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Disodium Ditungstate

BY K. OKADA, H. MORIKAWA, F. MARUMO AND S. IWAI

Research Laboratory for Engineering Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo, Japan

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Abstract. $Na_2W_2O_7$, orthorhombic, *Cmca*, $a=7{\cdot}216$ (1), $b=11{\cdot}899$ (1), $c=14{\cdot}716$ (3) Å, $Z=8$, $D_x=5{\cdot}53$. The crystals were prepared by heating an intimate mixture of $Na_2WO_4.2H_2O$ and H_2WO_4 at 800°C in a platinum crucible for several hours. Colourless transparent long prismatic crystals were obtained. W–O bonds in the octahedra are of three lengths: 1·725 (9), 1·921 (4) and 2·252 (9) Å. Those in the tetrahedra are of two lengths: 1·76 (1) and 1·807 (9) Å.

Introduction. The Weissenberg photographs showed orthorhombic symmetry. The systematic absences were *hkl* for $h+k$ odd, *h*0*l* for *l* odd and *hk*0 for *h* odd as reported by Lindqvist (1950). A prismatic crystal with dimensions about $0{\cdot}12\times0{\cdot}12\times0{\cdot}15$ mm was used for the intensity collection. Intensities were measured on a Philips automated four-circle diffractometer with Mo $K\alpha$ radiation, monochromated with graphite, up to $2\theta=100°$ by the ω–2θ scan technique. The scan speed was 2° min^{-1} in ω and scanning was repeated twice when the total counts were less than 10000. The scan width was determined according to the formula $1{\cdot}0°+0{\cdot}2°\tan\theta$. The intensities were corrected for Lorentz–polarization factors. Corrections for secondary extinction and absorption factors were carried out in the course of refinement, assuming a sphere of 0·07 mm radius for the crystal shape. In all, 2051 independent intensity data were obtained and used for the structure determination.

Starting with the atomic coordinates of $Na_2Mo_2O_7$ given by Seleborg (1967), the structure was refined by the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) with anisotropic temperature factors for W atoms and isotropic for the remainder. The final conventional *R* value is 0·054. The atomic scattering factors and dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1967). Unit weights were assigned for all the terms. The positional and the thermal parameters are listed in Table 1.*

Table 1. *Final positional and thermal parameters for* $Na_2W_2O_7$

	x	*y*	*z*	B_{iso}
W(1)	0·25	0·08606 (4)	0·25	0·72 (1)*
W(2)	0	0·24688 (5)	0·08537 (4)	0·80 (1)*
Na(1)	0·2507 (22)	0	0	1·64 (9)
Na(2)	0	0·3259 (8)	0·3443 (6)	1·76 (11)
O(1)	0·2042 (13)	0·2323 (7)	0·1554 (6)	1·33 (11)
O(2)	0·1991 (14)	0·4927 (7)	0·3361 (7)	1·34 (11)
O(3)	0	0·1256 (10)	0·2816 (8)	0·99 (13)
O(4)	0	0·3755 (11)	0·0289 (9)	1·31 (15)
O(5)	0	0·3590 (13)	0·5019 (9)	1·42 (18)

* Calculated from anisotropic thermal parameters according to the formula: $4(a^2B_{11}+b^2B_{22}+c^2B_{33})/3$.

Anisotropic thermal parameters ($\times10^5$) for the W atoms expressed in the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	287 (5)	147 (2)	86 (1)	0	−3 (3)	0
W(2)	357 (6)	151 (2)	94 (2)	0	0	18 (2)

Discussion. The crystals of $Na_2W_2O_7$ had been reported to be isostructural with those of $Na_2Mo_2O_7$ by Lindqvist (1950). The crystal structure of $Na_2Mo_2O_7$ was later refined by Lindqvist (1960) and Seleborg (1967); no crystallographic data on $Na_2W_2O_7$ have been reported to date. The coordinates of $Na_2W_2O_7$ obtained in the present refinement are quite similar to those of $Na_2Mo_2O_7$ reported by Seleborg (1967). The structure viewed along the *c* axis ($0\le c\le0{\cdot}5$) is shown in Fig. 1. The interatomic distances and bond angles of $Na_2W_2O_7$ are given in Table 2 with their estimated standard deviations in parentheses. The W(1) atom is octahedrally surrounded by six oxygen atoms, the coordination octahedron being largely distorted. The W(2) atom is

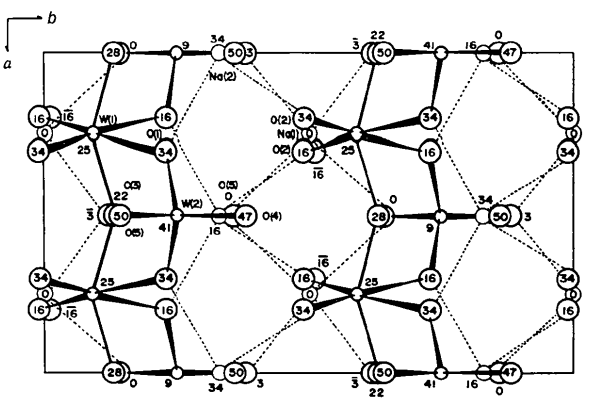

Fig. 1. The crystal structure of $Na_2W_2O_7$ viewed along the *c* axis ($0\leqq c\leqq0{\cdot}5$). Heights of atoms from the *ab* plane are indicated as percentages of the *c* length.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30793 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances and bond angles with their estimated standard deviations in parentheses*

