# $[Se_2MoO_8]_n{}^{2n-}$: A Novel Selenium-rich Chain-like Heteropolyanion

**Christian Robl* and Karin Haake**

*Institut für Anorganische Chemie der Universität München, Meiserstr. 1, D-8000 München 2, Germany*

The novel highly selenium-rich heteropolyanion $[Se_2MoO_8]_n{}^{2n-}$ with an unprecedented chain structure has been synthesized in aqueous solution and characterized by X-ray structure analysis of a single crystal of $K_2[Se_2MoO_8]\cdot 3H_2O$.

Most heteropolyanions for which the general formula $[A_xB_yO_z]^{n-}$ applies (A = Te, P, Si, Se *etc.* 'hetero-element', B = V, Nb, Mo *etc.* 'poly-element') have oligomeric cluster-like structures and possess a rather low A:B ratio. *E.g.* the well-known Keggin-type anions[1] such as $[PW_{12}O_{40}]^{3-}$ have a stoichiometric P:W ratio of 1:12 and the Te:Mo ratio in anions of the Anderson–Evans type[2] as $[TeMo_6O_{24}]^{6-}$ is 1:6.

Infinite heteropolyanions (chain-like, layer-like or anions with a three-dimensional framework structure) have been observed rarely.† Nevertheless, anions like these would promise interesting applications, in particular, those with anisotropic structural characteristics since heteropoly compounds show a high electron storage capacity and should be capable of providing new electrically conducting materials.

A chain-like molybdosulfate anion was prepared by Fuchs *et al.* in melts of $MoO_3$ and $Rb_2SO_4$ and isolated as $Rb_2[SMo_3O_{13}]$.[3] This anion is made up by chains of edge-sharing $MoO_6$ coordination octahedra. One $SO_4$ tetrahedron is attached at one time to a group of three $MoO_6$ octahedra sharing common corners with them. The $[SMo_3O_{13}]_n{}^{2n-}$ anion and the analogous molybdoselenate anion $[SeMo_3O_{13}]_n{}^{2n-}$ can be obtained conveniently in aqueous solution as well.[4]

The novel chain-like and highly selenium-rich heteropolyanion $[Se_2{}^{IV}MoO_8]_n{}^{2n-}$ was synthesized in aqueous solution applying a high excess of $SeO_3{}^{2-}$; 6 mmol $MoO_3$, 90 mmol $H_2SeO_3$ and 60 mmol $K_2CO_3$ were dissolved in 20 ml $H_2O$ and heated to boiling temperature. The clear solution had pH = 7 and was allowed to cool slowly. Small colourless crystal plates of $K_2[Se_2MoO_8]\cdot 3H_2O$ were formed within one week.‡§

---

† Alumosilicates are not regarded as heteropoly compounds in this consideration.

‡ *Crystal data* for $K_2[Se_2MoO_8]\cdot 3H_2O$, monoclinic with $a = 932.5(2)$, $b = 1233.0(2)$, $c = 1058.0(1)$ pm, $\beta = 112.31(1)°$, $V = 1125.4 \times 10^6$ pm$^3$, space group $P2_1/a$ (no. 14). $Z = 4$, $M_r = 514.1$, $D_c = 3.03$ g cm$^{-3}$, $\mu = 77.5$ cm$^{-1}$ (Mo-K$\alpha$). 2809 reflections were collected on a Siemens R3m/V four-circle diffractometer (graphite-monochromated Mo-K$\alpha$ radiation) in the $\omega$–$2\theta$ scan mode to $2\theta_{max} = 54°$; $T = 295$ K; a numerical absorption correction and an empirical extinction correction were applied. 2475 unique reflections ($R_{int} = 0.0129$) of which 1964 were considered observed with $|F| > 3\sigma_{|F|}$. The phase problem was solved by direct methods (SHELXTL-Plus programme package). Hydrogen atoms have not been located. All non-hydrogen atoms were refined anisotropically (146 parameters). $R = 0.0424$, $R_w = 0.0303$, $R_g = 0.0268$, $w = \sigma_{|F|}^{-2}$; maximum features in final difference Fourier synthesis $+0.92/-0.81$ e $\times 10^{-6}$ pm$^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

