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Cuboidal oxalate cluster complexes with the $Mo_3CuQ_4^{5+}$ cluster core (Q = S or Se): synthesis, structure, and electrochemical properties*

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The reactions of the $[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3(H_2O)_3(C_2O_4)_3]^{2-}$ complex (Q = S or Se) with CuX salts (X = Cl, Br, I, or SCN) in water produce the cuboidal heterometallic clusters $[Mo_3(CuX)(\mu_3\text{-}Q)_4(H_2O)_3(C_2O_4)_3]^{2-}$, which were isolated as the potassium and tetraphenylphosphonium salts. Two new compounds, $K_2[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]\cdot 6H_2O$ and $(PPh_4)_2[Mo_3(CuBr)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]\cdot 7H_2O$, were structurally characterized. All compounds were characterized by elemental analysis and IR spectroscopy. The $K_2[Mo_3(CuI)(\mu_3\text{-}Se)_4(H_2O)_3(C_2O_4)_3]$ compound was characterized by the ^{77}Se NMR spectrum; the $(PPh_4)_2[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]$, $(PPh_4)_2[Mo_3(CuI)(\mu_3\text{-}Se)_4(H_2O)_3(C_2O_4)_3]$ and $K_2[Mo_3(CuSCN)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]\cdot 7H_2O$ compounds, by electrospray mass spectra.

Key words: molybdenum, copper, chalcogenide clusters, oxalate complexes, cuboidal clusters, cyclic voltammetry, X-ray diffraction study.

Clusters with the cuboidal core $M_3M'Q_4$ (M = Mo or W; Q = Se or Se; M′ = Ru, Os, Ir, Ni, Pd, Pt, *etc.*) have attracted interest because of the unusual reactivity of heterometals in the clusters and a great scope for modifications of the properties of the clusters by varying the nature of the main metal (Mo or W), the bridging chalcogen atoms, and the ligands coordinated to Mo or W.[1] Nickel- and palladium-containing clusters of this family exhibit high catalytic activity in the addition reactions of carboxylic acids and alcohols with alkynes, the cyclization of acetylenecarboxylic acids into lactones, and the hydrodesulfurization of thiophene derivatives. These clusters also promote the isomerization of hydrophosphoryl compounds into the corresponding pyramidal tautomers and coordinate π-acceptor ligands (CO, alkenes, and alkynes) under mild conditions.[2—8]

Copper-containing clusters can exist in two oxidation states (diamagnetic 60-electron $M_3CuQ_4^{5+}$ complexes and paramagnetic 61-electron $Mo_3CuQ_4^{4+}$ complexes). Recently, it has been demonstrated that the $[Mo_3(CuCl)S_4(dmpe)_3Cl_3]$ cluster (dmpe is 1,2-bis(dimethylphosphino)ethane) and its analogs efficiently catalyze reactions of organic diaza compounds, for example, the intramolecular cyclopropanation of 1-diazo-5-hex-2-one.[9] Since the $[M_3(CuX)Q_4Z_3X_3]$ clusters (Z is dppe or dmpe; M = Mo or W; Q = S or Se; X = Cl or Br) have nonlinear optical properties, they hold promise as optical filters.[10,11] Other copper-containing clusters of the $[M_3CuQ_4]^{5+}$ family, in which the molybdenum (tungsten) atoms are coordinated by dithiophosphates,[12,13] dithiocarbamates,[14] dithiophosphinates,[15,16] cyclopentadienyl ligands,[17] triaminocyclohexane derivatives,[18] ammonia molecules,[19] or nitrilotriacetate,[20] as well as aqua complexes, which are stable only in a strongly acidic media,[21—23] were described in the literature. The reactivity of these compounds remains virtually unknown. In particular, copper-containing clusters would be expected to catalyze reactions of alkynes.[24] The synthesis of water-soluble derivatives of the $[M_3CuQ_4]^{5+}$ clusters stable in neutral media is of particular interest in view of modern trends in the catalysis of organic reactions (search for catalytically active systems in aqueous solutions at nearly neutral pH).[25]

In the present study, we synthesized a series of the oxalate derivatives $[Mo_3(CuX)Q_4(C_2O_4)_3(H_2O)_3]^{2-}$ (Q = S or Se; X = Cl, Br, I, or NCS) and investigated their structures and properties.

