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Solvothermal synthesis and crystal structure of $[NEt_4]_6[\{Mo_3(\mu_3\text{-}Se)(\mu\text{-}\eta^2\text{-}Se_2)_3(\eta^2\text{-}Se_2)(\mu\text{-}\eta^2\text{-}Se_5)(\eta^1\text{-}Se_5)\}_2(\mu\text{-}\eta^2\text{-}Se_4)]$. The first trinuclear molybdenum polyselenide dimer containing two $[Mo_3Se_7]^{4+}$ cluster cores bridged by a Se_4^{2-} chain

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Two equivalent $[Mo_3Se_{19}]^{2-}$ moieties, each composed of a $[Mo_3Se_7]^{4+}$ cluster core, two ligating Se_5^{2-} chains and a $(\eta^2\text{-}Se_2)^{2-}$ group, are bridged by a Se_4^{2-} chain to form the $[Mo_6Se_{42}]^{6-}$ ion.

The metal polychalcogenide complexes are of great interest due to their relevance to many important catalytic processes, such as hydrodesulfurization (HDS)[1] and enzymatic reactions in bioinorganic chemistry,[2] and as useful precursors to the generation of novel materials.[3] The well known molecular trinuclear molybdenum clusters with $[Mo_3S_4]^{4+}$ and $[Mo_3S_7]^{4+}$ cores have been extensively investigated.[4] In contrast, studies of analogous molybdenum selenides are quite underdeveloped due to the fact that the most convenient methods of synthesis for sulfides are not suitable for selenides. Recently, several trinuclear molybdenum selenides containing $[Mo_3Se_7]^{4+}$ and $[Mo_3Se_4]^{4+}$ cluster cores have been prepared by hydrothermal synthesis[5] and depolymerization of $[Mo_3Se_7]X_4$ (X = Cl or Br).[6] In this class of compound, formulated as $[\{Mo_3E_7L_3\}_2]X$ (E = S or Se, L = ligand, X = anion), two $[Mo_3E_7]^{4+}$ cluster cores are linked by a weak interaction between a bridging anion atom, X, and three axial atoms of the three bridging E_2 groups of each $[Mo_3E_7]^{4+}$ cluster core.[7] During the course of our study of heterometallic polychalcogenides[8] prepared under solvothermal conditions using K_2E_n (E = S, Se or Te; $n = 2$–6) as mineralizers, we have obtained the first trinuclear molybdenum polyselenide dimer containing two $[Mo_3Se_7]^{4+}$ cluster cores tethered by a Se_4^{2-} chain. The solvothermal synthesis and crystal structure of the new compound $[NEt_4]_6[Mo_6Se_{42}]$ are reported in this communication.

Molybdenum hexacarbonyl (60.4 mg, 0.229 mmol), metallic Ag (49.4 mg, 0.458 mmol), K_2Se_4† (180.3 mg, 0.458 mmol), $Et_4NCl\cdot H_2O$ (50 mg, 0.273 mmol) and EtOH (0.2 cm^3, 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 cm^3 after sealing). The tube was subsequently heated in a furnace to 100 °C for 72 h, and then slowly cooled to 50 °C at 6 °C per h. After opening the tube, black prismatic crystals of $[NEt_4]_6[Mo_6Se_{42}]$ ‡ (estimated yield 5%) were isolated from the powdery material and washed with ethanol. Scanning electron microscopy showed that the crystalline material contains Mo and Se but not Ag.

The structure of the apparently centrosymmetric $[Mo_6Se_{42}]^{6-}$ anion, as shown in Fig. 1, consists of two $[Mo_3Se_{19}]^{2-}$ units bridged by a Se_4^{2-} chain, which takes one of two possible configurations. A $[Mo_3Se_{19}]^{2-}$ unit comprises a $[Mo_3(\mu_3\text{-}Se)(\mu\text{-}\eta^2\text{-}Se_2)_2]^{4+}$ cluster core, two different ligating Se_5^{2-} chains and a $[\eta^2\text{-}Se_2]^{2-}$ group. The $[Mo_3Se_7]^{4+}$ cluster core is similar to those observed in $[Mo_{12}Se_{56}]^{12-}$,[5a] $[\{Mo_3Se_{18}\}_n]^{2n-}$ [5b] and $[Mo_9Se_{40}]^{8-}$,[5b] in which the Mo–Mo and Mo–Se bond distances are in good agreement. The average Se–Se bond distance of the three bridging diselenides in the present $[Mo_3Se_7]^{4+}$ cluster core is 2.327(5) Å, which is 0.123 Å shorter than that in the corresponding $[Mo_3Se_7]^{4+}$ cluster core of $[Mo_{12}Se_{56}]^{12-}$, but comparable to those in $[\{Mo_3Se_{18}\}_n]^{2n-}$ and $[Mo_9Se_{40}]^{8-}$. The Se–Se distance in the terminal diselenide is normal at 2.323(5) Å.

