Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1257). Services for accessing these data are described at the back of the journal.

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Triclinic sodium tungsten oxide, Na5W14O44

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Abstract

The structure of the title compound, pentasodium tetradecatungsten tetratetracontaoxide, is built up of groups of four layers of WO_6 octahedra similar to those found in the hexagonal tungsten bronzes, but displaced relative to each other so that no tunnels of trigonal and hexagonal sections are formed. These groups are linked together through a layer of a different type consisting of isolated WO_5 trigonal bipyramids. The Na atoms are distributed in the hexagonal holes of the above layers, being coordinated in all cases by eight O atoms in a hexagonal bipyramidal arrangement.
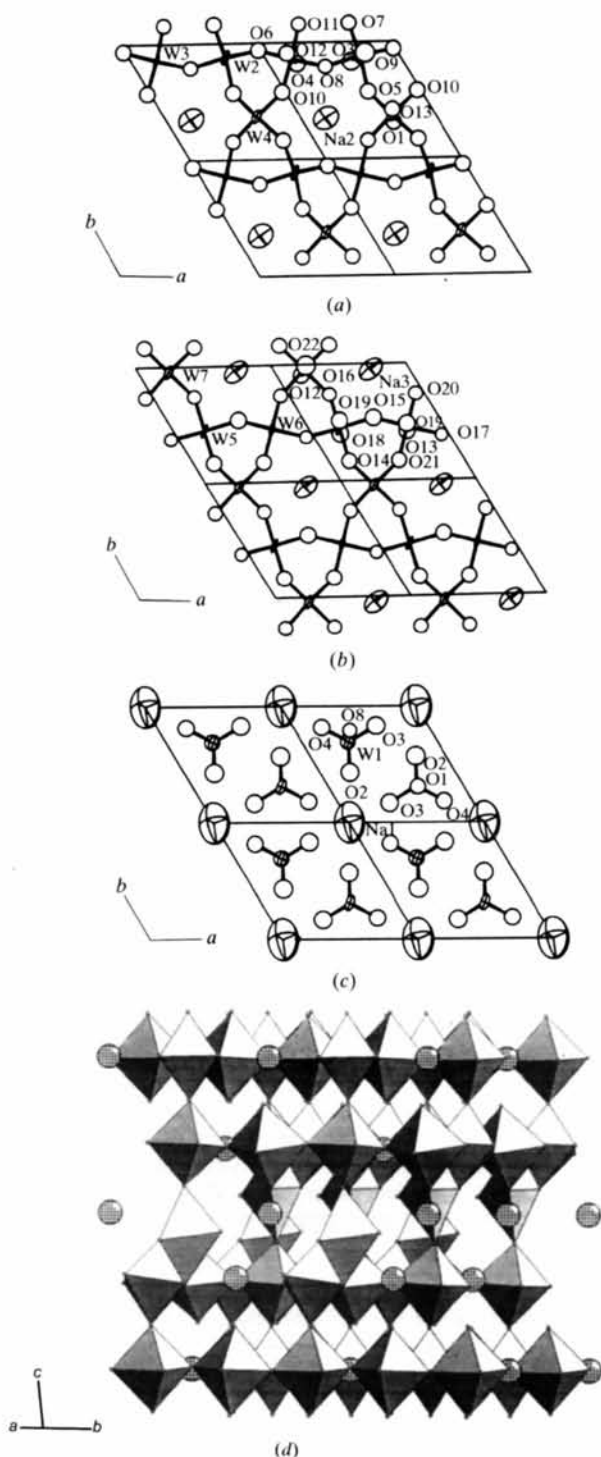
Comment

