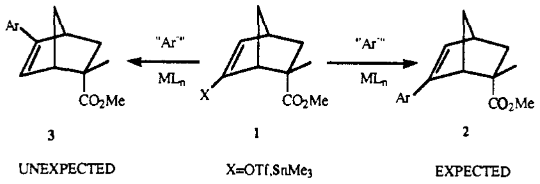
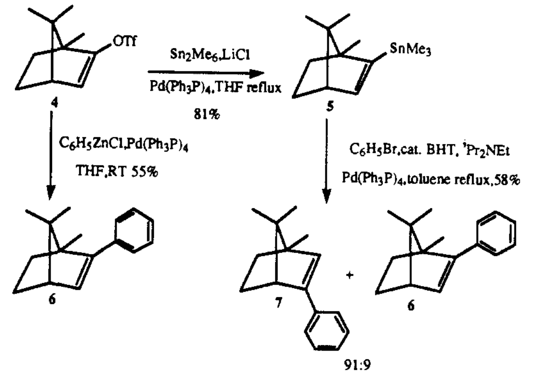
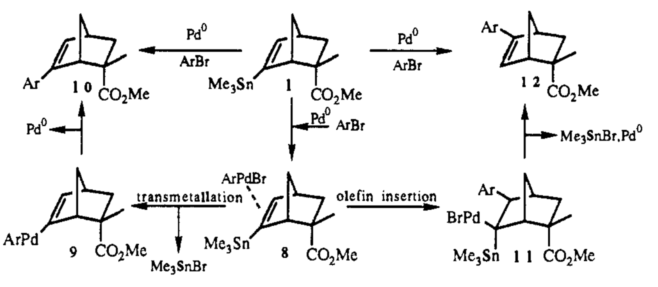
Scheme I



Scheme II



Scheme III



(d, $J = 3.4$ Hz)] and which was identical with the *minor* isomer we had obtained in the coupling of vinylstannane **5** with bromobenzene.[5]

Mechanistically, the initial steps of the reaction of compound **1**, $X = SnMe_3$, are probably oxidative insertion of the catalyst into the aryl bromide to give an $Ar-Pd^{II}-Br$ species followed by coordination of this species to the vinylstannane (Scheme III). For the "normal" ipso substitution to occur, transmetalation to a vinylpalladium species **9** would have to be the next step but is inhibited here by what we believe to be steric factors.[6,7] An alternative pathway could be Heck-type olefin insertion. The resulting intermediate **11** might then undergo the somewhat unusual trans β-hydride elimination which has been invoked to rationalize some Heck coupling products.[8] It might also conceivably proceed to **12** via 1,1-elimination to a carbene.

Whatever the precise factors that cause cine substitution of certain vinylstannanes, it is clear that cine substitution can sometimes entirely supplant the ipso substitution that is normally expected.

Acknowledgment. We thank Dr. Viresh Rawal for the details of the syntheses of the enol triflate and vinylstannane **1** we used in the synthesis of **2** and **3** and the National Science Foundation and the National Institutes of Health for their support of this work.

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[5] Due to the volatility of the products **6** and **7**, yields in the couplings of camphor derivatives **4** and **5** were only moderate. We performed a variety of coupling reactions using triflate **1**, stannane **1**, and various aryl halides. All of these were very efficient (80–100%) and regiospecific.

[6] When the vinylstannane analogue of **5** derived from (±)-epicamphor (4,7,7-trimethylbicyclo[2.2.1]heptan-2-one) was coupled with bromobenzene, the ratio of products **7**:**6** was 70:30. This suggests that steric crowding about the vinylstannane is in part responsible for steering the aryl group to the cine position. The vinylstannane derived from 4-*tert*-butylcyclohexanone gave the normal ipso-coupled product under these conditions. For an additional example of a cyclic vinylstannane that undergoes ipso coupling, see: Laborde, E.; Lesheski, L. E.; Kiely, J. S. *Tetrahedron Lett.* **1990**, *31*, 1837.