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Results and Discussion

Synthesis. The addition of solid Cu^I salts to aqueous solutions of $[Mo_3Q_4(H_2O)_3(C_2O_4)_3]^{2-}$ (**1**) is accompanied by a change in the color from green to red-brown (Q = S) or from brown to red-brown (Q = Se) and leads to the formation of the heterometallic complexes $[Mo_3(CuX)(\mu_3\text{-}Q)_4(H_2O)_3(C_2O_4)_3]^{2-}$ (X = Cl, Br, I, or SCN, Figs 1 and 2). The reactions of CuI and CuNCS proceed slowly and require prolonged stirring under moderate heating. More soluble CuCl reacts much more rapidly, and the color begins to change immediately after mixing of the reagents. The products can be isolated from solutions as amorphous or crystalline precipitates of the potassium salts $K_2[Mo_3(CuCl)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 2H_2O$ (**2**), $K_2[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 6H_2O$ (**3**), $K_2[Mo_3(CuI)(\mu_3\text{-}Se)_4(H_2O)_3(C_2O_4)_3]$ (**5**), and $K_2[Mo_3(CuSCN)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ (**7**) by evaporation of the solvents or, alternatively, these compounds can be precipitated as $(PPh_4)_2[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]$ (**4**), $(PPh_4)_2[Mo_3(CuI)(\mu_3\text{-}Se)_4(H_2O)_3(C_2O_4)_3]$ (**6**), and $(PPh_4)_2[Mo_3(CuBr)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ (**8**) by the addition of tetraphenylphosphonium salts. Satisfactory elemental analysis data were obtained for compounds **1**—**7**.

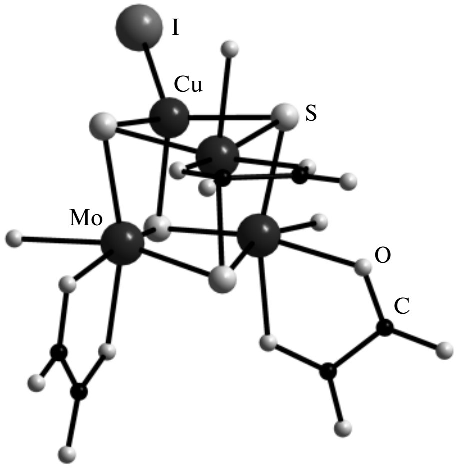

Fig. 1. Molecular structure of the cluster complex $[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]^{2-}$ in the crystal structure of compound **3** (Mo—Mo and Mo—Cu bonds are omitted).

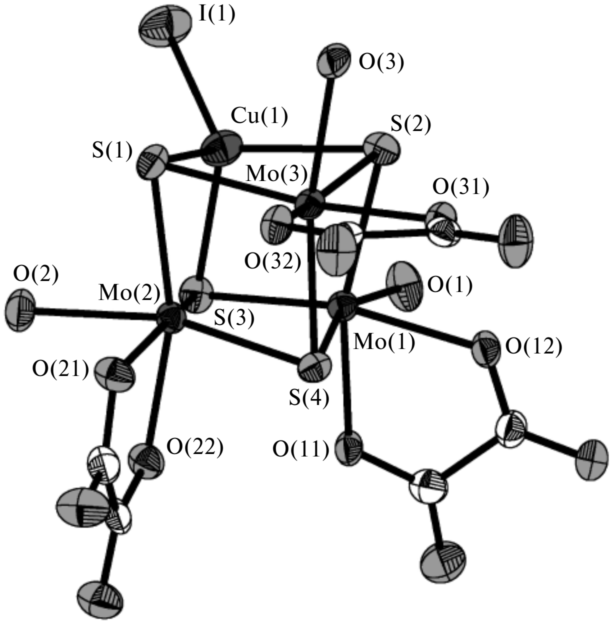

Fig. 2. Molecular structure of $[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]^{2-}$ in **3** (displacement ellipsoids are drawn at the 50% probability level; the Mo—Mo and Mo—Cu bonds are omitted).

