

# The Structure of $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ Synthesized under High Pressure and Temperature

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A new compound,  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ , has been found in the  $\text{Na}_2\text{O}-\text{WO}_3-\text{H}_2\text{O}$  system. It is the fourth compound in the  $\text{Na}_2\text{W}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  system and the second phase containing water. The crystals were prepared at a pressure of 1.5 GPa and a temperature of 900°C.  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  crystallizes in the triclinic space group,  $P\bar{1}$ ,  $Z=2$ , with lattice constants of  $a=8.4902(6)$  Å,  $b=7.6636(6)$  Å,  $c=5.1501(3)$  Å,  $\alpha=91.959(7)^\circ$ ,  $\beta=96.521(8)^\circ$  and  $\gamma=111.678(7)^\circ$ . The structure is built up from double chains of  $\text{WO}_6$  octahedra running along  $c$ , interconnected by two-dimensional nets of  $\text{NaO}_6$  polyhedra. Sodium coordinates to six oxygens forming both octahedra and trigonal prisms.

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**Key Words:** isopolytungstate;  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ ; high-pressure synthesis; single-crystal X-ray diffraction.

## INTRODUCTION

Tungstates have been used as radiation detectors for more than 100 years (1). The luminescent properties combined with high density and strong absorption make many tungstate compounds candidates to use in high-energy electromagnetic calorimetry (2, 3). One advantage with tungstate materials is that the electron transfer takes place within the tungstate group. The tungstate groups considered are  $\text{WO}_4^{2-}$  or  $\text{WO}_6^{6-}$  in which the W atom formally has an empty  $d$  shell. In the excited state the charge transfer is from the oxygen atoms to the central W atom.

One group of tungstates that has been much investigated due to their structural and electronic diversity is the isopolyoxotungstates (4), usually produced by acidification of aqueous solutions of monotungstates. While working with crystal growth of tungstates under high pressure and

temperature, a new phase was found in the  $\text{Na}_2\text{O}-\text{WO}_3-\text{H}_2\text{O}$  system. In this system 19 different solid phases have been reported so far, for a list of these with some crystallographic data see Table 1.

Simons (5) reported four phases in the system, the three disodium ditungstates,  $\text{Na}_2\text{W}_2\text{O}_7$ ,  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$  and  $\text{Na}_2\text{W}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ , and the paratungstate,  $\text{Na}_{10}(\text{H}_2\text{W}_{12}\text{O}_{42}) \cdot 28\text{H}_2\text{O}$ , all synthesized under normal pressure. The crystal structure of  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$  was published by Brüdgam *et al.* in 1998 (6). They also reported the presence of a tetrahydrate, referring only to IR and Raman spectra, i.e., no reliable confirmation of the composition.

The anhydrous compounds on the sodium-rich side of the system  $\text{Na}_2\text{O}-\text{WO}_3$  are  $\text{Na}_6\text{WO}_6$  (7) and  $\text{Na}_4\text{WO}_5$  (7, 8), of which only  $\text{Na}_4\text{WO}_5$  has been structurally characterized. The structure of anhydrous  $\text{Na}_2\text{W}_2\text{O}_7$  was determined by Okada *et al.* in 1975 (9). In 1990, Range and Haase (10) reported a new high-pressure phase of  $\text{Na}_2\text{W}_2\text{O}_7$ , resulting from the normal-pressure modification when pressure and temperature were increased to 3.2 GPa and 1475 K, respectively. The other tungsten-rich compounds are  $\text{Na}_2\text{W}_4\text{O}_{13}$  (11) and  $\text{Na}_2\text{W}_6\text{O}_{19}$  (12), of which only the first has been structurally characterized.

A special compound is  $\text{Na}_{0.17}\text{WO}_{3.085} \cdot 0.23\text{H}_2\text{O}$  (13) that has a typical hexagonal tungsten bronze structure (14). The W atom is, however, fully oxidized with a formal oxidation number of +6.

Of all the 'true isopolyoxotungstates' (4), with a discrete isopolyoxotungstate ion, found in the literature, only three different sodium salts have been structurally characterized. Those are  $\text{Na}_5[\text{H}_3\text{W}_6\text{O}_{22}] \cdot 18\text{H}_2\text{O}$  (15),  $\text{Na}_6\text{W}_7\text{O}_{24} \cdot 14\text{H}_2\text{O}$  (16) and  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot x\text{H}_2\text{O}$ ,  $x=20, 26, 27$  and  $28$  (17–19). The structure of  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$  was first published in 1976 by Evans (17), in space group  $P\bar{1}$ , and later redetermined in space group  $P2_1/n$  by Chrissafidou (19).  $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 27\text{H}_2\text{O}$  was the first isopolyoxotungstate to be structurally characterized, by Lindqvist (20) in the non-conventional space group  $C\bar{1}$ . That structure