§ *Characteristic IR absorption data* for $K_2[Se_2MoO_8]\cdot 3H_2O$: $\nu$/cm$^{-1}$ (Nujol) 3384vs, 1647m, 929s, 893vs, 865s, 859s, 776s, 743s, 592vs, 536s, 424m, 373m, 340s, 282s.

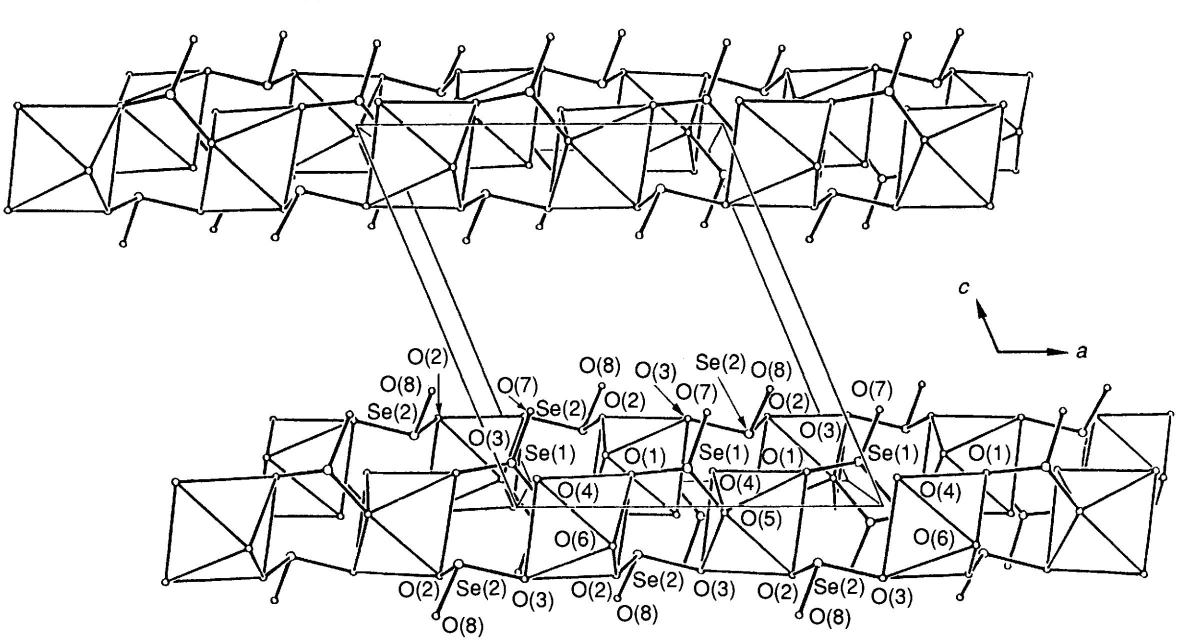

**Fig. 1** Viewed from the [010] direction: $[Se_2MoO_8]_n^{2n-}$ anions composed of $MoO_6$ coordination octahedra linked by $SeO_3$ pseudotetrahedra extend parallel to [100]. $K^+$ ions and water molecules are accommodated in the gap between layers of parallel anions. (The unit cell is outlined.) Selected bond lengths (pm) and angles (°): Mo–O(1) 203.0(4), Mo–O(2) 215.5(4), Mo–O(3) 200.0(4), Mo–O(4) 168.7(4), Mo–O(5) 217.6(4), Mo–O(6) 170.4(4), Se(1)–O(1) 174.5(4), Se(1)–O(5) 168.3(4), Se(1)–O(7) 164.9(5); Se(2)–O(2) 172.1(4), Se(2)–O(3) 175.7(3), Se(2)–O(8) 165.8(5); O(1)–Se(1)–O(5) 99.75(19), O(1)–Se(1)–O(7) 99.60(21), O(5)–Se(1)–O(7) 105.67(21); O(2)–Se(2)–O(3) 98.48(18), O(2)–Se(2)–O(8) 100.44(21), O(3)–Se(2)–O(8) 102.12(19).

