# Dalton Communications

## Synthesis and Crystal Structure of $[W_2Se_2(PPh_2Me)_2(SePh)_4]$: A Complex having Two Co-ordinatively Unsaturated Metal Centres

**P. Michael Boorman,* Heinz-Bernhard Kraatz and Masood Parvez**
*Department of Chemistry, University of Calgary, Calgary, Alberta, T2N 1N4, Canada*

The reaction of $[WCl_2(PPh_2Me)_4]$ with $SiMe_3(SePh)$ in tetrahydrofuran produces a centrosymmetric complex having terminal selenolate ligands and two co-ordinatively unsaturated tungsten centres.

Research into syntheses of new materials has provided much of the driving force for the latest developments in the field of selenido[1] and selenolato[2] complexes. However, despite the plethora of known thiolato complexes of early transition metals, the chemistry of analogous selenolates is still in its infancy and structural data on terminal selenolates in particular are rare.[3] As part of our ongoing investigation of the reactivity of selenolates, we report the synthesis and structure of the unprecedented tungsten(IV) selenido–selenolato complex $[W_2Se_2(PPh_2Me)_2(SePh)_4]$ **1** having two co-ordinatively unsaturated tungsten centres and terminal selenolate ligands.

The compound $SiMe_3(SePh)$ (0.044 g, 0.19 mmol) was added to a solution of $[WCl_2(PPh_2Me)_4]$ (0.1 g, 0.09 mmol) in tetrahydrofuran (thf) (10 $cm^3$) and stirred overnight at room temperature under an atmosphere of argon. After removal of all volatiles, the remaining brown oil was repeatedly triturated with hexane. The light yellow supernatant was removed, the solid was washed with *n*-hexanes (20 $cm^3$), dried *in vacuo* and redissolved in thf (5 $cm^3$) to give a green solution. An equal amount of hexane was added. At room temperature over a period of 2 weeks the solution deposited light green crystals, identified as $[W_2Se_2(PPh_2Me)_2(SePh)_4]\cdot 2thf$† by X-ray crystallography‡ (see below), in 28% yield (based on W). The $^1H$ NMR spectrum in $[^2H_8]$toluene gives a multiplet at δ 8.0–6.6 for the aromatic protons of the $PPh_2Me$ and SePh ligands and a doublet due to the methyl group of the $PPh_2Me$ ligands at δ 3.0 ($J_{PH}$ = 7.6 Hz). Two multiplets at δ 3.6 and 1.45 indicate the presence of thf. Unfortunately, the low solubility of the complex did not allow a characterization by $^{77}Se$ NMR spectroscopy; even the $^{31}P$ NMR spectrum only showed an unresolved signal at δ 6.2.

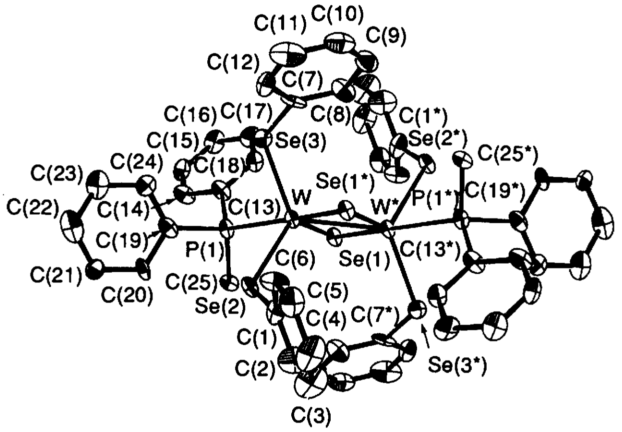

**Fig. 1** An ORTEP[6] plot (50% probability ellipsoids) of complex **1**. Selected bond lengths (Å) and angles (°): W–Se(1) 2.380(2), W–Se(2) 2.438(2), W–Se(3) 2.461(2), W–Se(1*) 2.473(1), W–P(1) 2.554(4), W–W 2.728(1), C(1)–Se(2) 1.914(10), C(7)–Se(3) 1.947(11), C(13)–P(1) 1.832(11), C(19)–P(1) 1.825(10), C(25)–P(1) 1.837(16); Se(2)–W–Se(1) 115.2(1), Se(3)–W–Se(1) 117.4(1), Se(3)–W–Se(2) 120.9(1), P(1)–W–Se(1) 81.0, P(1)–W–Se(2) 79.3(1), P(1)–W–Se(3) 83.9(1), W–Se(1)–W* 68.4(2), Se(1)–W–Se(1*) 111.6(1), Se(1*)–W–Se(2) 92.3(1), Se(1*)–W–Se(3) 92.2(1), Se(1*)–W–P(1) 167.1(1), C(1)–Se(2)–W 114.1(4), C(7)–Se(3)–W 111.6(3), C(13)–P(1)–W 121.2(3), C(25)–P(1)–W 112.0(6), C(19)–P(1)–W 115.5(4)

Complex **1** is a centrosymmetric dimer with distorted trigonal-bipyramidal geometry around each tungsten centre (see Fig. 1). Each $W^{IV}$ is bonded to two terminal selenolates, a terminal phosphine and two Se atoms that bridge the two W atoms. The presence of two unsaturated metal centres is unexpected, since the complex crystallizes with two thf as solvent of crystallization. Unsaturation of one metal centre in a dinuclear molybdenum complex was reported by Mayer and co-workers.[7] The W atom is displaced from the Se(2)–Se(3)–Se(1) plane by −0.3615 Å. The two selenolate ligands are both directed away from the phosphine. The W–Se(2) and W–Se(3) distances to the terminal selenolates are comparable to those found in $[W_2(OPr^i)_2(SeC_6H_2Me_3\text{-}2,4,6)_4]$.[8] The W–Se(1*) bond is 0.093(1) Å longer than W–Se(1). The $W_2Se_2$ cores of

---

† Satisfactory elemental analyses were obtained.