Spectra. The vibrational spectra are typical of bidentate coordinated oxalate ligands. The vibrational spectrum of $K_2[Mo_3(CuSCN)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ (**7**) shows additional bands belonging to the thiocyanate ligand coordinated through the sulfur atom (ν(CN) = 2141 cm^{-1}, ν(CS) = 721 cm^{-1}, δ(NCS) 429 = cm^{-1}).[26] The coordination through the sulfur atom is in agreement with the "soft" character of the copper atom in the cluster (formally Cu^I) and is observed also in other Cu^I complexes characterized by X-ray diffraction.[27] In the cuboidal cluster complex $[W_2(CuNCS)_2S_4(NCS)_6]^{4-}$ with the $[W^V{}_2Cu^I{}_2S_4]^{4+}$ core, the thiocyanate ligand is coordinated to the copper atom through the nitrogen atom, as evidenced by both the IR spectra and X-ray diffraction data.[28] We failed to grow single crystals of compound **7** suitable for X-ray diffraction. An attempt to replace the cation by the addition of PPh_4Br led to the replacement of the coordinated thiocyanate ligand by bromide and the formation of the $(PPh_4)_2[Mo_3(CuBr)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ complex (**8**).

The negative-ion electrospray mass spectra of compounds **4**, **6**, and **7** show the following fragmentation pattern for the cluster anions: the loss of two water molecules in the first step to form $[Mo_3(CuX)Q_4(H_2O)(C_2O_4)_3]^{2-}$, the loss of one more water molecule in the second step to form $[Mo_3(CuX)Q_4(C_2O_4)_3]^{2-}$, and the subsequent elimination of CuX to give $[Mo_3Q_4(C_2O_4)_3]^{2-}$. The addition of Cl^- or Br^- ions to solutions of iodide complexes **4** and **6** leads to the replacement of the iodide anion coordinated to the copper atom by the bromide or chloride anion, as evidenced by the appearance of the corresponding peaks in the mass spectra: $[Mo_3(CuCl)S_4(C_2O_4)_3]^{2-}$ (m/z = 389), $[Mo_3(CuBr)S_4(C_2O_4)_3]^{2-}$ (m/z = 412) (for **4**); $[Mo_3(CuCl)Se_4(C_2O_4)_3]^{2-}$ (m/z = 484), $[Mo_3(CuCl)Se_4(H_2O)(C_2O_4)_3]^{2-}$ (m/z = 491), and $[Mo_3(CuBr)Se_4(C_2O_4)_3]^{2-}$ (m/z = 505) (for **6**).

The ^{77}Se NMR spectrum of the $K_2[Mo_3(CuI)(\mu_3\text{-}Se)_4(H_2O)_3(C_2O_4)_3]$ complex (**5**) (aqueous solution) shows two signals in accordance with two types of selenium atoms in the $SeMo_3$ and $SeMo_2Cu$ environment at δ −56.08 and 325.34, which is comparable with the spectrum of the starting $[Mo_3Se_4(H_2O)_3(C_2O_4)_3]^{2-}$ complex (δ −67.25 and 309.81).

The cyclic voltammograms of compounds **2**, **3**, and **7** ($1.5 \cdot 10^{-3}$ mol L^{-1}) recorded in the range from 0.9 to −0.9 V on a glassy-carbon electrode in a 0.1 *M* Na_2SO_4 solution showed quasireversible reduction peaks at 0.03 and −0.35 V (**2**), −0.33 V (one two-electron reduction peak) (**3**), and −0.35 V (one peak) (**7**). The reduction of Cu^I to Cu^0 was not observed. This is evidenced by the fact that there are no analytical signals for copper dissolution on the electrode surface in the cyclic voltammogram after the cathodic scan and the presence of the deposition potential of −0.9 V for 120 s against the background of 0.5 *M* HCl in the absence of the $[Mo_3(CuX)Q_4(C_2O_4)_3]^{2-}$ complex. According to the published data, the molybdenum atoms are reduced, and the process can formally be described as

$$Mo^{IV}{}_3Cu^I \rightarrow Mo^{III}Mo^{IV}{}_2Cu^I \rightarrow Mo^{IV}Mo^{III}{}_2Cu^I.$$

