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$Na_2W_2O_7$ (II), A High-Pressure Phase of Disodium Ditungstate(VI)

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(*Received* 30 *March* 1989; *accepted* 18 *May* 1989)

Abstract. $Na_2W_2O_7$ (II), $M_r = 525{\cdot}68$, orthorhombic, $Cmc2_1$, $a = 3{\cdot}7777\,(7)$, $b = 26{\cdot}6067\,(38)$, $c = 5{\cdot}4290\,(7)$ Å, $V = 545{\cdot}68$ Å^3, $Z = 4$, $D_x = 6{\cdot}40$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 44{\cdot}654$ mm^{-1}, $F(000) = 855{\cdot}93$. The structure was refined to $R = 0{\cdot}038$, $wR = 0{\cdot}025$ for 1338 absorption-corrected observed reflections. $Na_2W_2O_7$ (II) has been synthesized from the normal-pressure phase at a hydrostatic pressure of 3·2 GPa and $T = 1475$ K. The structure comprises distorted perovskite-type slabs which are composed of WO_6 octahedra [W(1)—O 1·73–2·13, W(2)—O 1·72–2·29 Å] and Na atoms [Na(1)—O 2·46–2·95 Å]. Na(2) is situated between the slabs and has a sevenfold coordination by oxygen [Na(2)—O 2·39–2·89 Å].

Experimental. Experiments were carried out in a modified Belt-type high-pressure apparatus (Range & Leeb, 1975) using gold as the crucible material and starting with the normal-pressure modification $Na_2W_2O_7$ (I) (Okada, Morikawa, Marumo & Iwai, 1975). After quenching from 3·2 GPa and 1475 K a new phase was obtained and proved to be homogenous by Guinier photographs. Heating of this phase at ambient pressure and 1050 K results in complete retransformation to $Na_2W_2O_7$ (I). Therefore, the new phase [NaW_2O_7 (II)] is a high-pressure phase, metastable at normal conditions.

Single crystals, suitable for a crystal structure determination, could be isolated after very slow cooling from 1475 K at 3·2 GPa. A light-bluish crystal fragment (approx. 30 × 30 × 90 μm) was used for data collection on an Enraf–Nonius CAD-4 diffractometer (Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, graphite monochromator, $T = 296$ K). Lattice parameters were refined from 2θ values of 25 reflections in the range 4·8–16·4°. Intensities measured for $2 \le \theta \le 35°$; ω–2θ-scan technique [scan width $(1{\cdot}00 + 0{\cdot}34\tan\theta)°$]. Three standard reflections indicated no loss of intensity during data collection. Merging of the 4661 collected intensities ($\sin\theta_{\max}/\lambda = 0{\cdot}807$ Å^{-1}; $-6 \le h \le +6$, $-21 \le k \le +18$, $-8 \le l \le +8$) gave 1338 unique reflections ($R_{\rm int} = 0{\cdot}030$) with $F > 1\sigma(F)$, which were considered as observed and used for all calculations (program system *SHELX76*; Sheldrick, 1976).

From the systematic absences for hkl ($h + k$ odd) and $h0l$ (l odd) the diffraction symbol C^*c^* was derived, giving the possible space groups $C2cm$, $Cmc2_1$ and $Cmcm$. Statistics of the normalized E values suggested a non-centrosymmetric space group. This was confirmed by the results of the structure refinement which showed space group $Cmc2_1$ to be the correct one.

The W atom positions were derived from a Patterson map, the remaining atoms were found in successive difference Fourier maps. In least-squares refinement $|F|$ magnitudes were used to refine atomic coordinates and isotropic temperature factors. Convergence was obtained after a few cycles at $R = 0{\cdot}041$. At this stage a numerical correction for absorption (program *DIFABS*; Walker & Stuart, 1983) (max. and min. values 0·94 and 1·14) was

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0108-2701/90/020317-02$03.00

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Table 1. *Atomic coordinates and isotropic temperature factors* ($Å^2 \times 8\bar{u}^2$)

The equivalent isotropic B values for atoms refined anisotropically (designated by an asterisk) are defined as one-third of the trace of the orthogonalized B_{ij} tensor.

	x	y	z	B_{eq}/B_{iso}
W(1)	0	0·44470 (2)	0·10218†	0·32 (1)*
W(2)	0	0·34024 (2)	0·5745 (1)	0·43 (2)*
Na(1)	½	0·5508 (2)	0·1047 (16)	1·3(2)*
Na(2)	½	0·2874 (3)	0·0523 (17)	2·5 (3)*
O(1)	0	0·3936 (5)	0·9047 (22)	2·9 (6)*
O(2)	0	0·5076 (5)	0·3457 (25)	1·9 (5)*
O)3)	0	0·4084 (5)	0·3942 (22)	1·2 (2)
O(4)	½	0·3517 (4)	0·6240 (21)	1·9 (2)
O(5)	0	0·2910 (5)	0·7847 (22)	1·4 (2)
O(6)	½	0·4525 (5)	0·1483 (17)	1·7 (2)
O(7)	0	0·3059 (6)	0·3062 (25)	2·3 (3)

† Fixed.