‡ Crystal data: $M$ = 1694.538, triclinic, space group $P\bar{1}$, $a$ = 11.290(2), $b$ = 12.945(3), $c$ = 10.977(3) Å, $\alpha$ = 111.65(2), $\beta$ = 101.30(2), $\gamma$ = 98.20(2)°, $U$ = 1421.0 $Å^3$, $Z$ = 1, $D_c$ = 1.98 g $cm^{-3}$, $F(000)$ = 808, $R$ = 0.0814, $R'$ = 0.0838 for 3499 observed $[I > 3\sigma(I)]$ reflections. Crystal dimensions = 0.20 × 0.25 × 0.40 mm. The intensity data were collected on a Rigaku AFC6S diffractometer at 150(1) K, using the $\omega$–$2\theta$ scan method and monochromatized Mo-K$\alpha$ radiation ($\lambda$ = 0.710 69 Å) in the range $2 < \theta < 25°$. The data were corrected for Lorentz and polarization effects and absorption [$\mu$(Mo-K$\alpha$) = 80.32 $cm^{-1}$]. The structure was solved by direct methods using the TeXSAN program package,[4] then later refined using SHELX 76.[5] The refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic thermal parameters for the non-hydrogen atoms. The C–C bonds of the aromatic rings were constrained to 1.395 Å. Hydrogen atoms were included at geometrically idealized positions (C-H 0.95 Å) with a fixed common isotropic thermal parameter. In the refinement cycles, weights were derived from the counting statistics. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

$[W_2Se_9]^{2-}$ and $[W_2Se_{10}]^{2-}$ show a similar distortion.[9] The W–W separation of 2.728(1) Å and the diamagnetism strongly suggest the presence of a formal double bond.

The presence of $Me_3SiSiMe_3$ and $SiMe_3Ph$ in the hexane extract has been confirmed by gas chromatography–mass spectrometry and suggests an oxidative addition–reductive elimination type mechanism. The inherent weakness of the Se–C bond[10] allows the dearylation of the benzeneselenolate under very mild conditions, resulting in the formation of a μ-Se similar to what has been observed for $[Cl_3W(\mu\text{-Se})(\mu\text{-SePh})_2WCl_3]^{2-}$.[11] Investigations into the mechanistic aspects of this reaction and the reactivity of **1** are currently in progress.

## Acknowledgements

Financial support from NSERC (Canada) and the Department of Chemistry for a Graduate Scholarship (to H.-B. K.) is gratefully acknowledged.

## References

1 M. A. Ansari and J. A. Ibers, *Coord. Chem. Rev.*, 1990, **100**, 225; M. G. Kanatzidis, *Comments Inorg. Chem.*, 1990, **10**, 161.

2 M. L. Steigerwald and C. R. Sprinkle, *J. Am. Chem. Soc.*, 1987, **109**, 7200; S. M. Stuczynski, J. G. Brennan and M. L. Steigerwald, *Inorg. Chem.*, 1989, **28**, 4431; M. Bochmann, K. Webb, M. Harman and M. B. Hursthouse, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 638; M. Bochmann, A. P. Coleman, K. J. Webb, M. B. Hursthouse and M. Mazid, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 973; M. Bochmann, K. J. Webb, M. B. Hursthouse and M. Mazid, *J. Chem. Soc., Chem. Commun.*, 1991, 1735.

3 H. J. Gysling, in *The Chemistry of Organic Selenium and Tellurium Compounds*, eds. S. Patai and Z. Rappoport, Wiley, New York, 1986, vol. 1, ch. 18, pp. 741–754.

4 TeXSAN, Single Crystal Structure Analysis Software, version 1.2, Molecular Structures Corporation, Woodlands, TX, 1992.

5 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

6 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

7 K. A. Hall, S. C. Critchlow and J. M. Mayer, *Inorg. Chem.*, 1991, **30**, 3593.

8 M. H. Chisholm, I. P. Parkin, J. C. Huffman and W. B. Streib, *J. Chem. Soc., Chem. Commun.*, 1990, 920.

9 R. W. M. Wardle, S. Bhaduri, C.-N. Chau and J. A. Ibers, *Inorg. Chem.*, 1988, **27**, 1747.

10 L. Batt, in *The Chemistry of Organic Selenium and Tellurium Compounds*, eds. S. Patai and Z. Rappoport, Wiley, London and New York, 1986, vol. 1, ch. 4, pp. 157–160.

11 J. M. Ball, P. M. Boorman, J. F. Fait, H.-B. Kraatz, J. F. Richardson, D. Collison and F. A. Mabbs, *Inorg. Chem.*, 1990, **29**, 3290.

*Received 2nd July* 1992; *Communication* 2/03500F