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$(Et_4N)_2[(Mo_2O_2Se_6)_{0.20}(Mo_2O_2Se_7)_{0.18}(Mo_2O_2Se_8)_{0.62}]$, a New Dimeric Molybdenum Polyselenide Containing a $[Mo_2O_2(\mu\text{-}Se)_2]$ Core

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Introduction

Metal polychalcogenides are of long-standing interest because they are in general useful materials.[1] In particular, molybdenum and tungsten sulfides[2] have been studied as models of active sites in biological systems[3] and in industrial catalytic processes.[4] Molybdenum and tungsten polychalcogenides of the general formula $[M_2X_2(\mu\text{-}E)_2E_mE_n]^{2-}$ (M = Mo, W; X = O, S, Se; E = S, Se; m, n = 1−4) that have been isolated and structurally characterized include the sulfide conplexes $[Mo_2S_n]^{2-}$ (n = 6−10),[5−9] $[Mo_2OS_n]^{2-}$ (n = 6−9),[10,11] $[Mo_2O_2S_n]^{2-}$ (n = 6−9),[12−15] $[W_2S_{10}]^{2-}$,[16] $[W_2S_{12}]^{2-}$,[17] and $[W_2O_2S_{10}]^{2-}$.[18] In contrast, studies on their polyselenide analogues are much less extensively investigated. Several W−Se complexes such as $[W_2Se_6]^{2-}$, $[W_2Se_9]^{2-}$, $[W_2Se_{10}]^{2-}$, $[W_2OSe_8]^{2-}$, $[W_2(Se_9)_{0.66}(Se_{10})_{0.34}]^{2-}$, and two isomers of $[W_2Se_{10}]^{2-}$ have been reported by Ibers et al.[19] The Mo−Se analogues $[Mo_2X_2(\mu\text{-}Se)_2(Se_2)_2]^{2-}$ (X = O, Se) have been recently prepared in situ by Eichhorn et al.[20]

Development in the chemistry of molybdenum sulfides started with the initial reports on the synthesis and structure of $[(S_2)_2Mo(\mu\text{-}S_2)]_2^{2-}$[21a] and $[Mo_3S_{13}]^{2-}$[21b] by Müller et al. Numerous complexes containing the dimeric $[M_2X_2(\mu\text{-}E)_2]$ core are now generally prepared by the following synthetic methods: (1) reaction of $[MS_4]^{2-}$ (M = Mo, W) with sulfur or organic polysulfides,[7,9b,15,17a] in which an externally induced internal redox pathway has been proposed as the mechanism for the formation of dimeric complexes; (2) an intramolecular redox process based on the acidification or heating of the tetrathiomolybdates/tetrathiotungstates/tetraselenidotungstates;[11a,12e,h,19b] and (3) interconversion of various isomers of $[M_2E_n]^{2-}$ (M = Mo, W; E = S, Se; n = 6−12) by addition or removal of sulfur or selenium.[2b,8a,9a,10,13,17a,19c] Recently we became interested in the use of the hydro(solvo)thermal technique for the preparation of transition metal polychalcogenides.[22] In this paper we report the solvothermal synthesis and structure of the new compound $(Et_4N)_2[(Mo_2O_2Se_6)_{0.20}(Mo_2O_2Se_7)_{0.18}(Mo_2O_2Se_8)_{0.62}]$, in which the major component ion $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_4)]^{2-}$ is found for the first time.

Experimental Section

Synthesis. $Mo(CO)_6$ (109.6 mg, 0.416 mmol), K_2Se_4 (163.6 mg, 0.416 mmol),[23] and 0.2 mL of EtOH (99.7%) were loaded into a thick-walled Pyrex tube (13 mm in diameter). The mixture was frozen in liquid nitrogen and flame-sealed under vacuum (the total volume of reactants was ca. 6 mL after sealing). The tube was subsequently heated in a furnace at 100 °C for 72 h, and then slowly cooled to 60 °C at 6 °C/h to give a black powder. This product, $Et_4NCl{\cdot}H_2O$ (152.7 mg, 0.832 mmol), and 0.2 mL of EtOH were loaded into a Pyrex tube, and

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(23) K_2Se_4 was prepared by the reaction of elemental potassium and selenium in the appropriate stoichiometric ratio in an evacuated Pyrex tube. The tube was put into an autoclave under a nitrogen atmosphere, and then slowly heated to 400 °C for 5 h. **CAUTION:** *This highly exothermic reaction should always be carried out behind a blast shield in a fume cabinet.*

