Structure Refinement from Powder Neutron Diffraction Data of $Sn_{10}W_{16}O_{44}$, which contains a Metal–Metal Bonded W_6O_{12} Cluster

Simon J. Hibble and Siobhan A. McGrellis
Department of Chemistry, University of Reading, Whiteknights, PO Box 224, Reading RG6 6AD, UK

A powder neutron diffraction study of $Sn^{II}_{10}W_{16}O_{44}$ has shown that this is the correct composition for the compound previously assigned the formula $Sn_{10}W_{16}O_{46}$. The compound contains W_6O_{12} clusters with 14 electrons available for metal–metal bonding. This electron count is in agreement with the values found for octahedral Nb_6O_{12} units in related niobates. Six apical oxygens complete the co-ordination of the W_6 unit to give the formulation of the cluster as $W_6O^i_{12}O^a_6$. Two of these clusters are found in the unit cell, with the remaining four tungstens forming face-sharing octahedral $W^{VI}_2O_9$ units. The assignment of oxidation states and electron counting is supported by bond-valence calculations.

Metal cluster compounds have been known for transition-metal oxides since 1957 when $Zn_2Mo_3O_8$ was synthesised.[1] Since then a large number of molybdates and more recently niobates of this type have been prepared. The chemistry of reduced molybdates is especially rich; in addition to Mo_3 units, the range of cluster types synthesised includes Mo_4 units in $K_2Mo_8O_{16}$,[2] Mo_6 units in $Ca_{16.5}Mo_{13.5}O_{40}$[3] and Mo_{10} units in $LaMo_5O_8$.[4] Isolated Mo_6 clusters are rare in molybdenum oxide chemistry, but chains of condensed octahedral clusters, produced by edge sharing, provide the most common structural element. The parent of these compounds is $NaMo_4O_6$,[5] and a review containing a discussion of the electron counting in these compounds has been written by Simon.[6] Reduced niobates show a different type of chemistry which has recently been reviewed by Köhler *et al.*[7] Isolated Nb_6 clusters are a common structural feature and are found in a large number of compounds such as $Mg_3Nb_6O_{11}$[8] and $SrNb_8O_{14}$.[9] In these compounds 14 electrons fill the bonding molecular orbitals for the M_6O_{12} cluster. It is curious that for the corresponding third-row transition metals, tungsten and tantalum, only the metastable $Zn_2W_3O_8$,[10] containing W_3 triangles, and $Sn_{10}W_{16}O_{46}$[11] containing a W_6 octahedral cluster have been reported.

We were surprised to note that in the structure determination of $Sn_{10}W_{16}O_{46}$ by Goreaud *et al.*[11] the W_6 cluster was centred on an oxygen atom. This would mean that the structure contained M_6O_{13} units, in contrast to the M_6O_{12} units found in reduced niobates. Examination of the structure suggested that this was unlikely, because it gave an unreasonable bond-order sum around this central oxygen and an electron count of 12 for the cluster. Since this is the only known stable oxide containing a tungsten cluster, it was decided to carry out a powder neutron diffraction study to determine unequivocally the presence or otherwise of this central oxygen and to determine the electron count for the metal cluster.

Experimental

Preparation and Characterisation.—The red crystalline solid $Sn_{10}W_{16}O_{44}$ was prepared by heating SnO_2, WO_3 and W in the molar ratio 5:4:4 in a sealed silica ampoule at 800 °C for 1 week. The powder X-ray pattern was in agreement with that reported in the powder diffraction file[12] by Goreaud *et al.*[11] for '$Sn_{10}W_{16}O_{46}$'.

