prof. Dr. A. Müller, Dr. L. Cronin, Dr. C. Beugholt, E. Krickemeyer, M. Schmidtmann, Dr. H. Bögge, Dr. T. K. K. Luong
Lehrstuhl für Anorganische Chemie I
Fakultät für Chemie
Universität Bielefeld
Postfach 100131, 33501 Bielefeld (Germany)
Fax: (+49) 521-106-6003
E-mail: a.mueller@uni-bielefeld.de

Dr. P. Kögerler
Ames Laboratory
Iowa State University, Ames, IA 50014 (USA)

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