The incomplete reversibility of the process can be attributed to the transformation of the cluster after the reduction, for example, as a result of elimination of the ligand coordinated to the copper atom and the possible dimerization to a bis-cuboidal cluster at the Cu—S edge. The quasireversible redox process with Δ = (0.79—0.58) V = 0.21 V is also observed for iodide complex **3**. This process can be accounted by the $2I^-/I_2$ pair. For all the complexes under study, the peak intensities only slightly depend on the potential scan rate. Consequently, the diffusion to the electrode surface rather than the electron exchange is the rate-determining step.

Structures. The geometric parameters of the cluster fragment $Mo_3CuS_4{}^{5+}$ in compounds **3** and **8** (Tables 1 and 2, respectively) roughly resemble those in the $[Mo_3(CuX)S_4(dmpe)_3X_3]PF_6$ (X = Cl or Br) and $(NH_4)_2[Mo_3(CuCl)(Hnta)_3] \cdot 3H_2O$ (Hnta is nitrilotriaceate) complexes. The pronounced asymmetry of the coordination of Cu in complex **8** deserves notice: the Cu—S distances vary from 2.266(4) to 2.324(3) Å and the Cu—Mo distances are in the range of 2.799—2.847 Å. This may be attributed to the crystal packing effects taking into account the radical difference in the nature of the cationic moieties of **3** and **8**. Interestingly, the Cu—Br distance in complex **8** (2.324(3) Å) is substantially longer than that in the $[Mo_3(CuBr)S_4(dmpe)_3Br_3]PF_6$ cluster containing the same $Mo_3CuS_4{}^{5+}$ core (2.276 Å). At the same time, this distance is virtually equal to the corresponding distance in the $[Mo_3(CuBr)S_4(tdci)_3]Br_3 \cdot 11H_2O \cdot EtOH$ (2.336 Å) compound (tdci is 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inosite) derived from the $Mo_3CuS_4{}^{4+}$ cluster. This is evidence that the ligand environment of molybdenum atoms can play an

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the structure of compound **3**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Mo(1)—O(11)	2.123(4)	Mo(2)—O(21)	2.121(4)	Mo(3)—S(2)	2.3201(15)	S(1)—Cu(1)—S(2)	103.55(6)
Mo(1)—O(12)	2.138(4)	Mo(2)—O(2)	2.190(4)	Mo(3)—S(4)	2.3251(15)	S(2)—Cu(1)—S(3)	103.33(6)
Mo(1)—O(1)	2.176(4)	Mo(2)—S(3)	2.3225(15)	Mo(3)—S(1)	2.3307(15)	S(3)—Cu(1)—S(1)	102.95(6)
Mo(1)—S(3)	2.3202(15)	Mo(2)—S(4)	2.3248(15)	Mo(3)—Cu(1)	2.8175(8)	S(1)—Cu(1)—I(1)	119.28(5)
Mo(1)—S(4)	2.3297(15)	Mo(2)—S(1)	2.3430(15)	Cu(1)—S(3)	2.3021(16)	S(2)—Cu(1)—I(1)	116.33(5)
Mo(1)—S(2)	2.3327(15)	Mo(2)—Mo(3)	2.7561(7)	Cu(1)—S(1)	2.3052(16)	S(3)—Cu(1)—I(1)	109.50(5)
Mo(1)—Mo(2)	2.7408(7)	Mo(2)—Cu(1)	2.8405(9)	Cu(1)—S(2)	2.3192(17)		
Mo(1)—Mo(3)	2.7644(7)	Mo(3)—O(31)	2.110(4)	Cu(1)—I(1)	2.4491(8)		
Mo(1)—Cu(1)	2.8259(9)	Mo(3)—O(32)	2.145(4)				
Mo(2)—O(22)	2.118(4)	Mo(3)—O(3)	2.201(4)				

