DALTON
COMMUNICATION

# Synthesis and characterisation of tetramethylammonium selenosulfate(VI) tetrahydrate, $(NMe_4)_2SeSO_3{\cdot}4H_2O$

**Alexander J. Blake, Victoria Consterdine, Michael F. A. Dove,* Scott Lammas and Linda H. Thompson**

*Department of Chemistry, University of Nottingham, Nottingham, UK NG7 2RD*

Tetramethylammonium selenosulfate tetrahydrate has been synthesised and characterised; a single-crystal X-ray structure determination shows the presence of the dianion $SeSO_3^{2-}$, in which the central sulfur atom is bonded to three oxygens and one selenium atom [S–Se distance 2.1746(7) Å].

The solubility of elemental selenium in aqueous solutions of the sulfites of the more electropositive elements has been known since the middle of the nineteenth century.[1] Indeed, the dissolution in and subsequent precipitation of selenium from aqueous sulfite has been described as a means of separating selenium from tellurium.[2] In 1995 Ball and Milne[3] reported on their studies of the synthesis and spectroscopy of the selenosulfate anion; their data are fully consistent with the expected structure of this species and, like our earlier work,[4] refute the possible existence of both the isomeric thioselenate(VI) and the selenoselenate(VI) dianions.[2] Brunner *et al.*[5] had previously shown that a selenium-bridged dirhodium complex, $[(C_5Me_5)\text{-}Rh(CO)]_2Se$ could be converted by the action of $SO_3$ into the related μ-$SeSO_3$ complex, which they characterised by a single-crystal X-ray diffraction study. As part of our study of the chemistry of selenosulfates we attempted to isolate single crystals of a salt containing the free anion, searches of the October 1996 release of the Cambridge Structural Database[6] and of the latest Inorganic Crystal Structure Database having revealed the bridged dirhodium complex and the earlier study of a copper complex, $Cu(en)_2SeSO_3$ (en = ethane-1,2-diamine),[7] as the only relevant structures. Crystallographic studies of $M(en)_3SeSO_3$ compounds, $M^{II}$ = Cd,[8a] Mn, Fe, Co, Ni, Zn or Cd,[8b] had shown them to have disordered O and Se sites in the selenosulfate anion.

We have now succeeded in preparing crystals of the colourless tetrahydrate of tetramethylammonium selenosulfate. The compound was made from excess selenium, aqueous tetramethylammonium hydroxide (2 equivalents) and sulfur dioxide (1 equivalent) and isolated from the concentrated solution. It is stable in air at room temperature for more than a month in the dark; it may be partially dehydrated *in vacuo* and decomposes at 200 °C to a brown solid, which turns red with further heating. The hydrate was isolated in *ca.* 50% yield and gave satisfactory elemental analyses, $^{77}$Se NMR (in aqueous sulfite), infrared and Raman spectra fully consistent with the formulation.† Its crystal structure has been determined by single-crystal X-ray methods‡ and shows the presence of the tetramethylammonium ions and the free selenosulfate ion interacting *via* two of its oxygen atoms (O2 and O3) with a network of H-bonded water molecules, Fig. 1. There is also a long selenium–hydrogen interaction, Se1 ··· H3W1 2.58 Å, with a hydrogen bond angle of 173°. The S–Se bond length of 2.1746(7) Å in the anion is shorter than that reported earlier[7] for $Cu(en)_2SeSO_3$ in which selenium was said to complete the octahedral co-ordination of copper(II). The length of the S–Se bond in the dirhodium complex is significantly greater, 2.301 Å, consistent with it being a single bond; indeed, it is quite comparable with the related single bond in $O_n$S–Se ($n$ = 2 or 3) fragments listed in the Database,[6] for which the average value is 2.26 (±0.03) Å.

## Acknowledgements

Financial support from the EPSRC in the form of a studentship (to L. H. T.) and of funding for the purchase of the X-ray diffractometer is gratefully recorded.