[7] The regiochemical outcome of these reactions is also subject to electronic effects. Stille made the observation[1d] that the coupling of vinyltributylstannane with aryl halides is accelerated by the presence of electron-withdrawing substituents on the aromatic ring. We found that coupling of vinylstannane **5** with 1-bromo-4-nitrobenzene, under the usual conditions, gave a 55:45 mixture of products corresponding to **7** and **6**, respectively.

[8] We thank a referee for bringing this fact to our attention. Cf.: (a) Heck, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 2712. (b) Dieck, H. A.; Heck, R. F. *J. Organomet. Chem.* **1975**, *93*, 259.

Hydrothermal Synthesis of Metal Polychalcogenides. Structural Characterization of $[Mo_{12}Se_{56}]^{12-}$. A Cluster of Clusters

Ju-Hsiou Liao and Mercouri G. Kanatzidis*

Department of Chemistry and Center for Fundamental
Materials Research, Michigan State University
East Lansing, Michigan 48824

Received June 7, 1990

Recently, we have been exploring the chemistry of metal polychalcogenides with various synthetic methods such as traditional room temperature solution and unusual molten salt techniques with considerable success.[1] In order to expand the synthetic repertoire in this area, we have been experimenting with hydrothermal conditions to assess their potential as variable synthetic routes to novel metal polychalcogenides. Hydrothermal synthesis of chalcogenides is very little studied, despite its demonstrated usefulness in the synthesis of a variety of other important, and often inaccessible by other techniques, materials such as quartz and zeolites.[2] Hydro(methano)thermal conditions have been used to prepare some very interesting metal monochalcogenide compounds by using alkali carbonates as mineralizers.[3] Using Se_x^{2-} as mineralizers, we have uncovered a new route to novel polychalcogenides. We report here the first hydrothermal synthesis of a metal polychalcogenide complex, the remarkable $[Mo_{12}Se_{56}]^{12-}$ (I), possessing an extraordinary structure.[4,5]

The structure of $[Mo_{12}Se_{56}]^{12-}$ is shown in Figure 1. I is a discrete molecule which can be viewed as a cluster of four smaller

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[1] (a) Kanatzidis, M. G. *Comments Inorg. Chem.* **1990**, *10*, 161–195. (b) Kanatzidis, M. G.; Huang, S.-P. *Angew. Chem.* **1989**, *28*, 1513–1514. (c) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767–3769. (d) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3767–3769. (e) Kanatzidis, M. G.; Dhingra, S. *Inorg. Chem.* **1989**, *28*, 2024–2026. (f) Huang, S.-P.; Dhingra, S.; Kanatzidis, M. G. *Polyhedron* **1990**, *9*, 1389–1395. (g) Kanatzidis, M. G.; Huang, S.-P. *J. Am. Chem. Soc.* **1989**, *111*, 760–761.

[2] Barrer, R. M. In *Hydrothermal Chemistry of Zeolites*; Academic Press: 1982.

[3] (a) Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1988**, *562*, 23–30. (b) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 98–104. (c) Sheldrick, W. S.; Hauser, H.-J. *Z. Anorg. Allg. Chem.* **1988**, *557*, 105–111.

[4] For other Mo polyselenide complexes, see: (a) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.*, in press. (b) O'Neal, S. C.; Kolis, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 1971–1973. (c) Wardle, R. W. M.; Mahler, C. H.; Chau, C.-N.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2790–2795. (d) Adel, J.; Weller, F.; Dehnicke, K. *J. Organomet. Chem.* **1988**, *347*, 343–348.

[5] (a) A Pyrex tube containing Mo metal (0.048 g, 0.5 mmol), K_2Se_4 (0.394 g, 1.0 mmol), and 0.3 mL of water was sealed off under vacuum, and it was kept at ~140 °C for 60 h. The black chunky crystals that formed are insoluble in water. They were isolated by filtration and subsequently washed with water. The nature of these crystals, which are insoluble in all organic solvents, was established by X-ray diffraction analysis to be $K_{12}Mo_{12}Se_{56}$.[5b] (b) Semiquantitative analyses were run on a scanning electron microscope using an energy dispersive (EDS) microprobe technique. The crystals, though sufficiently large, diffract weakly. Thus the data had to be collected by using intense X-rays from a rotating anode source. Crystal data for $K_{12}Mo_{12}Se_{56}$: orthorhombic $Cmc2_1$, $Z = 4$, $a = 23.73$ (2) Å, $b = 17.70$ (1) Å, $c = 20.434$ (9) Å, $V = 8584$ (9) Å^3 at 23 °C. $2\theta_{max}$(Mo Kα) = 51°. The structure was solved by direct methods. Number of unique data: 4153. Number of data having $F_o^2 > 3\sigma(F_o^2)$: 2531. Number of variables: 174. Number of atoms: 80. $\mu = 258$ cm^{-1}. Final $R = 0.080$ and $R_w = 0.051$. In order to ensure product homogeneity, the X-ray powder diffraction diagrams of the product were compared with and found to be identical with that calculated from the single-crystal data.