Data Collection.—Time-of-flight powder neutron diffraction data were collected on the HRPD diffractometer at ISIS, Rutherford Appleton Laboratory, Chilton, Didcot. Approximately 5 g of powdered $Sn_{10}W_{16}O_{44}$ were loaded into a flat vanadium sample holder and placed 1 m in front of the back-scattering detectors. Data were collected over the time-of-flight range 35–118 ms (*d*-space range 0.72–2.4 Å). Profile plots were generated using GENIE.[13]

Structure Refinement

The model of Goreaud *et al.*[11] including the oxygen at the centre of the W_6 octahedra was used for the initial refinements. A standard Rietveld refinement was carried out using the program REFINE,[14] with the peak shape modelled by a pseudo-Voigt function convoluted with a double-exponential function. Data points which did not contribute to any reflections were excluded from the refinement. The coherent scattering lengths used for Sn, W and O were 0.6223×10^{-14}, 0.4770×10^{-14} and 0.5805×10^{-14} m, respectively.[15] The scale and ten polynomial background parameters were refined first, followed by the unit cell, zero point and peak parameters. A number of impurity peaks, not assignable to any known phase, were present in the pattern and where possible were excluded from the subsequent refinements (seven excluded regions). It is possible that these peaks arise from impurities produced by reaction with the ampoule during preparation. The atomic parameters were then refined with the isotropic thermal parameters fixed at the values of Goreaud *et al.*[11] The overall agreement index was poor, and attempts to refine the isotropic thermal parameters failed, because that for the central oxygen continued to increase without reaching a limit. The central oxygen was removed from the model, and a successful refinement was carried out by varying the atomic parameters, independent thermal parameters for the different tin and oxygen atoms, and a single thermal parameter for the tungsten atoms, see Fig. 1. The final atomic parameters are given in Table 1. A Fourier map for a section passing through the site proposed by Goreaud *et al.*[11] for an oxygen at the centre of the W_6 octahedra revealed no scattering density at this position.

Discussion

Although the final agreement factors remain a little high because of the presence of small amounts of unidentified impurity phases, the refinement and final Fourier map clearly show that there is no oxygen at the centre of the W_6 octahedra.

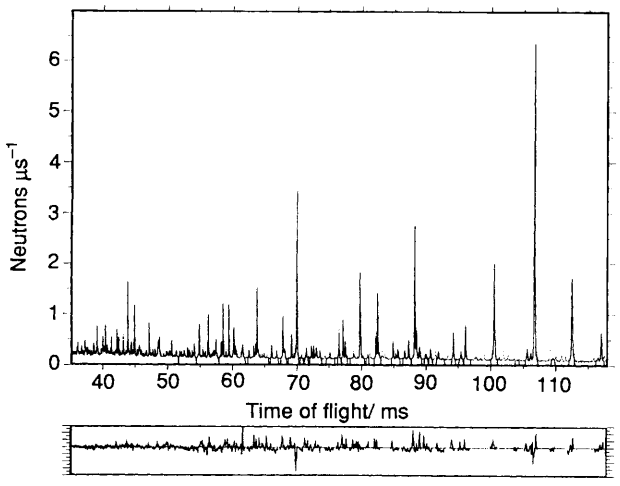

Fig. 1 Final fitted profile for $Sn_{10}W_{16}O_{44}$. Observed (points), calculated (line) and difference (lower) profiles are shown

Table 1 Refined atomic parameters for $Sn_{10}W_{16}O_{44}$ with estimated standard deviations in parentheses

Atom	Site	x	y	z	B/Å^2
W(1)	12i	0.2238(5)	0.0564(5)	0.0595(2)	0.10(4)
W(2)	4f	0.3333	0.6667	0.6716(3)	0.10(4)
Sn(1)	6h	0.1924(6)	0.3164(6)	0.25	0.48(7)
Sn(2)	4f	0.3333	0.6667	0.0708(2)	0.61(9)
O(1)	6h	0.4694(7)	0.2972(7)	0.25	0.65(8)
O(2)	12i	0.4657(4)	0.1175(5)	0.1248(1)	0.33(6)
O(3)	12i	0.1338(5)	0.4165(4)	0.0032(2)	0.29(5)
O(4)	12i	0.1794(6)	0.2379(3)	0.1223(1)	0.46(5)
O(5)	2a	0.0	0.0	0.25	0.72(6)

