transfer from the apical Se^{2-} atom to the electron-deficient Mo_3 core[10] resulting in partial $Se_{(ap)}$–$Se_{(a)}$ bonding (see Scheme I). The presence of the apical Se atom causes, in all subclusters, a significant lengthening of the $Se_{(a)}$–$Se_{(b)}$ bonds in the bridging formally "Se_2^{2-}" ligands. The average bond length becomes 2.45 (7) Å, compared to the 2.36 (3) Å average bond length of the terminal Se_2^{2-} ligands. In fact, there is an inverse correlation between the $Se_{(ap)}$–$Se_{(a)}$ bond lengths in the $[Se_7]^{8-}$ fragment (see Scheme I) and the $Se_{(a)}$–$Se_{(b)}$ bonds in the bridging "Se_2^{2-}" ligands themselves.

In conclusion, hydrothermal synthesis for polychalcogenide compounds is not only feasible but also an interesting and promising new alternative to the more traditional techniques usually employed in this area of chemistry. It may yield structurally and chemically unique compounds not accessible otherwise.[11] A number of other Mo/Se clusters have been made hydrothermally. Their structural characterization is in progress.

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Supplementary Material Available: Tables of atomic coordinates of all atoms, isotropic thermal parameters of all atoms, and all bond distances and angles for $K_{12}Mo_{12}Se_{56}$ (13 pages); listing of calculated and observed ($10F_o/10F_c$) structure factors for $K_{12}Mo_{12}Se_{56}$ (24 pages). Ordering information is given on any current masthead page.

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(9) Flomer, W. A.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 3682–3683.

(10) (a) Meerschaut, A.; Guemas, L.; Berger, R.; Rouxel, J. *Acta Crystallogr.* **1979**, *B35*, 1747–1750. (b) Sunshine, S. A.; Ibers, J. A. *Acta Crystallogr.* **1987**, *C43*, 1019–1022. (c) It is possible that lattice packing forces stabilize $Se_{(ap)}$ as may be implied by the close contacts of these atoms with two or three surrounding K^+ ions. The detailed structure of this complicated molecule will be published elsewhere.

(11) Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875–882.

(12) Preliminary work shows that this reaction is general to almost every metal/polychalcogenide combination. (a) Liao, J. H.; Kanatzidis, M. G., manuscript in preparation. (b) Liao, J. H.; McCarthy, T.; Sutorik, T.; Kanatzidis, M. G., work in progress.

A Novel Oxygen-Centered Hexanuclear Molybdenum Alkoxide Cluster, $Mo_6O(OEt)_{18}$

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The sol-gel approach, viz. hydrolysis of metal alkoxides and subsequent processing of the precipitated hydroxides or hydrous oxides, has become an important method for synthesis of oxide ceramics.[1] Using this approach, we have recently attempted to isolate reduced molybdenum oxides by hydrolysis of appropriate molybdenum alkoxides. In our study of the hydrolysis of $[Mo(OEt)_3]_4$ (**1**)[2] dissolved in toluene, addition of 12 mol of H_2O per mol of **1** resulted in complete precipitation of a gelatinous solid and, as expected, left an essentially colorless supernatant solution. Remarkably, however, if hydrolysis was performed with 14–16 mol of H_2O per mol of **1** a soluble brown species was formed in addition to the gelatinous solid. After separation of the solid and allowing the brown filtrate to stand for several days, dark brown crystals were deposited from the solution.[3] These crystals consisted of the compound $Mo_6O(OEt)_{18}\cdot4.8H_2O$, which contains a new oxygen-centered hexanuclear cluster unit, $Mo_6O(OEt)_{18}$ (**2**).