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the structure of compound **8**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Mo(1)—O(11)	2.119(7)	Mo(2)—O(21)	2.117(8)	Mo(3)—S(3)	2.317(3)	S(1)—Cu(1)—S(2)	103.73(12)
Mo(1)—O(12)	2.140(8)	Mo(2)—O(2)	2.185(7)	Mo(3)—S(2)	2.318(3)	S(2)—Cu(1)—S(3)	101.93(11)
Mo(1)—O(1)	2.180(7)	Mo(2)—S(1)	2.315(3)	Mo(3)—S(4)	2.334(3)	S(3)—Cu(1)—S(1)	103.74(12)
Mo(1)—S(3)	2.306(3)	Mo(2)—S(2)	2.317(3)	Mo(3)—Cu(1)	2.8466(18)	S(1)—Cu(1)—Br(1)	112.33(10)
Mo(1)—S(1)	2.311(3)	Mo(2)—S(4)	2.329(3)	Cu(1)—S(1)	2.266(4)	S(2)—Cu(1)—Br(1)	116.97(10)
Mo(1)—S(4)	2.333(3)	Mo(2)—Mo(3)	2.7601(14)	Cu(1)—S(3)	2.311(3)	S(3)—Cu(1)—Br(1)	116.44(11)
Mo(1)—Mo(3)	2.7595(13)	Mo(2)—Cu(1)	2.8077(19)	Cu(1)—S(2)	2.324(3)		
Mo(1)—Mo(2)	2.7652(13)	Mo(3)—O(31)	2.114(7)	Cu(1)—Br(1)	2.317(2)		
Mo(1)—Cu(1)	2.7983(18)	Mo(3)—O(32)	2.120(7)				
Mo(2)—O(22)	2.110(7)	Mo(3)—O(3)	2.177(8)				

equally important role as the oxidation state of the cluster fragment, the more so that the transition from the $Mo_3CuS_4^{5+}$ to $Mo_3CuS_4^{4+}$ state influences primarily the orbitals with the largest contribution of AOs of the Mo atom. The Cu—I distance in complex **3** (2.4491(8) Å) is virtually equal to those in the dithiophosphate derivatives $[Mo_3(CuI)S_4(dtp)_3(\mu\text{-}CH_3COO)(DMF)]$ (2.454 Å) and $[Mo_3(CuI)S_4(dtp)_3(\mu\text{-}CF_3COO)(CH_3CN)]$ (2.440 Å).[29,30]

The formation of cuboidal clusters by the incorporation of the Cu^I atom into the vacant vertex can be represented in the simplified form (without consideration for the Cu—Mo interaction) as the coordination of the tridentate sulfur-containing inorganic ligand. In this case, the mechanism of formation of cuboidal clusters is analogous to the mechanism of formation of $[Cu([9]ane\text{—}S_3)I]$-type complexes, its analogs with other aliphatic and aromatic cyclic thioesters, and $[Cu((EtNH)_2CS)_3I]$-type thiourea derivatives. The Cu—S distances both in complexes with these organic ligands and cuboidal clusters vary in the same range (2.27—2.32 Å).[31—34]

To summarize, we synthesized and structurally characterized a series of the water-soluble cuboidal heterometallic clusters $[Mo_3(CuX)(\mu_3\text{-}Q)_4(H_2O)_3(C_2O_4)_3]^{2-}$ stable in neutral media. It was demonstrated that ligands coordinated to the copper atoms can undergo reversible one-electron reduction and can be easily replaced. The copper atom in the cluster core was found to be "soft" in character.