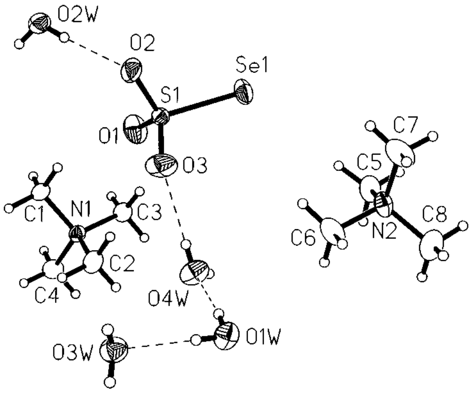

**Fig. 1** The asymmetric unit in the structure of tetramethylammonium selenosulfate tetrahydrate. Selected bond distances (Å) and angles (°): Se1–S1 2.1746(7), S1–O1 1.452(2), S1–O2 1.464(2), S1–O3 1.462(2); O1–S1–O3 110.90(13), O1–S1–O2 111.86(12), O3–S1–O2 108.79(12), Se1–S1–O1 108.57(8), Se1–S1–O2 108.35(8), Se1–S1–O3 108.28(9)

## References

1 *Gmelin's Handbuch der Anorganische Chemie*, *Selen*, *B*, Gmelin-Verlag GmbH, Clausthal-Zellerfeld, 1949.
2 K. W. Bagnall, *Comprehensive Inorganic Chemistry*, eds. J. C. Bailar, H. J. Emeléus, R. Nyholm and A. F. Trotman-Dickenson, Pergamon Press, 1973, vol. 2, p. 938.
3 S. Ball and J. Milne, *Can. J. Chem.*, 1995, **73**, 716.
4 L. H. Thompson, Ph.D. Thesis, University of Nottingham, 1993.
5 H. Brunner, N. Janietz, J. Wachter, H.-P. Neumann, B. Nuber and M. L. Ziegler, *J. Organomet. Chem.*, 1990, **388**, 203.
6 F. H. Allen and O. Kennard, *Chem. Design Automation News*, 1993, **8**, 1; 31.
7 N. V. Podbereskaya, S. V. Borisov and V. V. Bakakin, *Zh. Strukt. Khim.*, 1971, **12**, 840.
8 (*a*) N. V. Podbereskaya and S. V. Borisov, *Zh. Strukt. Khim.*, 1971, **12**, 1114; (*b*) V. L. Varand, N. V. Podbereskaya, V. M. Shulman, V. V. Bakakin and E. D. Ruchkin, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1967, 44.

*Received* 10*th October* 1997; *Communication* 7/07328C

---

† Spectroscopic data for the selenosulfate anion. Raman (solid state) 1144(E), 991($A_1$), 637($A_1$), 518(E), 303($A_1$), 279 (sh)(E) cm$^{-1}$; $^{77}$Se NMR in aqueous sulfite, a singlet at δ 650 relative to $Me_2Se$.

‡ Crystal data for: $C_8H_{32}N_2O_7SSe$, $M = 379.38$, monoclinic, $a = 8.2902(9)$, $b = 15.551(3)$, $c = 14.198(3)$ Å, $\beta = 94.924(15)°$, $U = 1823.7(6)$ Å$^3$, space group $P2_1/n$, $Z = 4$, $D_x = 1.382$ g cm$^{-3}$, Mo-Kα radiation, $\mu = 2.198$ mm$^{-1}$, $T = 150$ K, ω–θ scans, $2\theta \leqslant 50°$, 4499 total data, 3195 unique, $R_{int} = 0.024$ after a numerical absorption correction ($T_{max} = 0.758$, $T_{min} = 0.535$), 301 variables refined in full-matrix least squares against 3188 $F^2$ data to $R[F \geqslant 4\sigma(F)] = 0.0285$, $wR(F^2) = 0.0622$, $S = 0.99$, $\Delta\rho_{max} = 0.56$ e Å$^{-3}$. CCDC reference number 186/793.