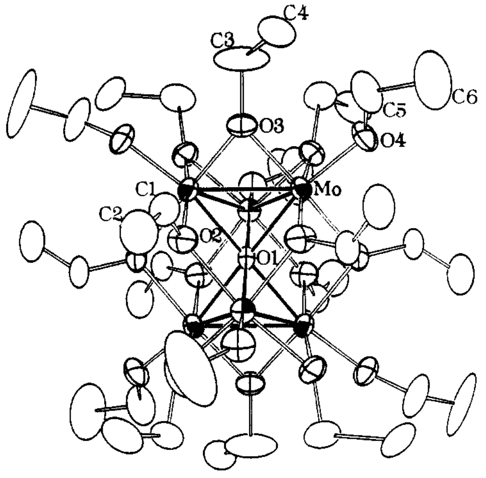

Figure 1. A view of the $Mo_6O(OEt)_{18}$ cluster unit **2** approximately perpendicular to the crystallographic 3-fold axis (50% thermal ellipsoids). Some significant bond distances are Mo–Mo = 2.6108 (3) Å, Mo–O1 = 2.1073 (4) Å, Mo–O2 = 2.098 (3) Å, Mo–O3 = 2.063 (4) Å, and Mo–O4 = 1.948 (3) Å. Only one orientation of the disordered ethyl groups is shown for clarity.

The molecular structure of **2**,[4] as shown in Figure 1, indicates a distorted octahedral cluster of Mo atoms with an oxygen atom in the center. The Mo_6 cluster unit is ligated by 12 edge-bridging OEt groups, and each Mo atom is also bonded to a terminal OEt ligand, as indicated by the formula $[Mo_6O(OEt)_{12}](OEt)_6$. The cluster unit is so severely distorted that two distinct triangular subunits can be recognized. The subunits can be thought of as two M_3X_{13} clusters joined together by sharing the central atom O1 and six inter-trimer bridging ethoxide ligands, as represented in the formulation $[Mo_3O_{1/2}(OEt)_{6/2}(OEt)_6]_2$. A measure of the distortion of the octahedral cluster unit is given by the deviation of the Mo–O1–Mo angle from 90°. In the distorted unit, this angle differs from 90° by 13.45°, i.e. the intra-trimer angle equals 76.55°. Also, if the Mo–O1 distance remained the same in the distorted and undistorted units, viz. 2.107 Å, a Mo–Mo bond distance of 2.98 Å would exist in the undistorted octahedral cluster. This distance is too long for a good Mo–Mo bonding interaction to occur. Thus, the cluster distorts so that six strong Mo–Mo bonds are formed at a distance of 2.6108 Å within the two triangular subunits. The six inter-trimer Mo–Mo distances of 3.309 Å represent essentially nonbonding separations.

Interstitially centered octahedral cluster species are well-known for scandium,[5] yttrium,[6] zirconium,[7] and the lanthanide elements.[8]

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(1) Mazdiyasni, K. S. *Cer. Int.* **1982**, *8*, 42.

(2) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

(3) In a typical preparation, **1** (1.08 mol) was dissolved in toluene and deoxygenated water (15.7 mol) was introduced by syringe under argon. Within minutes a solid brown material began precipitating from the solution. The reaction mixture was stirred for 1 h at room temperature before the solid was filtered off and the yellow-brown filtrate was recovered. A few crystals suitable for X-ray study were reproducibly grown directly from the filtrate solution within 1 to 2 weeks at −10 °C, or 4–5 days at room temperature.

(4) Compound **2** crystallized in the rhombohedral space group $R\bar{3}m$ with $a_H = 18.317$ (5) Å, $c_H = 15.359$ (3) Å, $Z = 3$, $d(\text{calc}) = 1.666$ g cm^{-3}. From data collected at −75 °C, the structure was refined to $R = 0.0311$ and $R_w = 0.0391$. An azimuthal scan of a reflection having χ near 90° indicated that no absorbtion correction was necessary. All non-hydrogen atoms were located and refined anisotropically. The ethyl groups of the ethoxide ligands, except C3 (bound to O3), were found to be disordered with respect to a mirror plane or a 2-fold axis. The $3m$ symmetry of the cluster unit thus results from averaging over the disordered C atom positions. Satisfactory refinement was obtained with the occupancy of each disordered C position set at 50%. Also, the solvent of crystallization evidenced by O5 was presumed to be water, since examination of the electron density map showed no peaks corresponding to C atoms of possible ethanol molecules. However, the possibility cannot be eliminated that O5 may belong to highly disordered ethanol molecules.

(5) Dudis, D. S.; Corbett, J. D.; Hwu, S. J. *Inorg. Chem.* **1986**, *25*, 3434.

(6) Ford, J. E.; Corbett, J. D.; Hwu, S. J. *Inorg. Chem.* **1983**, *22*, 2789.

(7) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 1927. Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 3272.