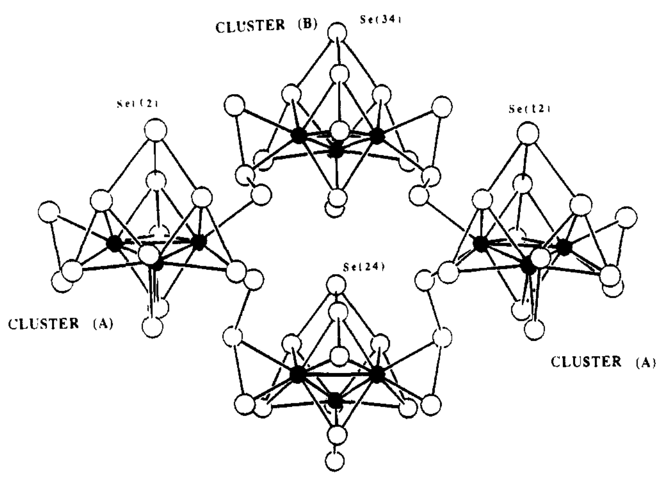
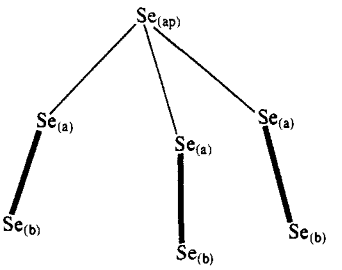


Figure 1. ORTEP representation of the molecular structure of the $[Mo_{12}Se_{56}]^{12-}$ anion. The black circles represent Mo atoms. The open circles represent Se atoms.

Scheme I



$[Mo_3Se_{14}]^{3-}$ trinuclear, slightly different subclusters.[6] Conceptually, I can be divided into two type A subclusters, one type B subcluster, and one type C subcluster as shown in Figure 1. I is situated in a crystallographic mirror plane which bisects the two trinuclear clusters B and C. These trinuclear subclusters are related to, but are distinctly different from, the $[Mo_3S_{13}]^{2-}$[7] cluster. Figure 2 shows the A, B, and C trinuclear subclusters individually. If we neglect the Mo–Mo bonds, each molybdenum atom has a coordination number of 7. In cluster A, two Mo atoms are bound each to one terminal Se_2^{2-} ligand, two bridging Se_2^{2-} ligands, and a triply bridging Se^{2-} ligand (capping the Mo_3 triangle). The other Mo center is also bound to two bridging Se_2^{2-} ligands and a triply bridging Se^{2-} ligand. The terminal ligand, however, is a Se_3^{2-} unit which also serves as the bridge to the other Mo trimers. The bonding mode of the Se_3^{2-} ligand is rare.[7]

In clusters B and C, one Mo center coordinates to one terminal Se_2^{2-} ligand, two bridging Se_2^{2-} ligands, and a triply bridging Se^{2-} ligand (capping the Mo_3 triangle). The other two Mo centers in B and C are bound to two bridging Se_2^{2-} ligands, a triply bridging Se^{2-} ligand (capping the Mo_3 triangle), and a terminal Se_3^{2-} ligand which also serves as the bridge to the other Mo trimers; see Figure 1. The formal Mo oxidation state is +4. Thus I can be described as $[Mo_{12}(Se_2)_{18}(Se_3)_4Se_8]^{12-}$.

