

Preparation, Structure, and Properties of the Mo/Se Ions $[\text{Mo}_2\text{O}_2(\mu_2\text{-Se})_2(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mo}_4(\mu_3\text{-Se})_4(\text{H}_2\text{O})_{12}]^{5+}$

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Preparation of the Mo^{V}_2 di- μ -selenido aqua ion, $[\text{Mo}_2\text{O}_2(\mu_2\text{-Se})_2(\text{H}_2\text{O})_6]^{2+}$, has enabled the cuboidal mixed-valence (3.25) ion $[\text{Mo}_4(\mu_3\text{-Se})_4(\text{H}_2\text{O})_{12}]^{5+}$ to be obtained; characterisation of both complexes including crystal structures of $\text{Na}(\text{Me}_4\text{N})[\text{Mo}_2\text{O}_2(\mu_2\text{-Se})_2(\text{Cys})_2] \cdot 7\text{H}_2\text{O}$ [Cys = L(+)-cysteine] and $[\text{Mo}_4(\mu_3\text{-Se})_4(\text{H}_2\text{O})_{12}](\text{MeC}_6\text{H}_4\text{SO}_3)_5 \cdot 14\text{H}_2\text{O}$ have been carried out and are reported.

Studies on metal/sulphido clusters¹⁻⁴ including Mo/S complexes⁵⁻⁷ is currently an active area of research. In this paper we turn to corresponding Mo/Se complexes, and describe two important lead-in compounds to this new area. One of these is the di- μ -selenido Mo^{V}_2 complex (which contains the cyclic

Mo_2Se_2 unit). On reduction the cuboidal Mo_4Se_4 unit is generated, the lower oxidation state (between III and IV) and electron count being more appropriate to such a tetrameric unit. Trimeric incomplete cuboidal ions are also obtained, the further characterisation of which is in progress.

The Mo^v dimer was prepared by a procedure involving reaction of heptamolybdate(vi), (NH₄)₆[Mo₇O₂₄]·6H₂O, with sodium hydroselenide (NaHSe) in aqueous solution. On addition of L(+)-cysteine and appropriate cations an orange-brown crystalline product is obtained (yield 33.7%). The structure of [Mo₂O₂(μ-Se)₂(Cys)₂]²⁻ in Na(Me₄N)[Mo₂O₂(μ-Se)₂(Cys)₂]·7H₂O was determined by standard low-temperature X-ray diffraction methods (150 K).† A graphics drawing of the complex ion is shown in Figure 1. The Mo–Mo distance of 2.92 Å obtained compares with 2.82 Å (di-μ-sulphido),⁸ and 2.57 Å (di-μ-oxo),⁹ for analogous complexes. The complex is diamagnetic consistent with Mo–Mo bonding, and in solution is a yellow colour similar to that observed for the sulphido and oxo analogues. Folding of the Mo₂Se₂ ring is evident in Figure 1, and the dihedral angle is ~ 31°. The folding is similar to that observed for the Mo₂S₂ structures, and allows closer approach of the Mo's as does the Mo–Se–Mo angle of 73°. Also relevant to the Mo–Mo interaction are the angles O–Mo–Se (101.8°) and Se–Mo–Se (103.8°). These various distortions give a structure which can be described as seven-coordinate capped octahedral, with a bent Mo–Mo bond in the seventh coordination position. Other selected bond distances (Å) are Mo–O(1) 1.670(7), Mo–O(2) 2.332(8), Mo–Se 2.441(2), Mo–Se' 2.475(2), Mo–S 2.489(3), Mo–N(1) 2.255(11) (standard deviations in brackets). The UV-VIS spectrum of the complex gives λ/nm (ε/M⁻¹ cm⁻¹ per dimer) of 205sh (3950), 237 (3190), 304 (9280) and 394sh (3460). On addition of 2 M HClO₄ to remove the cysteine, the aqua ion [Mo₂O₂(μ-Se)₂(H₂O)₆]²⁺ is obtained, peak positions at 247, 303 (with 330 sh) and 419 nm.

Sodium borohydride reduction of the MoV₂ cysteinato complex followed by adjustment of [H⁺] and air oxidation yields cuboidal and incomplete cuboidal (trimeric) complexes. The products are readily separated by a Dowex 50W-X2 cation-exchange chromatography. The first three bands are incomplete cuboidal products which are in the process of being further characterised. The fourth band of green

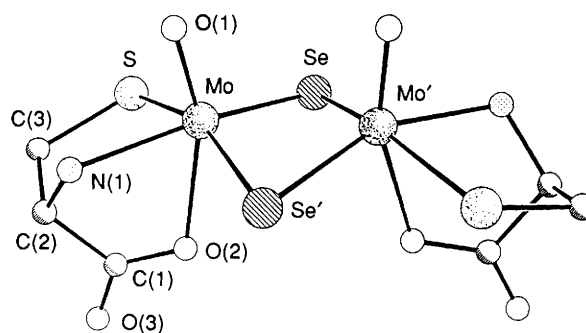


Figure 1. Structure of [Mo₂O₂(μ-Se)₂(Cys)₂]²⁻

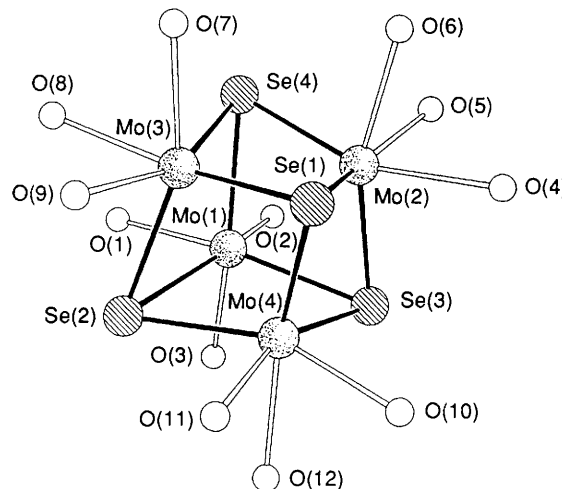


Figure 2. Structure of [Mo₄Se₄(H₂O)₁₂]⁵⁺.