Franzen *et al.* (1972) reported the preparation, crystal structure and physical properties of a triclinic phase of sodium tungsten oxide with a stoichiometry corresponding to the formula $Na_6W_{14}O_{45}$. The synthesis was achieved by electrolyzing fused mixtures of Na_2WO_4 and WO_3 of compositions used to prepare the well known tetragonal sodium tungsten bronze and at temperatures just above the melting point of the solution. At higher temperatures, the tetragonal sodium tungsten bronze phase was obtained. The single-crystal X-ray diffraction study revealed the positions of the W atoms, while the positions of the Na and O atoms could not be located due to the poor quality of the crystals obtained. However, Franzen *et al.* (1972) were able to propose a model for the structure based solely on the derived positions of the W atoms. Since there appeared to be considerable difficulty in relating the measured electrical properties of the studied phase with its structure, it was considered worthwhile to carry out a new structure investigation. The phase is pseudo-monoclinic, with a C-lattice type and cell constants, calculated from the reduced ones (*LEPAGE*; Spek, 1988), of $a = 12.672(2)$, $b = 7.274(1)$, $c = 18.551(3)$ Å, $\alpha = 89.29(1)$, $\beta = 97.75(1)$ and $\gamma = 90.27(1)°$. These values are comparable with the corresponding values calculated from the data given by Franzen *et al.* (1972) of $a = 12.577$, $b = 7.287$, $c = 18.474$ Å, $\alpha = 89.40$, $\beta = 95.66$ and $\gamma = 89.40°$.

There are three Na, seven W and 22 O atoms in the asymmetric unit of the structure, all lying in general positions, except for Na1 which lies on a symmetry centre. The present study confirmed the existence in the structure of groups of four layers, which consist of WO_6 octahedra sharing their corners in the *ab* plane. These layers are of the type found in the hexagonal bronzes, *e.g.* in $Rb_{0.27}WO_3$ (Magnéli, 1953), but of different stacking mode. While in the hexagonal bronzes the layers are superimposed along **c**, leading to tunnels of trigonal and hexagonal sections, in the structure of $Na_5W_{14}O_{44}$, the layers are displaced relative to each other, so that some WO_6 octahedra of a certain layer project onto the hexagonal holes of a lower one, thus hindering the formation of tunnels. The first layer in such a group comprises the metal atoms Na2, W2, W3 and W4 ($z = 0.16$–0.19; Fig. 1*a*). Similarly, the second layer comprises the metal atoms Na3, W5, W6 and W7 ($z = 0.37$–0.40; Fig. 1*b*). The third and fourth layers are derived from the second and first ones, respectively, *via* inversion through a symmetry centre with $z = \frac{1}{2}$. All the WO_6 octahedra are considerably distorted, the observed W—O distance range being $1.68(2)$–$2.39(2)$ Å. Such a range is not unexpected, *e.g.* in $Na_2W_4O_{13}$, it is $1.71(2)$–$2.28(5)$ Å (Viswanathan, 1974). There is also a fifth layer in the structure, comprising the metal atoms Na1 and W1 ($z = 0$–0.03; Fig. 1*c*), of a completely

(a)

(b)

(c)

(d)

Fig. 1. (a) and (b) are the first two layers in a structural unit, consisting of a group of four WO_6 layers. The next two layers are related to the above through a symmetry centre. (c) shows the fifth layer, consisting of isolated WO_5 trigonal bipyramids. For clarity, the O atoms which project upon the W atoms have been omitted in all unit cells but the reference one. The atomic displacement ellipsoids are drawn at the 95% probability level. (d) shows a perspective view of a WO_5 layer bridging two groups of WO_6 layers. For clarity, only the two closest layers of each group have been shown.