(8) Simon, A.; Warkentin, E. *Z. Anorg. Allg. Chem.* **1983**, *497*, 79.

0002-7863/90/1512-7402$02.50/0

A few examples are also known for niobium,[9] viz. $[Nb_6HI_8]^{n+}$ ($n = 2$ or 3) containing H as the centering element.[10] Up till now, it has been considered that these centered cluster species are stabilized by addition of electrons from the valence orbitals of the centering element to the bonding metal–metal orbitals of the cluster unit.[7] Thus, with few exceptions, these clusters exist only when the centering atom is present. However, in the case of $Mo_6O(OEt)_{18}$, which has 16 electrons for Mo–Mo bonding, the central oxygen atom should not be required for stability.[11] Addition of the 6 valence electrons from the central O atom gives a total of 22 electrons for the cluster unit. Presumably, these 6 additional electrons are placed at such a low energy relative to the metal–metal orbitals that they may be considered only as weakly interacting with the Mo–Mo bonding orbitals.

Another approach to the bonding of this cluster unit is to consider the latter as if it were two "independent" M_3X_{13} units, each with 8 electrons available for Mo–Mo bonding. Of main significance is the Mo–Mo distance of 2.6108 (3) Å, which is slightly greater than that of other 6-, 7-, or 8-electron M_3X_{13} clusters. For example, the 8-electron cases, $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2+}$[12] and $Zn_3Mo_3O_8$,[13] have d(Mo–Mo) of 2.550 (5) and 2.580 (2) Å, respectively. These distances are known to be influenced to some degree by interaction of the "capping" O atom with the Mo cluster orbitals of the triangular unit.[14] In the latter species, the Mo–O(cap) distances are 2.03 (1) and 2.06 (1) Å, respectively, whereas in **2**, this distance is 2.1073 (4) Å. The longer Mo–O1 distance is understandable because in **2** the O atom is 6-coordinate and in the other examples it is 3-coordinate.

Another significant difference between the triangular subunits of **2** and other M_3X_{13} clusters is the very short terminal Mo–O4 distance of 1.948 (3) Å. In the other known 8-electron M_3X_{13} examples, the corresponding distance is greater than 2.10 Å, viz. 2.13 (1) Å in $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2+}$ and 2.160 (8) Å in $Zn_3Mo_3O_8$. This suggests that significant Mo–O π interactions occur in the Mo–O terminal bonds of **2**, and this may in turn weaken the Mo–Mo bonding.

In another view, the structure of the cluster unit of **2** can be related to that of the isopolyanions $[M_6O_{19}]^{n-}$ (M = Mo or W, $n = 2$; M = Nb or Ta, $n = 8$).[15] Essentially, **2** is a reduced ethoxy analogue of the oxo anion. Specifically, the $[Mo_6O_{19}]^{2-}$ anion consists of an undistorted octahedral arrangement of Mo atoms centered by one O atom, bridged on each edge by twelve O atoms, and multiply bonded to six terminal O atoms. The isopolyanion is fully oxidized, and thus it has no d electrons available for Mo–Mo bonds. Electrons provided by the reduced oxidation state of molybdenum in the $Mo_6O(OEt)_{18}$ cluster, viz. Mo(3.33), are then utilized to form the Mo–Mo bonds of the distorted cluster.

Conceivably, it should be possible to oxidize the cluster unit by 1 and 2 electrons, leaving 15 and 14 electrons for metal–metal bonding. In the case of a 1-electron oxidation, the extent of delocalization of the unpaired electron over the entire cluster unit, as opposed to localization on one of the triangular subunits, would be of interest. At present, further efforts are underway to develop rational syntheses of compounds of this type and to elucidate their spectroscopic and chemical properties.

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Supplementary Material Available: A listing of crystal data, bond lengths and angles, and positional and thermal parameters for **2** (5 pages); tables of observed and calculated structure factors for **2** (4 pages). Ordering information is given on any current masthead page.

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[9] Simon, A. *Z. Anorg. Allg. Chem.* **1967**, *355*, 311.

[10] Also known, but less relevent to this finding, are the carbonyl cluster species containing C, P, and S centers. Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 123.

[11] Compare, for example, $[(Nb_6Cl_{12})Cl_6]^{n-}$ with $n = 4$, 3, or 2 and 16, 15, or 14 metal–metal bonding electrons, respectively.