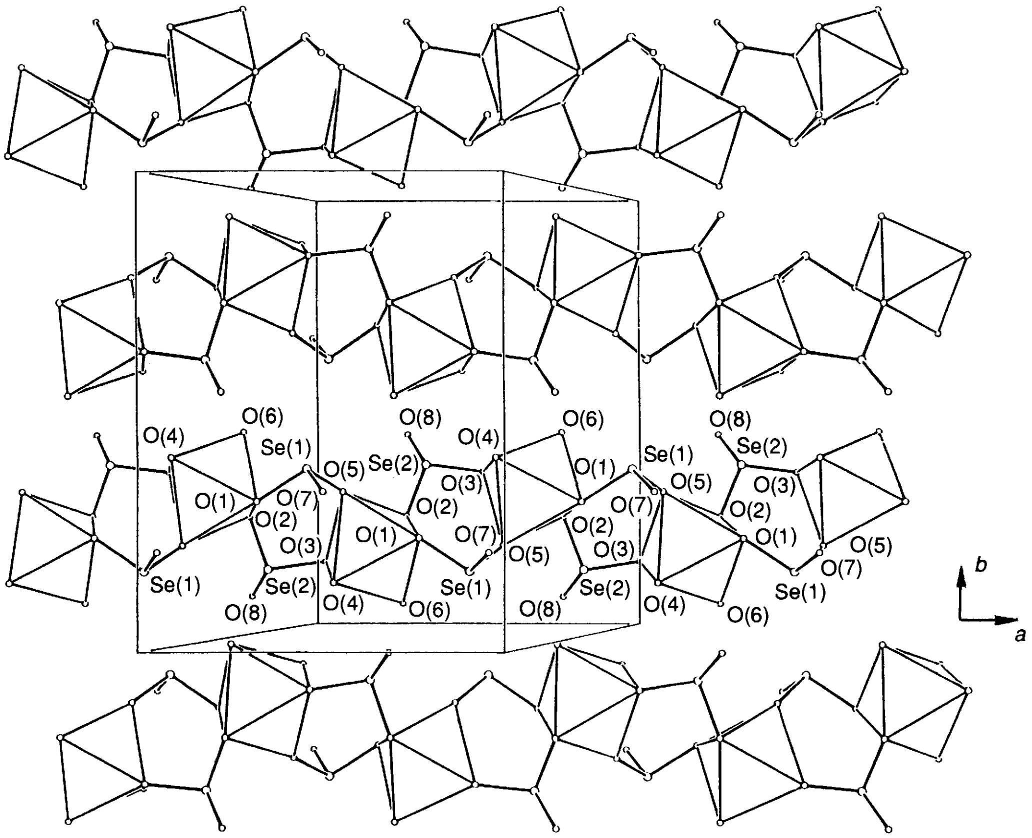

**Fig. 2** A view on (001) shows the corrugation of the $[Se_2MoO_8]_n^{2n-}$ chains. (The unit cell is outlined.)

$K_2[Se_2MoO_8]{\cdot}3H_2O$ is sparingly soluble in cold water, but soluble at 50 °C. This process is obviously accompanied by disintegration of the $[Se_2MoO_8]_n^{2n-}$ anion since single crystals of $K_4[Se_2Mo_5O_{21}]{\cdot}2H_2O$ were obtained after slow evaporation of the solvent; the cyclic $[Se_2Mo_5O_{21}]^{4-}$ anion is analogous to $[S_2Mo_5O_{21}]^{4-}$.[5] On the other hand the selenium-rich $K_2[Se_2MoO_8]{\cdot}3H_2O$ can be isolated as a second fraction from solutions with a moderate $SeO_3^{2-}$ excess prepared to synthesize $K_4[Se_2Mo_5O_{21}]{\cdot}2H_2O$; the mother liquor is depleted of molybdenum by separation of crystalline $K_4[Se_2Mo_5O_{21}]{\cdot}2H_2O$.[4]