different type with respect to those described above. In this layer, the W atoms are tetrahedrally coordinated by O atoms, with the W—O distances lying in the range 1.72 (2)–1.79 (2) Å. This distance range is typical for tetrahedrally coordinated W atoms, e.g. in $La_2W_3O_{12}$, it is 1.71 (2)–1.80 (2) Å (Gärtner et al., 1994). If the weak W1—O8 interaction of 2.84 (1) Å is also taken into account, the coordination polyhedron becomes a very distorted trigonal bipyramid. Franzen et al. (1972) also predicted the existence of a layer consisting of WO_5 trigonal bipyramids. The difference with respect to our results is that, while in their model the trigonal bipyramids appear in pairs, sharing an O atom lying on a symmetry centre, our study leads to isolated polyhedra with no O atom lying on a symmetry centre. This particular layer serves to join two adjacent groups of WO_6 layers (Fig. 1d). The Na atoms are distributed in the hexagonal holes formed within the WO_6 and WO_5 layers; in all cases, they are eightfold coordinated by O atoms in a hexagonal bipyramidal arrangement. The Na—O distances in the WO_6 layers are significantly shorter than in the WO_5 layer, in the first case lying in the range 2.26 (2)–2.76 (2) Å, with a mean value of 2.56 Å, and in the second case lying in the range 2.75 (2)–2.90 (2) Å, with a mean value of 2.80 Å. A point of special interest is that our study leads to a slightly different stoichiometry for the studied phase in comparison with that assumed by Franzen et al. (1972), lying, however, within the error limits given by those authors, i.e. $Na_5W_{14}O_{44}$ instead of $Na_6W_{14}O_{45}$. Assuming a valence of 6 for all the W atoms, which is supported by a bond-valence analysis, it appears that the proposed formula lacks electroneutrality, unless the sodium sites are partially occupied. This possibility was checked for two representative cases, both leading to the electroneutral formula $Na_4W_{14}O_{44}$, by assuming (i) equal occupation factors of 0.80 for all the sodium sites, and (ii) a smaller occupation factor of 0.50 for Na1, which possesses the larger displacement value and larger occupation factors of 0.75 for Na2 and Na3. Unfortunately, the experimental accuracy of this study did not permit a clear discrimination between the described models based solely on the refinement results. However, taking into account that the studied phase exhibits semiconducting properties (Franzen et al., 1972), the model of fully occupied Na sites seems more probable. The electroneutrality in the latter model can be accounted for by assuming an average valency for all the W atoms slightly less than 6 (i.e. 5.93), as in the case of tungsten bronzes of low sodium content.

Experimental

Samples of $Na_5W_{14}O_{44}$ were prepared by electrolyzing fused mixtures of Na_2WO_4 and WO_3 in a 1:1.667 molar ratio. The electrolysis was carried out at 1013 K using nichrome as cathode and graphite as anode. The current density was

about 10 mA cm^{-2}. The obtained phase was not pure, but co-existed with the orthorhombic $Na_2W_2O_7$ phase. After many attempts it has been possible to isolate from a sample a very small crystal fragment suitable for X-ray analysis.

Crystal data

$Na_5O_{44}W_{14}$	Mo $K\alpha$ radiation
$M_r = 3392.85$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 32
$P\bar{1}$	reflections
$a = 7.2740\,(11)$ Å	$\theta = 8.09-13.89°$
$b = 7.2911\,(11)$ Å	$\mu = 47.505$ mm^{-1}
$c = 18.551\,(3)$ Å	$T = 293\,(2)$ K
$\alpha = 96.375\,(9)°$	Crystal fragment
$\beta = 90.714\,(9)°$	$0.216 \times 0.062 \times 0.027$ mm
$\gamma = 119.656\,(8)°$	Dark blue
$V = 847.1\,(2)$ Å^3	
$Z = 1$	
$D_x = 6.651$ Mg m^{-3}	
D_m not measured	

Data collection

Upgraded Philips PW1100 diffractometer	2847 reflections with $I > 2\sigma(I)$
$\theta/2\theta$ scans	$R_{int} = 0.058$
Absorption correction:	$\theta_{max} = 27.5°$
ψ scan (EMPIR; Stoe & Cie, 1988a)	$h = -9 \rightarrow 9$
	$k = -9 \rightarrow 9$
$T_{min} = 0.043$, $T_{max} = 0.250$	$l = -24 \rightarrow 24$
9336 measured reflections	3 standard reflections
3900 independent reflections	frequency: 120 min
	intensity decay: 4%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 5.396$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.063$	$\Delta\rho_{min} = -6.298$ e Å^{-3}
$wR(F^2) = 0.159$	Extinction correction:
$S = 1.004$	SHELXL97
3900 reflections	Extinction coefficient:
177 parameters	0.0086 (4)
$w = 1/[\sigma^2(F_o^2) + (0.1111P)^2]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	International Tables for
$(\Delta/\sigma)_{max} < 0.001$	Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

