Crystal Structure of Sodium Tetratungstate, $Na_2W_4O_{13}$

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The structure of $Na_2W_4O_{13}$ has been determined by Patterson and Fourier methods from 426 independent reflections measured photographically. The basic units, consisting of four edge-shared octahedra, are linked along two crystallographic directions by corner sharing to form octahedral layers, which are held together by sodium atoms. The W–O linkage is similar to that in $K_2Mo_4O_{13}$, but is new for tungstates. Crystals are triclinic, space group $P\bar{1}$, with $Z = 1$, in a unit cell of dimensions: $a = 11{\cdot}163(5)$, $b = 3{\cdot}894(1)$, $c = 8{\cdot}255(3)$ Å, $\alpha = 90{\cdot}60(2)$, $\beta = 131{\cdot}36(2)$, $\gamma = 79{\cdot}70(2)°$. The structure was refined by least squares to R 0·117.

CAILLET [1] and later Bouillaud [2] reported the preparation of $Na_2W_4O_{13}$ and presented powder data. Crystals for the present investigation were obtained by a similar procedure. They were tabular and showed an excellent cleavage parallel to (100) plane.

EXPERIMENTAL

Powder data (Table 1) were obtained by use of a Guinier-type focusing camera internally calibrated with silicon. The lines were indexed according to my own method [3] and lattice parameters refined by use of a program based on least squares. The discrepancies between the present data and those observed by the earlier workers may be attributed to the inability to resolve many reflections, if cameras other than Guinier-type are used.

Crystal Data.—$Na_2O_{13}W_4$, Triclinic, $M = 0{\cdot}000(0)$, $a = 11{\cdot}163(5)$, $b = 3{\cdot}894(1)$, $c = 8{\cdot}255(3)$ Å, $\alpha = 90{\cdot}60(2)$, $\beta = 131{\cdot}36(2)$, $\gamma = 79{\cdot}70(2)°$, $U = 262{\cdot}2(3)$ Å^3, $D_c = 6{\cdot}27$, $Z = 1$, $D_m = 6{\cdot}49$, $F(000) = 550$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 439·9 cm^{-1}.

The structure was derived from three-dimensional Weissenberg data by Mo-K_α radiation. The intensities of the 426 independent reflections used for determining the structure were measured photometrically. An approximate correction for absorption effects of the prismatic crystal was made with the values given in ref. 4. Intensities were then corrected for Lorentz and polarisation factors. A Patterson projection then revealed the positions of the tungsten atoms. From the positions of the Patterson peaks and their relative heights, it could be concluded that an inversion centre exists between the four tungsten atoms. A three-dimensional difference Fourier synthesis using the tungsten parameters yielded the parameters of the thirteen oxygen atoms. A subsequent difference-Fourier calculated with tungsten and oxygen atoms indicated the positions of sodium atoms. All parameters together with individual temperature factors were then refined by full-matrix least-squares (a modified version of the Busing-Levy ORFLS program) to a final R of 0·117. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21082 (5 pp., 1 microfiche).* Atom co-ordinates are listed in Table 2.

DISCUSSION

The structure consists of infinite chains of shared WO_6 octahedra (Figure 1) running parallel to the c axis, the repeating unit consisting of only four edge-shared octahedra. Thus the structure is similar to that of $K_2Mo_4O_{13}$,[5] but not identical because the latter contains eight edge-shared octahedra within the basic unit. Thus this type of linkage can be considered new, especially for the tungstates. The octahedra, marked A and B in Figure 1 are related to those marked A′ and B′, through a centre of inversion. All four tungsten atoms lie almost in the plane (120). Each basic unit of four octahedra is

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

[1] P. Caillet, *Compt. rend.*, 1963, **256**, 1986.

[2] Y. Bouillaud, *Bull. Soc. France Mineral. Crist.*, 1968, **91**, 292.

[3] K. Viswanathan, *Amer. Mineral.*, 1968, **53**, 2047.

[4] K. Sagel, 'Tabellen zur Röntgenstrukturanalyse,' ch. 8, Band VIII, Seite 85, Springer Verlag, Berlin, 1958.