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Table 1. Crystallographic Data for $(Et_4N)_2[(Mo_2O_2Se_6)_{0.20}(Mo_2O_2Se_7)_{0.18}(Mo_2O_2Se_8)_{0.62}]$

empirical formula = $(Et_4N)_2[Mo_2O_2Se_2(Se_2)(Se_2)_{0.20}(Se_3)_{0.18}(Se_4)_{0.62}]$
$a = 16.167(1)$ Å
$b = 12.549(1)$ Å
$c = 15.265(1)$ Å
$\beta = 92.92(1)°$
$V = 3092.9(4)$ Å^3
$Z = 4$
fw = 1070.3
space group = $P2_1/c$
$T = 20$ °C
$\lambda = 0.710\ 73$ Å
$\rho_{calcd} = 2.298$ g cm^{-3}
$\mu = 95.58$ cm^{-1}
$R^a = 0.068$
$R_w{}^b = 0.070$

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

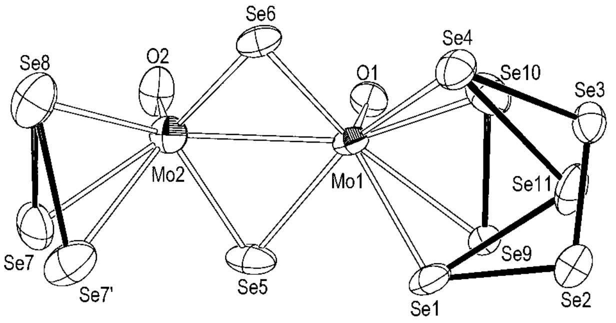

Figure 1. Structures of component anions in $[Et_4N]_2[(Mo_2O_2Se_6)_{0.20}(Mo_2O_2Se_7)_{0.18}(Mo_2O_2Se_8)_{0.62}]$. The atoms are represented as thermal ellipsoids at the 30% probability level. Note that Se7 and Se7′ are alternative sites of an atom belonging to the common terminal Se_2 ligand, and the terminal ligand on the other side can be Se_2, Se_3 or Se_4. Selected bond distances (Å): Mo(1)−Mo(2), 2.894(3); Mo(1)−Se(1), 2.522(3); Mo(1)−Se(4), 2.522(6); Mo(1)−Se(5), 2.503(3); Mo(1)−Se(6), 2.480(3); Mo(1)−O(1), 1.69(2); Mo(2)−Se(5), 2.415(3); Mo(2)−Se(6), 2.422(3); Mo(2)−Se(7), 2.530(5); Mo(2)−Se(7′), 2.58(3); Mo(2)−Se(8), 2.539(3); Mo(2)−O(2), 1.64(2); Se(1)−Se(2), 2.303(7); Se(2)−Se(3), 2.217(7); Se(3)−Se(4), 2.316(7); Se(7)−Se(8), 2.283(6); Se(7′)-Se(8), 2.70(2).

the procedure above was repeated. After the tube was opened, dark red plate crystals of $(Et_4N)_2[(Mo_2O_2Se_6)_{0.20}(Mo_2O_2Se_7)_{0.18}(Mo_2O_2Se_8)_{0.62}]$were isolated from the powdery material and washed with ethanol.

Crystallographic Studies. A well-developed single crystal (0.05 × 0.20 × 0.30 mm) was selected and mounted on a Rigaku AFC7R diffractometer for study using graphite-monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) radiation. Unit cell parameters were based on 25 carefully centered reflections in the range $15 < 2\theta < 30°$. Intensities of three standard reflections monitored after every 200 reflections did not show any appreciable decay during data collection. Absorption correction was applied using ψ scan data. The structure was solved by the direct method and refined by full-matrix least-squares on F using the Siemens SHELXTL PLUS (PC Version) package of crystallographic software.[24] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The data processing and structure refinement parameters are summarized in Table 1.

The site occupancies of Se7 and Se7′ (see Figure 1) were each initially set to $^1/_2$. They were then refined with the restriction that their sum should add up to unity; this resulted in site occupancies of 0.75 and 0.25, respectively. In the next stage of refinement the site occupancies (sof's) of atoms Se1, Se2, Se3, Se4, Se9, Se10, and Se11 were varied subject to the following conditions: sof(Se1) = sof(Se4), sof(Se2) = sof(Se3), sof(Se9) = sof(Se10), sof(Se1) + sof(Se9) =1, and sof(Se2) + sof(Se9) + sof(Se11) = 1. Final convergence resulted in site occupancies of 0.20, 0.18, and 0.62 for the diselenide, triselenide, and tetraselenide ligands, respectively.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å)