W1—O2	1.718 (17)	W6—O17	1.920 (15)
W1—O1	1.756 (15)	W6—O13	2.298 (16)
W1—O4	1.790 (17)	W7—O22	1.685 (17)
W1—O3	1.793 (17)	W7—O14	1.872 (16)
W2—O9	1.698 (17)	W7—O20^i	1.900 (15)
W2—O7	1.888 (16)	W7—O16^i	1.924 (16)
W2—O6^i	1.903 (16)	W7—O21	1.971 (15)
W2—O5^i	1.977 (16)	W7—O12^i	2.307 (16)
W2—O8^{ii}	1.993 (15)	Na1—O2^{viii}	2.747 (17)
W2—O3^{ii}	2.207 (16)	Na1—O2	2.747 (17)
W3—O12	1.737 (16)	Na1—O3^{ii}	2.754 (16)
W3—O10	1.842 (15)	Na1—O3^{ix}	2.754 (16)
W3—O8	1.869 (16)	Na1—O4^i	2.811 (17)
W3—O6	1.952 (16)	Na1—O4^{iv}	2.811 (17)
W3—O11^{iii}	1.957 (15)	Na1—O6^i	2.897 (14)
W3—O4	2.194 (15)	Na1—O6^{iv}	2.897 (14)
W4—O13	1.742 (16)	Na2—O18	2.212 (19)
W4—O5	1.852 (17)	Na2—O2	2.254 (18)
W4—O11	1.872 (15)	Na2—O11^v	2.58 (2)
W4—O7	1.924 (17)	Na2—O6^i	2.595 (19)

W4—O10	1.971 (15)	Na2—O7	2.661 (19)
W4—O1^{iv}	2.169 (15)	Na2—O5^v	2.688 (19)
W5—O18	1.683 (16)	Na2—O10	2.75 (2)
W5—O17	1.890 (15)	Na2—O8	2.763 (19)
W5—O16	1.897 (15)	Na3—O22^x	2.17 (2)
W5—O15^v	1.926 (16)	Na3—O9	2.191 (19)
W5—O14	1.935 (16)	Na3—O21^{vii}	2.62 (2)
W5—O19^{vi}	2.391 (16)	Na3—O16^{ii}	2.627 (19)
W6—O19	1.714 (16)	Na3—O15^i	2.63 (2)
W6—O21^{vii}	1.869 (16)	Na3—O17	2.719 (19)
W6—O15	1.903 (17)	Na3—O20^i	2.73 (2)
W6—O20	1.911 (15)	Na3—O14	2.744 (19)

O2—W1—O1	110.0 (7)	O2—W1—O3	111.2 (8)
O2—W1—O4	108.5 (8)	O1—W1—O3	108.8 (7)
O1—W1—O4	108.8 (7)	O4—W1—O3	109.6 (8)

Symmetry codes: (i) $x, y - 1, z$; (ii) $x - 1, y - 1, z$; (iii) $1 + x, 1 + y, z$; (iv) $-x, 1 - y, -z$; (v) $1 + x, y, z$; (vi) $-x, 1 - y, 1 - z$; (vii) $x - 1, y, z$; (viii) $-x, -y, -z$; (ix) $1 - x, 1 - y, -z$; (x) $-x, -y, 1 - z$.

Because of the irregular shape of the selected crystal and the lack of better shaped crystals in the sample, an empirical absorption correction (ψ-scan method) was applied to the measured intensities, although an accurate absorption correction based on the crystal shape would be desirable in this case (heavily absorbing compound and very anisotropic crystal shape). The inadequacy of the absorption correction resulted in some problems in the least-squares refinement of the structure. Thus, the O atoms could not be refined anisotropically, since the displacement tensor of many of them turned out to be non-positive definite. Also, the large anisotropies on the displacement parameters of W3, W5 and W6 may be attributed, at least partly, to the bias introduced by the same effect, a conclusion which is corroborated by the orientation exhibited by the atomic displacement ellipsoids, all being nearly parallel to the same direction (see Fig. 1). Despite these difficulties, however, the refinement converged smoothly. The extreme $\Delta\rho_{max}$ and $\Delta\rho_{min}$ peaks in the final difference density map are observed very close to the W sites (0.62 and 1.15 Å from W5 and W3, respectively). The same is also true for the rest of the significant difference density peaks, so that the presence of additional O atoms in the structure should be precluded. The resulting stoichiometry of the compound from this refinement corresponds to the formula $Na_5W_{14}O_{44}$ (see above).