Experimental

Compounds **1—8** were synthesized in air. Solvents were purified according to standard procedures. Other compounds of reagent grade were used without additional purification. The $K_2[Mo_3(\mu_3\text{-}Q)(\mu_2\text{-}Q_2)_3(C_2O_4)_3] \cdot 0.5KBr \cdot xH_2O$ compounds (Q = S or Se) were synthesized according to a procedure described earlier.[35]

The elemental analysis was carried out in the Laboratory of Microanalysis of the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The vibrational spectra were recorded in the 4000—400 cm^{-1} range in KBr pellets on a Scimitar FTS 2000 instrument at 1 cm^{-1} resolution. The ^{77}Se NMR spectra were measured on a Bruker MSL300 spectrometer at room temperature in H_2O with $SiMe_4$ as the internal standard. The mass spectra (ESI-MS) were obtained on a Quattro LC (quadrupole—hexapole—quadrupole) mass spectrometer (Micromass, Manchester, UK).[36] The cyclic voltammograms were measured on a Metrhom 797 VA Computrace instrument (Switzerland); 0.1 *M* Na_2SO_4 was used as the supporting electrolyte; the potential scan rate was 0.1 V s^{-1}.

Dipotassium(trioxalatotetrasulfidotrimolybdenum), $K_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(H_2O)_3(C_2O_4)_3]$ (1a). A solution of PPh_3 (0.80 g, 3.0 mmol) in chloroform (10 mL) was added to a solution of $K_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(C_2O_4)_3] \cdot 0.5KBr \cdot 3H_2O$ (0.77 g, 0.80 mmol) in H_2O (50 mL). The reaction mixture was magnetically stirred in a closed flask for 12 h and then stirred in the open flask until chloroform was completely evaporated. The white precipitate was filtered off. The solution was concentrated to dryness. The precipitate was dissolved in a minimum amount of water and then precipitated by the addition of a threefold volume of acetone. The green precipitate was filtered off, washed with acetone, and dried in air. The yield was 0.52 g (80%). Found (%): C, 8.60; H, 0.85; S, 16.21. $C_6H_6Mo_3O_{15}K_2S_4$. Calculated (%): C, 8.87; H, 0.74; S, 15.79. IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 3456 s, 3087 s, 1699 s, 1672 s, 1400 s, 1270 m, 907 m, 794 m, 610 w, 529 m, 500 m.

Dipotassium(trioxalatotetrasulfidomonochlorocoppertrimolybdenum), $K_2[Mo_3(CuCl)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 2H_2O$ (2). The $K_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(H_2O)_3(C_2O_4)_3]$ compound (**1a**) (0.10 g, 0.12 mmol) was dissolved in H_2O (10 mL), and CuCl (0.10 g, 1.0 mmol) was added to the solution. The reaction mixture was stirred under argon for ~1 h and then filtered off from unconsumed copper(I) chloride. The solution was concentrated in air, after which a brown powder was obtained. The yield was 0.09 g (77%). Found (%): C, 7.64; H, 1.12; S, 13.34. $C_6H_{10}ClCuMo_3O_{17}K_2S_4$. Calculated (%): C, 7.60; H, 1.06; S, 13.54. IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 3413 s, 1701 s, 1672 s, 1629 c, 1396 m, 1363 m, 1319 m, 1041 w, 905 w, 823 m, 791 w, 507 m, 491 m.

Dipotassium(trioxalatotetrasulfidomonochlorocoppertrimolybdenum), $K_2[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 6H_2O$ (3). A solution of PPh_3 (0.20 g, 0.76 mmol) in chloroform (10 mL) was added to an aqueous solution (10 mL) of $K_2[Mo_3S_7(C_2O_4)_3] \cdot 0.5KBr \cdot 3H_2O$ (0.14 g, 0.14 mmol). The reaction mixture was vigorously magnetically stirred in a closed flask for 12 h and then magnetically stirred in the open flask until chloroform was completely evaporated. The white precipitate that formed was filtered off, CuI (0.20 g, 1.1 mmol) was added to the green solution of $[Mo_3S_4(H_2O)_3(C_2O_4)_3]^{2-}$, and the mixture was stirred for 10 h. The brown solution was filtered off from unconsumed copper(I) iodide. The slow evaporation of the solution at room temperature for 7 days afforded brown crystals of **3**, which were separated by decantation, washed with ethanol, and dried in air. The yield was 0.12 g (77%). Found (%): C, 6.24; H, 1.29. $C_6H_{18}CuIMo_3O_{21}K_2S_4$. Calculated (%): C, 6.49; H, 1.63. IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 3447 s, 1700 s, 1673 s, 1378 s, 1273 w, 1240 w, 904 m, 788 m, 532 m, 491 w, 427 w.