[5] M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), 1971, 2107.

linked with identical units through common corners, parallel to b and c axes, thus giving rise to an octahedral layer parallel to the (100) plane. Such rigid octahedral layers are held together by the comparatively weak

TABLE 1

Powder pattern of $Na_2W_4O_{13}$ obtained on a Guinier focusing-type camera with Cu-$K_{\alpha 1}$ radiation

h	k	l	d_o	d_c	I_o
1	0	−1	8·203	8·205	18
0	0	1	6·129	6·130	30
2	0	−1	5·499	5·491	28
2	0	−2	4·108	4·103	40
2	0	0	4·073	4·080	70
1	0	−2	3·843	3·838	23
1	1	0	3·792	3·784	100
0	1	0	3·792	3·790	
3	0	−2	3·513	3·514	80
0	−1	−1	3·459	3·457	22
0	0	2	3·064	3·065	42
1	1	1	3·005	3·006	9
2	−1	−1	2·889	2·889	20
3	1	−2	2·762	2·769	35
3	0	−3	2·736	2·735	32
2	−1	−2	2·736	2·736	
3	0	0	2·716	2·719	25
2	0	−3	2·684	2·683	6
1	1	−2	2·601	2·601	22
0	−1	−2	2·573	2·574	5
4	0	−3	2·512	2·512	3
2	−1	0	2·503	2·505	11
3	1	0	2·495	2·497	18
2	1	1	2·439	2·442	13
1	0	−3	2·396	2·396	9
3	−1	−1	2·336	2·337	7
3	1	−3	2·258	2·256	3
2	−1	−3	2·232	2·233	14
4	1	−3	2·201	2·200	3
3	−1	−3	2·182	2·182	10
5	0	−3	2·164	2·164	24
5	0	−2	2·164	2·160	
0	0	3	2·042	2·043	22
3	−1	0	2·001	2·003	3
4	−1	−3	2·001	2·001	
3	1	1	1·979	1·981	5
1	2	0	1·948	1·947	22
1	1	−3	1·937	1·937	4
0	−2	−1	1·891	1·890	4
1	2	−1	1·861	1·861	5
2	1	2	1·861	1·861	
1	2	1	1·850	1·850	16
6	0	−3	1·831	1·830	23
3	1	−4	1·782	1·782	6
4	−1	−4	1·775	1·778	12
6	1	−3	1·775	1·777	
3	2	−2	1·766	1·766	6
2	−1	−4	1·766	1·766	
3	2	0	1·753	1·755	9
1	−2	−2	1·753	1·752	
6	0	−2	1·753	1·751	
2	2	−2	1·743	1·744	4
1	0	−4	1·731	1·731	2
2	2	1	1·731	1·729	
4	2	−2	1·706	1·708	16
2	−2	−1	1·699	1·701	17
0	−1	3	1·699	1·698	
1	1	3	1·684	1·685	9
6	1	−4	1·677	1·679	4
1	2	−2	1·649	1·650	15
1	−1	−4	1·649	1·649	

Na–O bonds, thus accounting for the excellent cleavage parallel to (100). The alkali-metal atom has only five oxygens as near neighbours (Na–O distances varying between 2·16 and 2·65 Å, Table 3), the co-ordinating polyhedron approaching the shape of a tetragonal pyramid.

TABLE 2

Co-ordinates of the atoms, with standard deviations in parentheses

Atom	x	y	z	β/Å²
W(1)	0·1938(5)	0·8382(2)	0·2132(5)	0·12(03)
W(2)	0·1744(5)	0·9774(3)	0·8054(3)	0·11(04)
O(1)	0·0	0·0	0·5	2·14(80)
O(2)	0·663(6)	0·160(7)	0·195(5)	1·77(52)
O(3)	0·684(7)	0·166(5)	0·892(7)	1·43(71)
O(4)	0·995(5)	0·005(4)	0·157(8)	1·10(74)
O(5)	0·346(3)	0·855(5)	0·485(3)	0·13(52)
O(6)	0·198(4)	0·389(7)	0·223(3)	0·43(65)
O(7)	0·148(7)	0·422(5)	0·827(6)	0·93(46)
Na	0·430(8)	0·285(4)	0·736(6)	0·82(55)

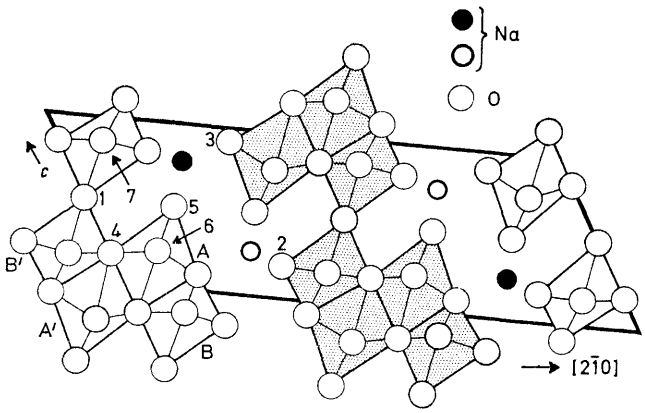

FIGURE 1 Projection of the structure on the (120) plane; projection axis approximately b. The plane, defined by b and $2\bar{1}0$, is exactly centred. Hence the relationship between the octahedral chains, shaded and unshaded, is given by the vector $\left[\frac{b}{2}+\frac{[2\bar{1}0]}{2}\right]$. Sodium atoms (solid circles) are at height 0·5, others are at 0. The basis oxygen atoms have been numbered (see Table 3)