Space group = $P6_3/m$, a = 7.6697(1), c = 18.6391(3) Å, number of reflections used in the refinement = 873, $\chi^2 = (R_{wp}/R_{ex})^2$ = 18.48 for 3185 observations and 43 basic variables, $R_{wp} = [\Sigma_i w_i |Y_i(obs) - Y_i(calc)|^2/\Sigma_i w_i Y_i(obs)^2]^{\frac{1}{2}}$ = 0.081, $R_{ex} = [(N - P + C)/\Sigma_i w_i Y_i(obs)^2]^{\frac{1}{2}}$ = 0.0204; R_{wp} is the weighted profile R factor, R_{ex} is the expected R factor, w_i is the weight for point i, N = no. of observations, Y_i is the intensity of point i, P = no. of variables and C = no. of constraints.

Table 2 Selected interatomic distances (Å) in $Sn_{10}W_{16}O_{44}$

W(1)–W(1)	2.704(5) × 2	W(1)–O(4)	1.989(4)
	2.678(5) × 2		1.974(5)
W(1)–O(2)	2.067(5)	W(2)–W(2)	2.923(8)
W(1)–O(3)	2.023(6)	W(2)–O(1)	2.020(6) × 3
	1.999(4)	W(2)–O(2)	1.824(4) × 3

The structure of $Sn_{10}W_{12}O_{44}$ is shown in Fig. 2 with the $W_6O^i{}_{12}O^a{}_6$ units as heavily shaded polyhedra and the W_2O_9 units as lightly shaded face-sharing octahedra. Fig. 3 shows the metal–metal and metal–oxygen bonds in the $W_6O^i{}_{12}O^a{}_6$ unit {O^i refers to oxygen atoms above the edges of the octahedron [O(3) and O(4)] and O^a to apical oxygen atoms O(2)}. It should be noted that the centre of the octahedron is unoccupied. For a more detailed discussion of other structural features the papers of Goreaud *et al.*[11] should be consulted.

Selected bond distances are given in Table 2. The atomic parameters determined for the oxygen atoms have much lower uncertainties than those from the single-crystal X-ray study and are suitable for bond-valence calculations. Tungsten–oxygen bond orders (s) were calculated using $s = (R/R_1)^{-6}$ with R_1 = 1.904 (for a bond order of 1).[16] The W–O bond-order sum for W(1) is 3.63 and for W(2) is 5.99. These values would support the assignment of oxidation states 3.67 and 6 to W(1) and W(2) respectively, consistent with the chemical formula $Sn^{II}{}_{10}W_{16}O_{44}$. This would leave 2.33 electrons per

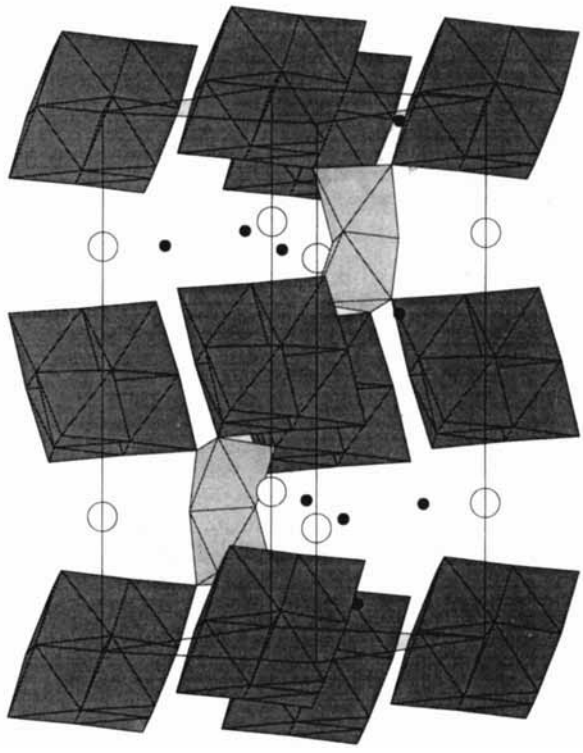

Fig. 2 Structure of $Sn_{10}W_{16}O_{44}$ ($W_6O^i{}_{12}O^a{}_6$ units, heavily shaded polyhedra; W_2O_9 units lightly shaded polyhedra; Sn, small dark circles; O large circles)