Table 2. *Interatomic distances* (Å)

W(1)—O(1)	1·73 (1)	W(2)—O(7)	1·72 (1)
—O(3)	1·86 (1)	—O(5)	1·74 (1)
—O(2)	1·88 (1)	—O(4)	1·932 (2) (×2)
—O(6)	1·916 (2) (×2)	—O(3)	2·06 (1)
—O(2)	2·13 (1)	—O(1)	2·29 (1)
Na(1)—O(3)	2·460 (9) (×2)	Na(2)—O(5)	2·385 (9) (×2)
—O(6)	2·48 (1)	—O(7)	2·39 (1) (×2)
—O(2)	2·57 (1) (×2)	—O(5)	2·44 (1)
—O(4)	2·60 (1)	—O(7)	2·82 (2)
—O(6)	2·63 (1)	—O(4)	2·89 (1)
—O(2)	2·82 (1) (×2)		
—O(1)	2·90 (1) (×2)		
—O(6)	2·95 (1)		

applied before performing the final refinement [anisotropic for W, Na, O(1) and O(2), isotropic for O(3)–O(7)].

Final $R = 0{\cdot}038$, $wR = 0{\cdot}025$. $w = 1{\cdot}51/\sigma^2(F)$. $(\Delta/\sigma)_{max} < 0{\cdot}002$ in final refinement cycle, 51 parameters. Max. features in the final $\Delta\rho$ map ($+7{\cdot}5$, $-5{\cdot}4$ e $Å^{-3}$) near the heavy atoms, obviously resulting from insufficient absorption correction. Atomic scattering factors and f', f'' values were taken from *International Tables for X-ray Crystallography* (1974). Bond distances and angles were calculated using the program *SADIAN* (Baur & Wenninger, 1969). Final atomic coordinates and equivalent or isotropic temperature factors are given in Table 1, derived interatomic distances in Table 2.*

The structure (Fig. 1) comprises perovskite-type slabs which are composed of tilted and rather distorted WO_6 octahedra and Na atoms. The W(1)—O and W(2)—O distances range from 1·73 to 2·13 and 1·72 to 2·29 Å, respectively. Na(1) is surrounded by 12 O atoms with distances ranging from 2·46 to 2·95 Å. Na(2) is situated between the slabs and has a sevenfold coordination by oxygen (Table 2).

Related literature. The structure of the normal-pressure phase $Na_2W_2O_7$ (I) has been determined by Okada *et al.* (1975). At the $Na_2W_2O_7$ (I)→(II) transition the coordination number of the W atoms increases from [4] and [6] to [6] and [6], in accordance with the pressure-coordination rule. In the homologous compounds $K_2W_2O_7$ and $Rb_2W_2O_7$ (Hegenbart & Range, 1982) the W atoms are octahedrally coordinated as in $Na_2W_2O_7$ (II). The connection pattern of the WO_6 octahedra, however, is quite different. $Na_2W_2O_7$ (II) is isostructural with $Sr_2Nb_2O_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1975) and closely related to the centrosymmetric (*Cmcm*) compound $Sr_2Ta_2O_7$ (Ishizawa, Marumo, Kawamura & Kimura, 1976).

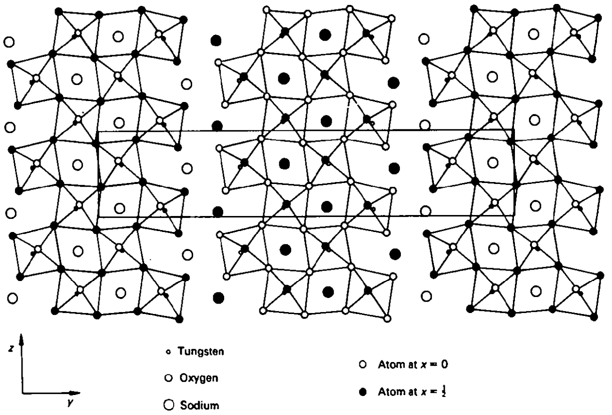

Fig. 1. The crystal structure of $Na_2W_2O_7$ (II) viewed along [100].

We thank Dr U. Klement for the collection of diffraction data and Dr M. Zabel for many helpful discussions. The generous support given by the Fonds der Chemischen Industrie is gratefully acknowledged.

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* Lists of structure factors, anisotropic thermal parameters, and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52247 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.