Bis(tetraphenylphosphonium)trioxalatotetrasulfidomonoiodocoppertrimolybdenum, $(PPh_4)_2[Mo_3(CuI)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3]$ (4). An aqueous solution of $[Mo_3S_4(CuI)(H_2O)_3(C_2O_4)_3]^{2-}$ (see above) was mixed with an aqueous solution (10 mL) of PPh_4Br (0.30 g, 0.72 mmol). The precipitate that formed was filtered off, washed portionwise with hot water, and dried on the filter. The yield was 0.10 g (45%). IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 3451 s, 1700 s, 1669 s, 1589 w, 1484 m, 1437 s, 1393 s, 1259 w, 1188 w, 1167 w, 1109 s, 997 m, 902 m, 785 m, 756 m, 723 s, 690 s, 527 s, 489 w. Compound **4** is readily soluble in CH_2Cl_2 and DMF. ESI-MS (in CH_3CN), *m/z*: 340 $[Mo_3S_4(C_2O_4)_3]^{2-}$, 435 $[Mo_3(CuI)S_4(C_2O_4)_3]^{2-}$.

Dipotassium(trioxalatotetraselenidomonochlorocoppertrimolybdenum), $K_2[Mo_3(CuI)(\mu_3\text{-}Se)_4(H_2O)_3(C_2O_4)_3]$ (5). Copper(I) iodide (0.15 g, 0.79 mmol) was added to an aqueous solution of $[Mo_3Se_4(H_2O)_3(C_2O_4)_3]^{2-}$ (**1b**), which was prepared from $K_2[Mo_3Se_7(C_2O_4)_3] \cdot 0.5KBr \cdot 4H_2O$ (0.13 g, 0.10 mmol)

Table 3. Crystallographic data and the X-ray data collection and refinement statistics for compounds **3** and **8**

Parameter	**3**	**8**
Molecular formula	$C_6H_{18}CuIK_2Mo_3O_{21}S_4$	$C_{54}H_{40}BrCuMo_3O_{22}P_2S_4$
M_r	1110.90	1662.31
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	10.7815(5)	13.344(2)
b/Å	19.0463(9)	15.772(3)
c/Å	14.6132(7)	17.482(2)
α/deg	90	81.420(4)
β/deg	108.128(2)	69.799(5)
γ/deg	90	73.140(4)
V/Å^3	2851.8(2)	3299.8(9)
Z	4	2
ρ_{calc}/g cm^{-3}	2.587	1.673
μ/mm^{-1}	3.773	1.727
$2\theta_{max}$/deg	55	51.36
Temperature/K	293	150
Number of measured/independent/ observed ($I > 2\sigma(I)$) reflections	19742/6507/4142	21784/12182/6310
R_{int}	0.0583	0.0852
Number of variables	361	812
R_1 ($I > 2\sigma(I)$)	0.0383	0.0775
wR_2 (based on all reflections)	0.0865	0.2150
Residual electron density (max/min)	0.744/–0.940	1.548/–1.269

as described above for **3**. The reaction mixture was stirred for 7 h. The red-brown solution was filtered and slowly concentrated in air. An amorphous precipitate of $K_2[Mo_3(CuI)Se_4(H_2O)_3(C_2O_4)_3]$ was filtered off and washed with ethanol. The yield was 0.060 g (50%). Found (%): C, 6.41; H, 0.86. $C_6H_6CuIMo_3O_{15}K_2Se_4$. Calculated (%): C, 6.05; H, 0.51. IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 3424 s, 1669 s, 1671 s, 1392 s, 1254 w, 1233 w, 904 m, 787 m, 525 m, 471 w. ^{77}Se NMR (H_2O), δ: –56.08, 325.34.