The average Mo–Mo distance in I is 2.75 (2) Å. What is remarkably striking in the A, B, and C subclusters is that an extra selenium atom (see Figure 2) interacts with the selenium atoms of the three bridging Se_2^{2-} ligands to form what is formally a $[Se_7]^{8-}$ "umbrella"-like fragment, Scheme I ($Se_{(ap)}$–$Se_{(a)}$ average distance of 2.76 (15) Å).

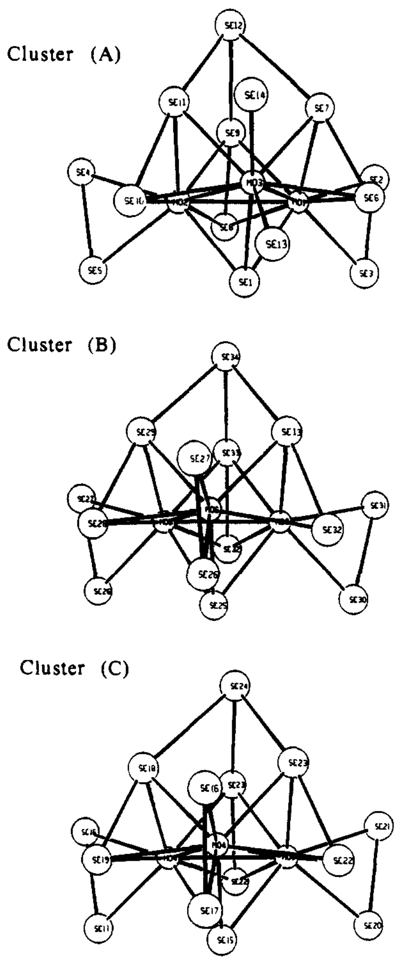


Figure 2. The individual structures and labeling scheme of the Mo/Se trinuclear subclusters. Top: cluster A. Middle: cluster B, situated on a mirror plane. Bottom: cluster C, situated on a mirror plane. Selected distances (Å): Mo(1)–Se(1) 2.505 (8), Mo(2)–Se(1) 2.489 (8), Mo(3)–Se(1) 2.522 (8), Mo(1)–Se(2) 2.611 (9), Mo(1)–Se(3) 2.586 (9), Mo(2)–Se(4) 2.669 (8), Mo(2)–Se(5) 2.620 (8), Mo(3)–Se(13) 2.658 (8), Mo(3)–Se(14) 2.647 (8), Se(2)–Se(3) 2.35 (1), Se(4)–Se(5) 2.37 (1), Se(6)–Se(7) 2.375 (9), Se(8)–Se(9) 2.407 (9), Se(10)–Se(11) 2.568 (9), Se(13)–Se(14) 3.000 (9), Se(11)–Se(12) 2.561 (9), Se(12)–Se(7) 2.934 (9), Se(12)–Se(9) 2.796 (9), Mo(6)–Se(25) 2.520 (10), Mo(7)–Se(25) 2.59 (10), Mo(6)–Se(26) 2.598 (8), Mo(6)–Se(27) 2.671 (9), Mo(7)–Se(30) 2.620 (10), Mo(7)–Se(31) 2.610 (10), Se(26)–Se(27) 2.33 (1), Se(30)–Se(31) 2.35 (1), Se(28)–Se(29) 2.41 (1), Se(32)–Se(33) 2.493 (9), Se(34)–Se(29) 2.83 (1), Se(34)–Se(33) 2.67 (1), Mo(4)–Se(15) 2.486 (9), Mo(5)–Se(15) 2.540 (10), Mo(4)–Se(16) 2.712 (8), Mo(4)–Se(17) 2.622 (8), Mo(5)–Se(20) 2.590 (10), Mo(5)–Se(21) 2.580 (10), Se(16)–Se(17) 2.418 (9), Se(20)–Se(21) 2.37 (1), Se(18)–Se(19) 2.35 (1), Se(22)–Se(23) 2.487 (9), Se(24)–Se(18) 3.03 (1), Se(23)–Se(24) 2.65 (1). Selected angles (deg): Se(7)–Se(12)–Se(11) 71.6 (2), Se(7)–Se(12)–Se(9) 69.0 (2), Se(9)–Se(12)–Se(11) 72.7 (3), Se(12)–Se(7)–Se(6) 162.6 (3), Se(12)–Se(9)–Se(8) 165.0 (4), Se(12)–Se(11)–Se(10) 167.5 (3), Se(29)–Se(34)–Se(33) 73.0 (3), Se(33)–Se(34)–Se(33) 74.8 (4), Se(34)–Se(33)–Se(32) 163.7 (4), Se(34)–Se(29)–Se(28) 160.2 (5), Se(18)–Se(24)–Se(23) 70.7 (3), Se(23)–Se(24)–Se(23) 74.3 (3), Se(24)–Se(18)–Se(19) 160.2 (5), Se(24)–Se(23)–Se(22) 166.0 (3).