† Crystal data. Syntex P2₁ four circle diffractometer, Mo-K_α radiation (λ = 0.71069 Å), graphite monochromator, scintillation counter, 150 K, empirical absorption corrections.

For Na(Me₄N)[Mo₂O₂(μ-Se)₂(Cys)₂]·7H₂O: C₁₀H₃₆Mo₂N₃NaO₁₃S₂Se₂, M = 843.33, orthorhombic, a = 19.092(6), b = 12.296(4), c = 24.068(6) Å, V = 5650.1 Å³, space group P22₂1, Z = 8, D_c = 1.983 g cm⁻³, μ(Mo-K_α) = 3.6 mm⁻¹, 2θ_{max} = 54°, crystal dimensions ca. 0.50 × 0.45 × 0.45 mm, 6797 unique reflections of which 5245 are 'observed' [I ≥ 2σ(I)]; superstructure problem (reflections hkl, l = 2n + 1 very weak), solution and refinement based on the reflections of the orthorhombic subcell [c' = c/2, space group I222; Mo, Se, Na and O(1) follow the symmetry elements of the space group Immm]; 1735 subcell reflections, R (R_w) = 0.049 (0.059) for 1707 observed reflections; direct methods combined with Fourier techniques, full-matrix least-squares refinements, 142 variables, H atoms omitted, anisotropic temperature factors for the atoms of the anion, otherwise isotropic ones, 1 scale factor.

For [Mo₄Se₄(H₂O)₁₂](MeC₆H₄SO₃)₅·14H₂O: C₃₅H₈₇Mo₄O₄₁S₅Se₄, M = 2023.98, triclinic, a = 12.603(9), b = 16.384(16), c = 16.946(8) Å, α = 90.16(6), β = 92.91(6), γ = 95.99(6)°, V = 3475.4 Å³, space group P1, Z = 2, D_c = 1.934 g cm⁻³, μ(Mo-K_α) = 2.9 mm⁻¹, 2θ_{max} = 48°, crystal dimensions ca. 0.19 × 0.14 × 0.12 mm, 10946 unique reflections, R (R_w) = 0.074 (0.079) for 5147 reflections with I ≥ 3σ(I); direct methods in combination with Fourier procedures, full-matrix least-squares refinement (2 blocks), 380 variables, phenyl rings as rigid groups, H atoms of the H₂O molecules omitted, H atoms of the anions calculated at idealised positions, anisotropic temperature factors for the Mo, Se and S atoms, otherwise isotropic ones, 1 scale factor. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[Mo₄Se₄(H₂O)₁₂]⁵⁺ was re-columned under N₂, followed by elution from a short column with 4 M HPTS (*p*-MeC₆H₄-SO₃H). Crystals were obtained after leaving to stand under N₂ for a few days. The presence of air results in more rapid oxidation to Mo₃Se₄⁴⁺ and deposition of red selenium is sometimes observed. Solutions in ~2 M HClO₄, stored under N₂, could be kept for weeks with little or no decomposition.

The structure of [Mo₄Se₄(H₂O)₁₂]⁵⁺ in crystals of [Mo₄Se₄(H₂O)₁₂](MeC₆H₄SO₃)₅·14H₂O was also determined from a low temperature set of data (150 K).† A graphics representation is shown in Figure 2. Selected mean bond distances (Å) and bond angles (°) are: Mo–Mo 2.865(4), Mo–Se 2.480(4), Mo–O 2.199 (15), Se–Mo–Se 106.4(1). The Mo–Mo distance compares with 2.349 Å in [Mo₄S₄(H₂O)₁₂]⁵⁺.¹⁰ No Mo₄O₄ cube has been characterised at this oxidation level, see e.g. ref. 11. Shibahara and colleagues¹² have however prepared a Mo₄OS₃⁵⁺ cube incorporating a single, μ₃-oxo group, which gives Mo–μ₃(O) of 1.96 Å, as compared to Mo–μ₃(S) of 2.36 Å (2.35 Å in Mo₄S₄⁵⁺), and in the present case Mo–μ₃(Se) of 2.48 Å.

Aqueous acidic solutions (2 M HClO₄) of [Mo₄Se₄(H₂O)₁₂]⁵⁺ give peak positions λ/nm (ε/M⁻¹ cm⁻¹ per cube) at 435(sh) (669), 662 (407), and 1188 (117). The latter is consistent with a mixed valence structure, the average oxidation state of which is 3.25 per Mo. The peaks at 662 nm (645) and 1188 nm (1100) are shifted to higher wavelengths as compared to those (in brackets) for [Mo₄S₄(H₂O)₁₂]⁵⁺.¹³ Cyclic voltammograms for the complex in 2 M HPTS show two quasi-reversible one-electron waves demonstrating the existence of [Mo₄Se₄(H₂O)₁₂]^{4+·5+·6+} states. Reduction poten-

tials for the 5+/4+ couple of 193 mV, and for 6+/5+ couple 792 mV compare with corresponding values of 210 mV and 860 mV for the Mo₄S₄ cube.

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