Known examples of metal polyselenides containing the Se_5^{2-} ligand include $[Ti(\eta^5\text{-}Cp)_2(\eta^2\text{-}Se_5)]$ ($Cp = C_5H_5$),[10] $[Fe_2Se_2(\eta^2\text{-}Se_5)_2]^{2-}$,[11] $[V_2(Se_2)_4(\mu\text{-}\eta^2\text{-}Se_5)]^{2-}$,[12] $[In_2(Se_4)_4(\mu\text{-}\eta^2\text{-}Se_5)]^{4-}$,[13] $[Cu_2(Se_4)(\eta^2\text{-}Se_5)(\mu\text{-}\eta^2\text{-}Se_5)]^{4-}$ [14] and $[GaSe_2(\eta^2\text{-}Se_5)_2]^{2-}$.[15] However, none of these involves a Group 6 element. In the present $[Mo_6Se_{42}]^{6-}$ anion, the $\mu\text{-}\eta^2\text{-}Se_5$ unit acts as a bidentate ligand bridging across two adjacent Mo atoms to form a seven-membered Mo_2Se_5 ring, which adopts a chair conformation similar to that found in $[V_2(Se_2)_4(\mu\text{-}\eta^2\text{-}Se_5)]^{2-}$.[12] The other monodentate Se_5^{2-} unit is bonded to atom Mo(2), and the end

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† 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 cupboard.

‡ A well developed single crystal (0.2 × 0.2 × 0.2 mm) was selected and mounted on a Rigaku RAXIS IIC imaging plate system equipped with graphite-monochromated Mo-Kα ($\lambda = 0.710\,73$ Å) radiation. Crystal data for $[NEt_4]_6[Mo_6Se_{42}]$: $M = 4673.4$, monoclinic, $P2_1/c$, $Z = 2$, $a = 14.678(1)$, $b = 13.630(1)$, $c = 28.237(1)$ Å, $\beta = 96.73(1)°$, $U = 5610.2(6)$ Å^3, $T = 293$ K, $D_c = 2.767$ Mg m^{-3}, $F(000) = 8520$, $\mu = 14.308$ mm^{-1}, relative transmission factor in the range 0.452–1.0. A total of 15 787 reflections were collected in the 2θ range 3.0–55.0° ($0 \leqslant h \leqslant 18$, $-17 \leqslant k \leqslant 17$, $-35 \leqslant l \leqslant 35$), yielding 9758 unique reflections (R_{int} 0.059), 3192 of which with $F > 4\sigma(F)$ were considered as observed. The structure was solved by direct methods and refined by full-matrix least squares on F using the Siemens SHELXTL PLUS (PC Version)[9] package of crystallographic software. All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions of the three independent NEt_4^+ cations were generated and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. At convergence $R_F = 0.058$, $R_{wF}^2 = 0.0651$, $S = 1.09$, maximum and minimum peaks in final difference map: 2.12 and -0.96 e Å^{-3} in the vicinity of the Mo and Se atoms. The $[Mo_6Se_{42}]^{6-}$ anion is located at a crystallographic inversion centre. This necessitates positional disorder of the atoms of the bridging Se_4^{2-} unit which exhibits two different and equally populated chain configurations in the structure. Accordingly the independent Se(10), Se(11), Se(12) and Se(13) atoms of the bridging Se_4^{2-} chain were refined with half site-occupancy. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/406.