TABLE 3

Distances (Å) in $Na_2W_4O_{13}$

(*a*) W(1) octahedron

W(1)–O(3′)	2·04	W(1)–O(5)	1·71
W(1)–O(4)	1·92	W(1)–O(6)	1·74
W(1)–O(4′)	2·28	W(1)–O(6^I)	2·16

O–O 2·54—3·07, mean 2·77

(*b*) W(2) octahedron

W(2)–O(1)	1·90	W(2)–O(9′)	2·10
W(2)–O(2′)	1·80	W(2)–O(7)	2·26
W(2)–O(3′)	1·88	W(2)–O(7^I)	1·73

O–O 2·57—2·98, mean 2·72

(*c*) Na polyhedron

Na–O(2′)	2·44	Na–O(5)	2·45
Na–O(2′^{I})	2·41	Na–O(5^I)	2·65
Na–O(3)	2·16		

(*d*) W distances

W(1)–W(2)	3·272	edge linked
W(1)–W(1)	3·274	edge linked
W(1)–W(1)	3·894	corner linked
W(1)–W(2)	3·944	corner linked

Primed and unprimed atoms are related by a centre of inversion; Roman numeral superscript I denotes atoms related by translation along b.

The tungsten octahedra are considerably distorted and the observed range in the W–O distances of 1·71—2·28 Å is typical of tungstates.

This structure bears no resemblance to the tunnel

structure of the analogous tungstate, $K_2W_4O_{13}$, which contains WO_6 octahedra linked by corners to form six-membered rings.[6] Considering that both are tetratungstates, this change of structure is radical, and must be attributed to the environment of the sodium. The bigger potassium ion requires a larger number of neighbours and the rigid single chain of $Na_2W_4O_{13}$ cannot be distorted to any extent. However, it should be theoretically possible for the band structure of $K_2Mo_4O_{13}$ to accommodate the bigger potassium ions and to produce an analogous $K_2W_4O_{13}$. Incidentally, the sodium atom in $Na_2W_4O_{13}$ has almost the same co-ordination as one of the sodium atoms in $Na_2W_2O_7$ or $Na_2Mo_2O_7$.[7,8]

A comparison of the structures of the bimolybdates of sodium and potassium [9] reveals that replacement of the alkali-metal atoms does cause a change in the nature of the bond between the molybdenum polyhedra, although the chain structure remains.

A comparison of the structure of $Na_2W_4O_{13}$ with that of $Li_2W_2O_7$ (ref. 10) is interesting, since both contain four edge-shared octahedra in the fundamental unit (Figure 2). In the former the three shared edges within the unit lie almost on a single plane (120) and the basic units are linked in two directions by sharing corners to form octahedral layers, giving rise to a tetratungstate polyanion, $(W_4O_{13})^{2-}$. On the other hand, the three shared edges do not lie on a plane in $Li_2W_2O_7$ and the basic units are linked by sharing edges to form octahedral double chains, giving rise to a polyanion, $(W_4O_{14})^{4-}$.

A study of the structures of the different tungstates suggests that the W–O co-ordination is determined by the tungsten : oxygen ratio; thus in bronzes, M_xWO_3, with a W : O ratio of 1 : 3, in the parent oxide, WO_3, and in the tetratungstate (4 : 13), the co-ordination is exclusively octahedral, whereas in the ditungstate, $Na_2W_2O_7$, both tetrahedral and octahedral co-ordinations are observed. At the extreme ratio of 1 : 4, as in Na_2WO_4, only tetrahedral co-ordination has been observed. The molybdates of potassium behave similarly.[5]

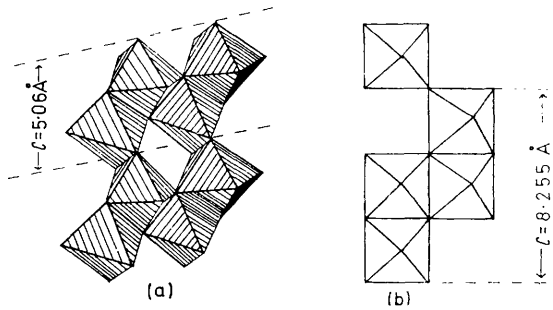

FIGURE 2 (*a*) Band of W octahedra with the composition (W_4O_{14}) in the structure of $Li_2W_2O_7$. (*b*) Idealised octahedral chain of composition (W_4O_{13}) in the $Na_2W_4O_{13}$ structure

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