[12] Bino, A.; Cotton F. A.; Dori, Z. *Inorg. Chim. Acta* **1979**, *33*, L133.

[13] Torardi, C. C.; McCarley, R. E. *Inorg. Chem.* **1985**, *24*, 476.

[14] Bursten, B. E.; Cotton, F. A.; Hall, M. B.; Najjar, R. C. *Inorg. Chem.* **1982**, *21*, 302.

[15] Lindquist, I. *Ark. Kemi.* **1952**, *5*, 247. Lindquist, I.; Aronsson, B. *Ark. Kemi.* **1954**, *7*, 49. Fuchs, J.; Jalr, K. F. *Z. Naturforsch.* **1968**, *23b*, 1380. Allcock, H. R.; Bissell, E. C.; Shawl, E. T. *Inorg. Chem.* **1973**, *12*, 2963. Fuchs, J.; Freiwald, W.; Hartl, H. *Acta. Crystallogr.* **1978**, *B34*, 1764.

Synthesis of the First Optically Pure, Fluorinated Inositol 1,4,5-Trisphosphate of *myo*-Inositol Stereochemistry and Its Effect on Ca^{2+} Release in Swiss 3T3 Cells

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The importance of inositol phosphates for intracellular signalling is now well established.[1,2] Stimulation of cell surface receptors by a variety of ligands initiates the hydrolysis of a membrane-located phosphoinositide to give D-*myo*-inositol 1,4,5-trisphosphate (Ins $1,4,5P_3$) and diacylglycerol. Ins $1,4,5P_3$ releases Ca^{2+} from intracellular stores associated with the endoplasmic reticulum, causing an increase in cytoplasmic free Ca^{2+} concentration.[3] A large number of inositol phosphates, apart from Ins $1,4,5P_3$, have been found in eukaryotic cells, but their role remains to be elucidated.[1,2,4-7] The complexity in inositol phosphate metabolism arises primarily because of the phosphorylation of Ins $1,4,5P_3$ by a 3-kinase to give D-*myo*-inositol 1,3,4,5-tetrakisphosphate (Ins $1,3,4,5P_4$).[8] In some, but not all, systems, Ins $1,3,4,5P_4$ may control intracellular Ca^{2+} movement,[9-11] thus regulating the amount of Ca^{2+} available to Ins $1,4,5P_3$. The extent to which the anabolism of Ins $1,4,5P_3$ occurs in different cell preparations used for studying inositol phosphate second messenger action is not clear, but an agent that could prevent metabolism by the 3-kinase pathway would be a useful probe for studying inositol phosphate function.[12-14]

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[1] Berridge, M. J.; Irvine, R. F. *Nature* **1989**, *341*, 197.

[2] Putney, J. W.; Takemura, H.; Hughes, A. R.; Horstman, P. A.; Thastrup, O. *FASEB J.* **1989**, *3*, 1899.

[3] Nishizuka, Y. *Nature* **1988**, *334*, 661.

[4] For a recent review on the chemistry and pharmacology of other novel inositol phosphate analogues, see: Nahorski, S. R.; Potter, B. V. L. *Trends Pharmacol. Sci.* **1989**, *10*, 139.

[5] Downes, C. P.; Mussat, M. C.; Michell, R. H. *Biochem. J.* **1982**, *203*, 169.

[6] Inhorn, R. C.; Bansal, V. S.; Majerus, P. W. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2170.

[7] Irvine, R. F.; Brown, K. D.; Berridge, M. J. *Biochem. J.* **1984**, *221*, 269.

[8] Irvine, R. F.; Letcher, A. J.; Heslop, J. P.; Berridge, M. J. *Nature* **1986**, *320*, 631.

[9] Irvine, R. F.; Moor, R. M.; Pollock, W. K.; Smith, P. M.; Wreggett, K. A. *Phil. Trans. R. Soc. London, B* **1988**, *320*, 281.

[10] Petersen, O. H. *Cell Calcium* **1989**, *10*, 375.

[11] Whitaker, M. *Nature* **1990**, *343*, 701.

[12] Strupish, J.; Cooke, A. M.; Gigg, R.; Potter, B. V. L.; Nahorski, S. R. *Biochem. J.* **1988**, *253*, 901.