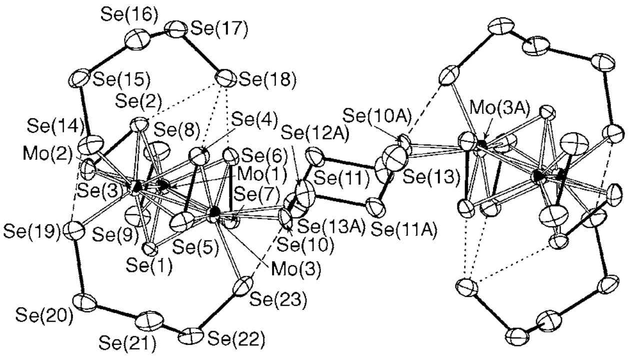

Fig. 1 Molecular structure of the $[\{(Mo_3Se_7)(Se_5)_2(Se_2)\}_2Se_4]^{6-}$ cluster showing the atom labelling scheme (30% thermal ellipsoids). Sets of atoms Se(10), Se(11), Se(12), Se(13) and Se(10A), Se(11A), Se(12A), Se(13A) represent two possible configurations of the central bridging Se_4^{2-} chain. Metal–ligand bonds are indicated by double lines, covalent bonds between the selenium atoms are represented by solid lines, and weak interactions that decrease in strength are represented by broken lines and dotted lines. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 2.784(3), Mo(1)–Mo(3) 2.777(4), Mo(2)–Mo(3) 2.781(3), Mo(2)–Se(14) 2.660(4), Mo(2)–Se(19) 2.616(4), Mo(3)–Se(10) 2.623(8), Mo(3)–Se(23) 2.617(4), Mo(3)–Se(13A) 2.77(1), Se(10)–Se(11) 2.36(1), Se(11)–Se(12) 2.33(1), Se(12)–Se(13) 2.27(1), Se(14)–Se(15) 2.335(5), Se(15)–Se(16) 2.316(6), Se(16)–Se(17) 2.310(5), Se(17)–Se(18) 2.313(5), Se(19)–Se(20) 2.380(5), Se(20)–Se(21) 2.338(5), Se(21)–Se(22) 2.364(6), Se(22)–Se(23) 2.366(5), Se(10)–Se(23) 2.736(8), Se(14)–Se(19) 2.917(5); Mo(2)–Mo(1)–Mo(3) 60.0(1), Mo(1)–Mo(2)–Mo(3) 59.9(1), Mo(1)–Mo(2)–Se(14) 143.0(1), Mo(1)–Mo(2)–Se(19) 130.1(1), Mo(1)–Mo(3)–Se(10) 150.6(2), Mo(1)–Mo(3)–Se(13A) 125.8(2), Mo(1)–Mo(3)–Se(23) 130.7(1), Se(10)–Se(11)–Se(12) 103.0(4), Se(11)–Se(12)–Se(13) 97.7(4), Se(12)–Se(13)–Mo(3A) 98.4(4), Mo(2)–Se(14)–Se(15) 112.1(2), Mo(2)–Se(19)–Se(20) 114.3(1), Mo(3)–Se(23)–Se(22) 112.0(2), Se(14)–Mo(2)–Se(19) 67.1(1), Se(10)–Mo(3)–Se(23) 63.0(2). Symmetry transformation: A $1 - x, -y, 1 - z$)

Se atom [Se(18)] of the pendant chain stretches out to interact with three axial Se atoms of the three bridging diselenides in the same $[Mo_3Se_7]^{4+}$ cluster core, with an averaged distance of 3.214(5) Å between them. This forms an unusual polyselenide fragment similar to that found in $[\{Mo_3Se_{18}\}_n]^{2n-}$.[5b] It is noteworthy that weak interactions between chalcogen atoms have been observed in several molybdenum polychalcogenide compounds[5a,5b,8,16] prepared by the hydrothermal technique.

It is interesting to note that there is an apparent intracluster interaction between the μ-η^2-Se_5 ligand and one configuration of the bridging Se_4^{2-} chain. The intracluster Se(10) · · · Se(23) distance of 2.736(8) Å is *ca.* 0.25 Å shorter than those found in $[Mo_9Se_{40}]^{8-}$ (Se · · · Se = 2.98 Å)[5b] and $[W(CO)_5Se_2]_2^{2+}$ (Se · · · Se = 3.015 Å).[17] Another unusual intracluster interaction is that between two different co-ordinated chains of Se_5^{2-}. The Se(14) · · · Se(19) distance of 2.917(5) Å is 0.180 Å longer than that of Se(10) · · · Se(23), but still much shorter than 3.6 Å, the sum of the van der Waals radii of two selenium atoms. It is strange that the covalent bond distances involving atoms Se(10), Se(23), Se(14) and Se(19) are normal, but atom Se(13) has abnormally elongated Mo–Se [Mo(3)–Se(13A) 2.77(1) Å] and shortened Se–Se [Se(12)–Se(13) 2.27(1) Å] bond distances. This may give a hint that the close Se · · · Se distance and the disorder in the Se_4^{2-} chain arise from crystal packing forces. The intermolecular Se · · · Se distances range from 3.470(5) to 3.933(5) Å.

The present study reaffirms that the hydrothermal technique offers a useful avenue for the synthesis of novel metal polychalcogenides which are otherwise difficult or impossible to obtain using conventional techniques.[18]

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