The $[Se_7]^{8-}$ unit has never been previously observed. The considerable variation in the $Se_{(ap)}$–$Se_{(a)}$ type distances, ranging from 2.56 (1) to 3.03 (1) Å, is noteworthy. The longest $Se_{(ap)}$–$Se_{(a)}$ distance is 3.03 Å, still substantially shorter than 3.6 Å, the sum of the van der Waals radii of two selenium atoms. Interestingly, in cluster C the $Se_{(ap)}$–$Se_{(a)}$ distance dispersion is minimum, with distances ranging from 2.67 (2) to 2.83 (2) Å. The factors stabilizing this unusual and unique $[Se_7]^{8-}$ polyselenide fragment are not obvious. However, they may be similar to those responsible for the stability of other unique polychalcogenides found in $[NbTe_{10}]^{3-}$[8] and in Nb_2Se_9.[9] One can envision partial electron

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(6) The $[Mo_{12}Se_{56}]^{12-}$ clusters are spaced apart by K^+ ions. There is no evidence for significant intercluster bonding Mo–Se or Se–Se contacts (less than 3.2 Å). The minimum K–Se contacts are 3.30 Å.

(7) Müller, A.; Sarkar, S.; Bhattacharyya, R.G.; Pohl, S.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 535.

(8) The recently reported polysulfide $Cp^*_2Ru_2(CO)(S_2)(S_3)$ contains a S_3^{2-} ligand in a similar coordination. Brunner, H.; Janietz, N.; Wachter, J.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1988**, *356*, 85.

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.

Acknowledgment. Financial support from the Center for Fundamental Materials Research (CFMR), Michigan State University, and the National Science Foundation (Presidential Young Investigator Award, CHE-8958451) is gratefully acknowledged.

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, $Mo_6O(OEt)_{18}$

Judith A. Hollingshead and Robert E. McCarley*

Department of Chemistry and Ames Laboratory
U.S. DOE, Iowa State University, Ames, Iowa 50011

Received June 28, 1990

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 $Mo_6O(OEt)_{18}$·$4.8H_2O$, which contains a new oxygen-centered hexanuclear cluster unit, $Mo_6O(OEt)_{18}$ (**2**).

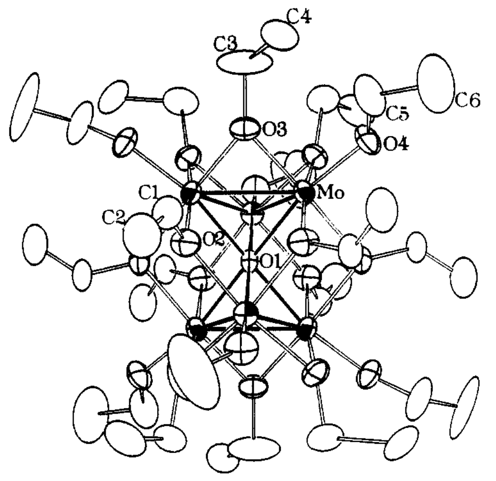

Figure 1. A view of the $Mo_6O(OEt)_{18}$ cluster unit **2** approximately perpendicular to the crystallographic 3-fold axis (50% thermal ellipsoids). Some significant bond distances are Mo–Mo = 2.6108 (3) Å, Mo–O1 = 2.1073 (4) Å, Mo–O2 = 2.098 (3) Å, Mo–O3 = 2.063 (4) Å, and Mo–O4 = 1.948 (3) Å. Only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