atom	x	y	z	$U_{eq}{}^a$
Mo(1)	0.7787(1)	0.0556(1)	0.8157(1)	0.047(1)
Mo(2)	0.7914(1)	−0.0548(2)	0.6505(1)	0.056(1)
Se(1)	0.7072(2)	0.2336(2)	0.8243(3)	0.065(1)
Se(2)	0.6583(4)	0.2680(4)	0.9605(3)	0.086(2)
Se(3)	0.7125(3)	0.1348(4)	1.0397(3)	0.058(2)
Se(4)	0.7034(4)	−0.0103(3)	0.9459(4)	0.065(2)
Se(5)	0.7588(2)	0.1320(2)	0.6647(2)	0.077(1)
Se(6)	0.7459(2)	−0.1341(2)	0.7845(2)	0.062(1)
Se(7)	0.7405(3)	−0.0480(4)	0.4911(3)	0.085(2)
Se(7')	0.708(1)	0.000(2)	0.509(2)	0.098(9)
Se(8)	0.7208(2)	−0.2045(2)	0.5634(2)	0.091(1)
Se(9)	0.7078(8)	0.2166(9)	0.893(1)	0.054(5)
Se(10)	0.717(2)	0.044(2)	0.963(2)	0.10(1)
Se(11)	0.691(1)	0.193(2)	0.994(2)	0.086(9)
O(1)	0.8795(8)	0.068(1)	0.8478(9)	0.064(6)
O(2)	0.892(1)	−0.069(1)	0.647(1)	0.084(7)
N(1)	0.004(1)	0.257(1)	0.576(1)	0.051(6)
N(2)	0.448(1)	0.420(1)	0.233(1)	0.050(6)
C(11)	0.014(2)	0.157(2)	0.628(2)	0.080(8)
C(12)	−0.075(2)	0.255(2)	0.520(2)	0.081(8)
C(13)	−0.003(2)	0.353(2)	0.638(2)	0.087(8)
C(14)	0.081(2)	0.269(2)	0.523(2)	0.077(7)
C(15)	0.079(2)	0.145(2)	0.691(2)	0.11(1)
C(16)	−0.077(2)	0.168(2)	0.450(2)	0.080(7)
C(17)	−0.066(2)	0.348(2)	0.703(2)	0.100(9)
C(18)	0.077(2)	0.364(2)	0.464(2)	0.081(8)
C(21)	0.373(2)	0.493(2)	0.240(2)	0.091(8)
C(22)	0.431(2)	0.345(2)	0.162(2)	0.100(9)
C(23)	0.464(2)	0.359(2)	0.318(2)	0.099(9)
C(24)	0.526(2)	0.486(2)	0.217(2)	0.092(9)
C(25)	0.294(1)	0.452(2)	0.266(2)	0.072(7)
C(26)	0.496(2)	0.272(2)	0.135(2)	0.12(1)
C(27)	0.469(2)	0.418(2)	0.401(2)	0.11(1)
C(28)	0.521(2)	0.541(2)	0.137(2)	0.11(1)

[a] $U_{eq} = (^1/_3)\sum_i\sum_j U_{ij}a_ia_j\mathbf{a}_i\cdot\mathbf{a}_j$. Site occupancy factors: Se1, Se4, 0.80; Se2, Se3, 0.62; Se9, Se10, 0.20; Se11, 0.18; Se7, 0.75; Se7′, 0.25.

Results and Discussion

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. The crystal structure of $(Et_4N)_2[(Mo_2O_2Se_6)_{0.20}(Mo_2O_2Se_7)_{0.18}(Mo_2O_2Se_8)_{0.62}]$ contains $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_2)]^{2-}$, $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_3)]^{2-}$, and $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_4)]^{2-}$ ions (Figure 1) with site occupancies of 0.20, 0.18, and 0.62, respectively, all sharing the same $[Mo_2O_2(\mu\text{-}Se)_2]$ core and one terminal diselenide unit. The difference between them is in the other terminal polyselenide unit, which can be $\eta^2\text{-}Se_2{}^{2-}$, $\eta^2\text{-}Se_3{}^{2-}$, or $\eta^2\text{-}Se_4{}^{2-}$, respectively. The skeletal geometry and Mo−Mo distance of the $[Mo_2O_2(\mu\text{-}Se)_2]$ core are similar to those found in $[Mo_2X_2(\mu\text{-}Se)_2(Se_2)_2]^{2-}$ (X = O, Se), but the asymmetric coordination of the bridging selenium atoms to the molybdenum atoms (average difference of Mo−Se$_b$ distances = 0.073 Å) is apparently different from that in $[Mo_2X_2(\mu\text{-}Se)_2(Se_2)_2]^{2-}$ (X = O, Se).[20] Asymmetrically bound chalcogenide bridges have been reported for similar polysulfide analogues[14c,9a,11b] of molybdenum and tungsten and polyselenide analogues of tungsten.[19a,b] Both molybdenum atoms in the present complex are coordinated by four selenium atoms and one oxygen atom in a distorted square-pyramidal arrangement. Each metal atom is situated above the basal plane and displaced toward the axial oxygen atom by a distance ranging from 0.694 to 0.881 Å.