Data collection: DIF4 (Stoe & Cie, 1988b). Cell refinement: DIF4. Data reduction: REDU4 (Stoe & Cie, 1988c). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: DIAMOND (Bergerhoff, 1996). Software used to prepare material for publication: SHELXL97.

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γ-Mo₄O₁₁

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Abstract

The space group of the title compound, tetramolybdenum undecaoxide, has been confirmed to be $Pna2_1$. Three out of the four Mo atoms are each coordinated by six O atoms to form MoO_6 octahedra. The remaining Mo atom is coordinated by four O atoms to form an MoO_4 tetrahedron. In the crystal, all the octahedra share their corner O atoms to form stacked quasi-two-dimensional layers which are connected by the tetrahedra.

Comment

The transport, structure and charge-density-wave (CDW) properties of γ-phase molybdenum oxide, *i.e.* γ-Mo_4O_{11}, have been extensively studied (Schlenker, 1989; Kihlborg, 1959; Koyano *et al.*, 1988; Inoue *et al.*, 1988; Gao *et al.*, 1995, 1996). However, this structure has been assigned different space groups, *Pnma* and $Pna2_1$, based on consideration of the packing and powder diffraction data, respectively (Wyckoff, 1967; JCPDS, card 5–337; Ghedira *et al.*, 1985; Magresi, 1948). To resolve this space-group ambiguity, a single-crystal structure determination was carried out.

The space group of γ-Mo_4O_{11} has been confirmed to be $Pna2_1$. In the crystal, Mo atoms Mo1, Mo2 and Mo3 are each coordinated by six O atoms to form MoO_6 octahedra and the remaining Mo4 atoms are each coordinated by four O atoms to form MoO_4

tetrahedra. The coordination and the bond lengths are as shown in Fig. 1 and Table 1, respectively. The octahedra share their corners to form stacked quasi-two-dimensional layers which are interconnected by MoO_4 tetrahedra through mutual sharing of the O1, O4, O6 and O7 atoms. The minimum and maximum Mo—O bond lengths are 1.702 (4) (Mo4—O6) and 2.117 (4) Å (Mo3—O6), respectively, which are close to reported values (Orpen *et al.*, 1989). The axial O—Mo—O angles in the octahedra vary from 161.09 (13) to 176.4 (2)° for O11—Mo3—O4 and O3—Mo1—O5, respectively. Similarly, the bond angles in the tetrahedra range from 108.5 (2) (O6—Mo4—O1 and O1—Mo4—O7) to 113.1 (2)° (O4—Mo4—O7).
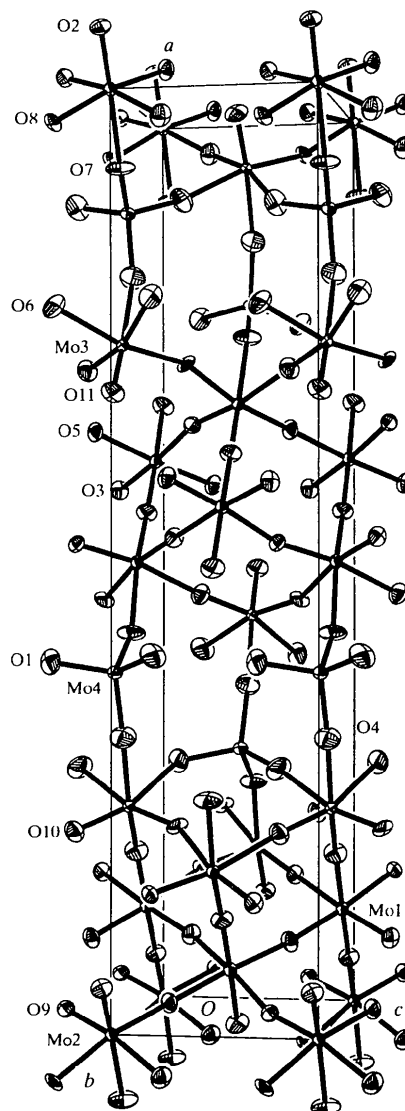

Fig. 1. The structure of the title compound showing 90% probability displacement ellipsoids. For clarity, some of the atoms are marked at symmetry-related positions. The origin of the coordinates is shifted to the Mo2 atom site.