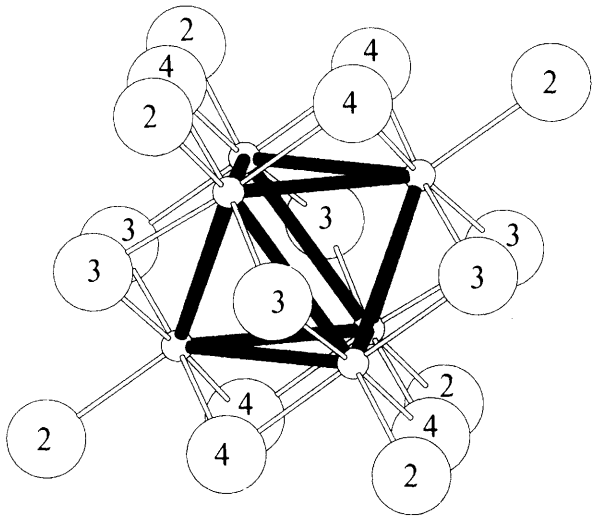

Fig. 3 The $W_6O^i{}_{12}O^a{}_6$ unit (W, small circles; O, large circles) showing the numbering scheme used in the tables

W(1) available for metal–metal bonding, giving a total electron count of 14 for the W_6 cluster which is in good agreement with the values known for Nb_6O_{12} clusters.[7–9] This can be contrasted with the Mo_6O_{12} cluster in $Ca_{16.5}Mo_{13.5}O_{40}$[3] which would appear to have an electron count close to 16.

Acknowledgements

We thank the University of Reading Endowment Fund for a studentship for S. A. M. and the EPSRC for the provision of neutron scattering facilities.

References

1 W. H. McCarrol, L. Katz and R. Ward, *J. Am. Chem. Soc.*, 1957, **79**, 5410.

2 C. C. Torardi and J. C. Calabrese, *Inorg. Chem.*, 1984, **23**, 3281.
3 B. Lindblom and R. Strandberg, *Acta Chem. Scand.*, 1989, **43**, 825.
4 S. J. Hibble, A. K. Cheetham, A. R. L. Bogle, H. R. Wakerley and D. E. Cox, *J. Am. Chem. Soc.*, 1988, **110**, 3295.
5 C. C. Torardi and R. E. McCarley, *J. Am. Chem. Soc.*, 1979, **101**, 3963.
6 A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 159.
7 J. Köhler, G. Svensson and A. Simon, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1437.
8 B. O. Marinder, *Chem. Scr.*, 1977, **11**, 97.
9 J. Köhler, A. Simon, S. J. Hibble and A. K. Cheetham, *J. Less-Common Met.*, 1988, **142**, 123.
10 G. Tourne and H. Czeskleba, *C. R. Hebd. Seances Acad. Sci., Ser. C*, 1970, **271**, 136.
11 M. Goreaud. Ph. Labbe and B. Raveau, *Acta Crystallogr., Sect. B*, 1980, **36**, 15, 19.
12 JCPDS Powder Diffraction File, JCPDS, International Center for Diffraction Data, Swathmore, PA, Card 32–1362.
13 W. I. F. David, M. W. Johnson, K. J. Knowles, C. M. Moreton-Smith, G. D. Crosbie, E. P. Campbell, S. P. Graham, and J. S. Lyall, GENIE, A Language for Spectral Manipulation and Display, Rutherford Appleton Laboratory, Chilton, Didcot, 1986.
14 W. I. F. David, REFINE, Rutherford Appleton Laboratory, Chilton, Didcot, 1986.
15 L. Koester and W. B. Yelon, *Summary of Low Energy Neutron Scattering Lengths and Cross Sections*, Netherland Research Foundation, Department of Physics, Petten, 1982.
16 I. D. Brown and K. K. Wu, *Acta Crystallogr., Sect. B*, 1976, **32**, 1957.

Received 8*th February* 1995; *Paper* 5/00754B