There is no obvious source of oxygen atoms from the reactants. However, the relevant metal−ligand distance of about 1.65 Å in the initial structural model showed that such bonds can be assigned as Mo−O double bonds. In the final stage of refinement the average Mo−O distance of 1.67(2) Å is

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[24] Sheldrick, G. M. *SHELXTL PLUS*; Siemens Analytical Instruments Inc.: Madison, WI, 1990.

consistent with those found in the aforementioned compounds containing a $[Mo_2O_2E_2]$ (E = S, Se) core. A similar case was found in the hydrothermal synthesis of $[V_2O_2Se_{10}]^{4-}$ and $[V_2O_2Se_8]^{4-}$.[25] Hence a plausible explanation is that the source of oxygen atoms comes from ethanol.

The major component ion $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_4)]^{2-}$ in the disordered structure, which resembles the polysulfide analogue $[Mo_2O_2(\mu\text{-}S)_2(S_2)(S_4)]^{2-}$, has a five-membered metal-selenium ring that rarely occurs in molybdenum compounds, some known examples being $[MoSe(Se_4)_2]^{2-}$,[26a] $[MoO(Se_4)_2]^{2-}$,[26b] and $[CpMo(Se_4)_2]^{-}$.[26c] The symmetric coordination of the bidentate Se_4^{2-} ligand chelated to the Mo1 atom differs from those found in $[MoSe(Se_4)_2]^{2-}$,[26a] $[MoO(Se_4)_2]^{2-}$,[26b] and $[CpMo(Se_4)_2]^{-}$ [26c] but is similar to that found in $[Mo_2O_2S_2(S_2)(S_4)]^{2-}$,[14c] The chelating Se_4^{2-} ligand adopts a half-envelope conformation in which the Se2 and Se3 atoms are 0.780 and 1.542 Å above the Mo1Se1Se4 plane, respectively. As in many compounds[8,9,13,14b,c,27] containing a ME_4 (E = S, Se, Te) ring, the tetraselenide ligand shows an alternation in the lengths of the Se−Se bonds. The pair of outer Se−Se bonds (mean 2.305(9) Å) are significantly longer than the inner Se−Se bond (2.217(8) Å). A plausible explanation may be that M(dπ)−E(dπ) interactions depopulate the HOMO of the E_4^{2-} ligand, and thereby decrease the antibonding effect between the two inner chalcogen atoms.[28]

Intermolecular selenium−selenium contacts substantially shorter than the van der Waals contact distance of 3.6 Å are observed (Figure 2). The Se···Se distances between adjacent bridging selenium atom and terminal polyselenide atoms are 3.552(2) Å in $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_4)]^{2-}$ and 3.541(2) Å in $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_3)]^{2-}$, respectively. This kind of short inter-ligand contacts has been pointed out previously.[9,17a] However, it is noteworthy that an abnormally short inter-ligand contact, namely Se2···Se7′ = 3.097(2) Å, between different terminal polyselenide atoms in $[Mo_2O_2(\mu\text{-}Se)_2(Se_2)(Se_4)]^{2-}$ is observed. Although the Se−Se bond distances involving Se7′ are longer than those involving Se7, and the Se2−Se3 distance of 2.219(8) Å is shorter than that in various compounds containing MSe_4 rings,[27] it is difficult to ascertain whether the Se2···Se7′ short contact and disordered arrangement of Se7 and Se7′ originate from crystal packing force[22a] or from subtle electronic effects,[17a] as inherent crystallographic disorder severely limits the precision of the present crystal structure determination.[9a,28b]

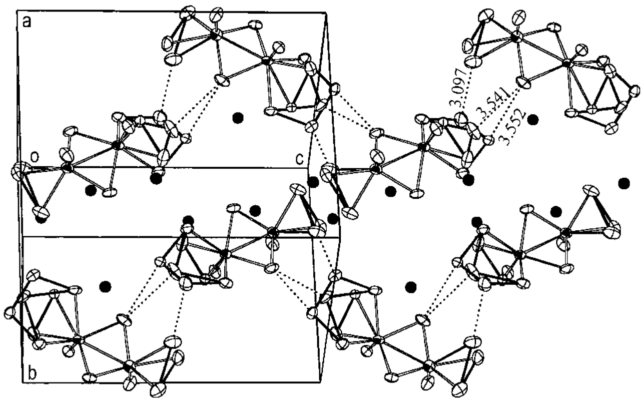

Figure 2. Crystal structure showing the packing of molecules. For clarity the Et_4N^+ ions are shown as filled spheres. The shorter intermolecular interactions between Se atoms are represented by broken lines.

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Supporting Information Available: Tables of crystal data and structure refinement parameters, all bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, H-atom coordinates and isotropic temperature factors (7 pages). Ordering information is available on any current masthead page.

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