Symmetry code

0	x, y, z	viii	$\frac{1}{2}+x, \frac{1}{2}+y, z$
i	$x, \bar{y}, \bar{z}$	ix	$\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$
ii	$x, \frac{1}{2}-y, \frac{1}{2}+z$	x	$\frac{1}{2}+x, \bar{y}, \frac{1}{2}+z$
iii	$x, \frac{1}{2}+y, \frac{1}{2}-z$	xi	$\frac{1}{2}+x, y, \frac{1}{2}-z$
iv	$\bar{x}, \bar{y}, \bar{z}$	xii	$\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$
v	$\bar{x}, y, z$	xiii	$\frac{1}{2}-x, \frac{1}{2}+y, z$
vi	$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$	xiv	$\frac{1}{2}-x, y, \frac{1}{2}-z$
vii	$\bar{x}, \frac{1}{2}-y, \frac{1}{2}+z$	xv	$\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$

W(1)–O($1^{0,xiv}$) (2×)	2·252 (9) Å	O(1^{0})–W(1)–O(1^{xiv})	78·9 (3)°
W(1)–O($2^{iii,xiii}$) (2×)	1·725 (9)	O(1^{0})–W(1)–O(2^{iii})	90·7 (4)
W(1)–O($3^{0,xiv}$) (2×)	1·921 (4)	O(1^{0})–W(1)–O(2^{xiii})	169·4 (4)
W(2)–O($1^{0,v}$) (2×)	1·807 (9)	O(1^{0})–W(1)–O(3^{0})	78·4 (4)
W(2)–O(4^{0})	1·759 (14)	O(1^{0})–W(1)–O(3^{xiv})	79·8 (4)
W(2)–O(5^{ii})	1·762 (13)	O(2^{0})–W(1)–O(2^{iii})	99·8 (4)
Na(1)–O($2^{ii,iii}$) (2×)	2·44 (1)	O(2^{0})–W(1)–O(3^{0})	100·4 (5)
Na(1)–O($4^{xiii,ix}$) (2×)	2·37 (2)	O(2^{0})–W(1)–O(3^{xiv})	97·8 (5)
Na(1)–O($5^{ii,iii}$) (2×)	2·47 (2)	O(3^{0})–W(1)–O(3^{xiv})	151·7 (5)
Na(2)–O($1^{xi,xiv}$) (2×)	2·41 (1)	O(1^{0})–W(2)–O(1^{v})	109·3 (3)
Na(2)–O($2^{0,v}$) (2×)	2·45 (1)	O(1^{0})–W(2)–O(4^{0})	110·9 (4)
Na(2)–O(3^{0})	2·56 (1)	O(1^{0})–W(2)–O(5^{ii})	109·1 (3)
Na(2)–O(5^{0})	2·35 (2)	O(4^{0})–W(2)–O(5^{ii})	107·6 (6)

tetrahedrally surrounded by four oxygen atoms. The distortion of the tetrahedron is rather small. The WO_6 octahedron is linked sharing corners to two neighbouring WO_6 octahedra and two WO_4 tetrahedra, forming infinite $[W_2O_7]^{2-}$ ion chains parallel to the *a* axis. Of the W(1)–O distances within each octahedron two are long [W(1)–O(1)], two are medium [W(1)–O(3)] and two are short [W(1)–O(2)]; of the W(2)–O distances within a tetrahedron two are long [W(2)–O(1)] and two are short [W(2)–O(4), W(2)–O(5)]. Assuming that the bond strength is expressed in the form $s=s_0(R/\bar{R})^{-N}$ given by Brown & Shannon (1973), the sums of bond strengths at individual oxygen atoms were calculated in order to examine the valence balance around each oxygen atom: O(1) 2·15, O(2) 2·08, O(3) 2·31, O(4) 2·00, O(5) 2·10. (In the above expression, $s=$ strength of a bond with length R, $s_0=$ ideal strength of the bond with length $\bar{R}$, and $N=$a constant to be determined for each cation–anion pair.) The values of s_0, $\bar{R}$ and N tabulated by Brown & Shannon (1973) were used for Na^+–O^{2-} bonds and those for W^{6+}–O^{2-} bonds were deduced from the mean W–O bond lengths for the W^{6+} cations with tetrahedral and octahedral coordinations. Within the accuracy of the approximations made O(1), O(2), O(4) and O(5) can be considered balanced, but O(3) seem to be a little unbalanced. The Na(1) atom is octahedrally surrounded by six oxygen atoms, whereas the Na(2) atom is not octahedrally but pentagonal-pyramidally surrounded by six oxygen atoms. The Na(1) octahedron shares corners with the two $W(1)O_6$ octahedra, two $W(2)O_4$ tetrahedra and two $Na(2)O_6$ coordination polyhedra, and shares edges with the neighbouring $Na(1)O_6$ octahedra. The Na(2) coordination polyhedron shares corners with the four $W(1)O_6$ octahedra, two $W(2)O_4$ tetrahedra and two $Na(1)O_6$ octahedra. Thus, Na^+ ions link the $(W_2O_7)^{2-}$ ion chains laterally.

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References

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

International Tables for X-ray Crystallography (1967). Vol. III, pp. 201–216. Birmingham: Kynoch Press.

LINDQVIST, I. (1950). *Acta Chem. Scand.* **4**, 1066–1074.

LINDQVIST, I. (1960). *Acta Chem. Scand.* **14**, 960.

SELEBORG, M. (1967). *Acta Chem. Scand.* **21**, 499–504.