Differential thermal analysis of $K_2[Se_2MoO_8]{\cdot}3H_2O$ in air showed endothermic processes obviously caused by gradual decomposition at 110, 270 and 320 °C yielding a red residue in which $K_4MoO_5$ and Se were identified by their X-ray powder diffraction patterns.

The structure of the $[Se_2MoO_8]_n^{2n-}$ anion is unprecedented in heteropolyanion chemistry. Distorted $MoO_6$ coordination octahedra are linked by two crystallographically independent $SeO_3$ pseudo-tetrahedra to yield a sinusoidally corrugated chain running parallel to [100] with the amplitude of corrugation parallel to [010] (Figs. 1 and 2). Only two oxygen atoms of each $SeO_3$ group are shared with the $MoO_6$ octahedra. As a consequence of the high stoichiometric Se content, the $MoO_6$ octahedra are separated from each other. Hence the $[Se_2MoO_8]_n^{2n-}$ anion lacks a continuous -O-Mo-O-Mo-O- bond sequence as is characteristic of most heteropoly compounds. A further anion with this particular feature is the recently prepared cyclic $[Te_6Mo_{12}O_{60}]^{12-}$ anion.[6]

Pairs of edge-sharing $MoO_6$ coordination octahedra linked by bridging $MoO_4$ coordination tetrahedra were found in the chain-like isopolyanion $[Mo_2O_7]_n^{2n-}$ of $(NH_4)_2[Mo_2O_7]$.[7]

Inspite of the one-dimensionally infinite $[Se_2MoO_8]_n^{2n-}$ anions the single crystals of $K_2[Se_2MoO_8]\cdot 3H_2O$ do not cleave to fibres. This is obviously caused by the connection mode of the $K^+$ coordination polyhedra. They are linked by common edges to form a layer-like arrangement parallel to (001) establishing a sturdy connection between adjacent anions.

The bond orders calculated according to the method of Brown[8] are 5.9 for Mo, 3.8 for Se(1) and 3.7 for Se(2), respectively. For both unique Se atoms the terminal Se–O bond is the shortest [Se(1)–O(7) 164.9, Se(2)–O(8) 165.8 pm]. Application of a riding model bond[9] length correction yields 166.2 [Se(1)–O(7)] and 167.1 pm [Se(2)–O(8)]. The other Se–O bond lengths as well as the Mo–O bonds are not significantly affected by artificial foreshortening due to thermal vibration.

Financial support by Fonds der Chemischen Industrie is gratefully acknowledged.

*Received, 14th August 1992; Com. 2/04414E*

## References

1 J. F. Keggin, *Nature*, 1933, **131**, 908.
2 H. T. Evans, *J. Am. Chem. Soc.*, 1948, **70**, 1291.
3 J. Fuchs, H.-U. Kreusler and A. Förster, *Z. Naturforsch., B Chem. Sci.*, 1979, **34**, 1683.
4 C. Robl and K. Haake, unpublished results.
5 K. Y. Matsumoto, M. Kato and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 106.
6 C. Robl and M. Frost, *J. Chem. Soc., Chem. Commun.*, 1992, 248.
7 I. Knöpnadel, H. Hartl, W.-D. Hunnius and J. Fuchs, *Angew. Chem.*, 1974, **86**, 894.
8 I. D. Brown and K. K. Wu, *Acta Crystallogr., Sect. B*, 1976, **32**, 1957.
9 W. R. Basing and H. A. Levy, *Acta Crystallogr.*, 1964, **17**, 142.