Bis(tetraphenylphosphonium)trioxalatotetraselenidomonoiodocoppertrimolybdenum, $(PPh_4)_2[Mo_3(CuI)(\mu_3\text{-}Se)_4(H_2O)_3(C_2O_4)_3]$ (6). An aqueous solution of $[Mo_3(CuI)Se_4(H_2O)_3(C_2O_4)_3]^{2-}$ was mixed with an aqueous solution (15 mL) of PPh_4Br (0.30 g, 0.72 mmol). The precipitate that formed was filtered off, washed with hot water, and dried in air. The yield was 0.075 g (42%). ESI-MS (in CH_3CN), *m/z*: 530 $[Mo_3(CuI)Se_4(C_2O_4)_3]^{2-}$, 537 $[Mo_3(CuI)Se_4(H_2O)(C_2O_4)_3]^{2-}$.

Dipotassium(trioxalatotetrasulfidomonorhodanocoppertrimolybdenum), $K_2[Mo_3(CuSCN)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ (7). Copper thiocyanate (0.080 g, 0.66 mmol) was added to an aqueous solution of $[Mo_3S_4(H_2O)_3(C_2O_4)_3]^{2-}$, which was prepared from $K_2[Mo_3S_7(C_2O_4)_3] \cdot 0.5KBr \cdot 3H_2O$ (0.13 g, 0.13 mmol). The reaction mixture was stirred at 50 °C for 15 h. The solution was filtered and slowly concentrated in air. An amorphous precipitate of $K_2[Mo_3S_4(CuSCN)(H_2O)_3(C_2O_4)_3]$ was filtered off and washed with ethanol. The yield was 0.065 g (54%). Found (%): C, 7.56; H, 1.56; N, 1.39. $C_7H_{20}NCuMo_3O_{22}K_2S_5$. Calculated (%): C, 7.93; H, 1.90; N, 1.32. IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 3423 s, 2141 m, 2091 w, 1703 s, 1674 s, 1393 s, 1256 w, 1130 w, 948 w, 904 m, 788 m, 721 m, 525 w, 479 m, 429 w. ESI-MS (H_2O, *m/z*): 341 $[Mo_3S_4(C_2O_4)_3]^{2-}$, 401 $[Mo_3S_4(CuSCN)(C_2O_4)_3]^{2-}$, 412 $[Mo_3S_4(CuSCN)(H_2O)(C_2O_4)_3]^{2-}$.

Bis(tetraphenylphosphonium)trioxalatotetrasulfidomonobromocoppertrimolybdenum, $(PPh_4)_2[Mo_3(CuBr)(\mu_3\text{-}S)_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ (8). An aqueous solution of $[Mo_3S_4(CuSCN)(H_2O)_3(C_2O_4)_3]^{2-}$ (see above) was mixed with an aqueous solution (10 mL) of PPh_4Br (0.30 g, 0.72 mmol). The precipitate that formed was centrifuged, decanted, washed with water, and dried in air. Recrystallization of the reaction product from hot water afforded red crystals of $(PPh_4)_2[Mo_3(CuBr)S_4(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$. The yield was 0.080 g (38 %). IR (KBr, 4000—400 cm^{-1}), ν/cm^{-1}: 3430 s, 1699 s, 1669 s, 1586 w, 1484 m, 1437 s, 1382 s, 1258 w, 1188 w, 1165 w, 1109 s, 996 m, 900 m, 782 m, 756 m, 722 s, 689 s, 527 s, 489 w.

X-ray diffraction study. The structures of the $K_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(CuI)(H_2O)_3(C_2O_4)_3] \cdot 6H_2O$ (**3**) and $(PPh_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S)_3(CuBr)(H_2O)_3(C_2O_4)_3] \cdot 7H_2O$ (**8**) complexes were determined by X-ray diffraction. The X-ray diffraction data were collected on a four-circle automated Bruker X8APEX diffractometer equipped with a CCD area detector (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator).[37] The crystallographic data and the X-ray data collection and refinement statistics are given in Table 3. The semiempirical absorption corrections were applied based on the intensities of equivalent reflections with the use of the SADABS program.[37] The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms with the use of the SHELXTL program package.[38] The hydrogen atoms of the H_2O molecules were not located. Selected bond lengths and bond angles are given in Tables 1 and 2.

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