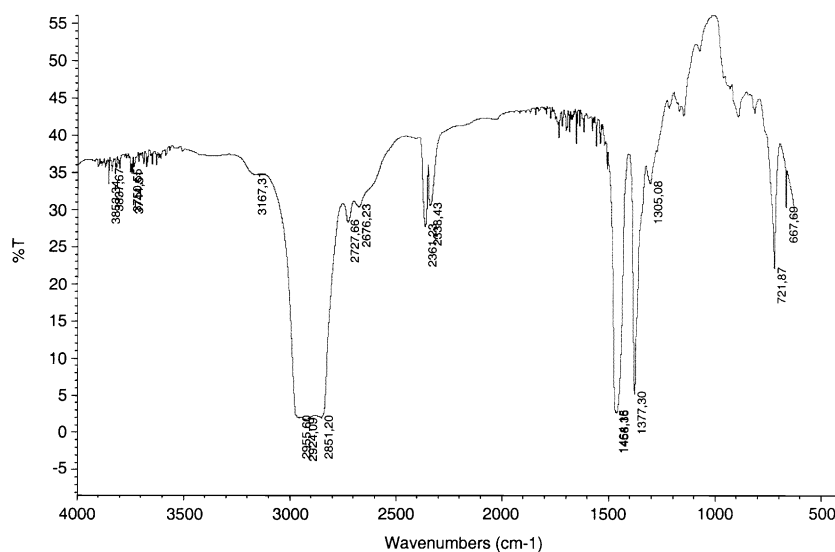
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**TABLE 1**  
**Compounds with General Formula  $(\text{Na}_2\text{O})_x(\text{WO}_3)_y(\text{H}_2\text{O})_z$**

| Compound  | <i>x</i>                 | <i>y</i> | Analysis  | Space group   | Volume | Reference |
|---|--------------------------|----------|-----------|---------------|--------|-----------|
| <i>Anhydrous</i>  |                          |          |           |               |        |           |
| $\text{Na}_6\text{WO}_6$  | 3                        | 1        | XDP       | Orthorhombic  | 1305   | (7)       |
| $\text{Na}_4\text{WO}_5$  | 2                        | 1        | XDS       | $P\bar{1}$    | 241.3  | (8)       |
| $\text{Na}_2\text{WO}_4$  | 1                        | 1        | XDS       | $Fd\bar{3}m$  | 761.8  | (42)      |
| $\text{Na}_2\text{W}_2\text{O}_7$   | 1                        | 2        | XDS       | <i>Cmca</i>   | 1263.6 | (9)       |
| $\text{Na}_2\text{W}_2\text{O}_7(\text{II})$                                      | 1                        | 2        | XDS       | <i>Cmc2_1</i> | 545.7  | (10)      |
| $\text{Na}_2\text{W}_4\text{O}_{13}$  | 1                        | 4        | XDS       | $P\bar{1}$    | 262.2  | (11)      |
| $\text{Na}_2\text{W}_6\text{O}_{19}$  | 1                        | 6        | XDP       |               |        | (12)      |
| $\text{Na}_{0.17}\text{WO}_{3.085} \cdot 0.23\text{H}_2\text{O}$                  | 0.085<br><i>z</i> = 0.23 | 1        | NDP       | <i>P6/mmm</i> | 181.1  | (13)      |
| $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$                                | 1                        | 1        | XDS       | <i>Pbca</i>   | 1245.7 | (43)      |
| $\text{Na}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$                        | 1                        | 2        | XDS       | $P\bar{1}$    | 337.25 | (6)       |
| $\text{Na}_2\text{W}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$                       | 1                        | 2        | IR, Raman |               |        | (6)       |
| $\text{Na}_2\text{W}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$                       | 1                        | 2        | XDP, TG   |               |        | (5)       |
| $\text{Na}_3[\text{H}_3\text{W}_6\text{O}_{22}] \cdot 18\text{H}_2\text{O}$       | 2.5<br><i>z</i> = 19.5   | 6        | XDS       | $P\bar{1}$    | 1791.7 | (15)      |
| $\text{Na}_6\text{W}_7\text{O}_{24} \cdot 14\text{H}_2\text{O}$                   | 3                        | 7        | XDS       | <i>Pc2_1b</i> | 3660.4 | (16)      |
| $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 21\text{H}_2\text{O}$    | 3<br><i>z</i> = 22       | 12       | IR, TG    |               |        | (21)      |
| $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$ | 5<br><i>z</i> = 0.21     | 12       | XDS       | <i>P2_1/n</i> | 2721.1 | (19)      |
| $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 26\text{H}_2\text{O}$ | 5<br><i>z</i> = 0.27     | 12       | XDS       | $P\bar{1}$    | 1490.2 | (18)      |
| $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 27\text{H}_2\text{O}$ | 5<br><i>z</i> = 0.28     | 12       | XDS       | $P\bar{1}$    | 2915.3 | (19)      |
| $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 28\text{H}_2\text{O}$ | 5<br><i>z</i> = 0.29     | 12       | XDS       | <i>C2/c</i>   | 6079.5 | (19)      |

was later redetermined by Chrissafidou (19), but now in the conventional space group  $P\bar{1}$ . The metatungstate,  $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 21\text{H}_2\text{O}$  (21), is known from spectroscopic

measurements. The  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  ion is thought to be isostructural with the Keggin complex  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  (22) with the two hydrogens replacing the phosphorous atom.



**FIG. 1.** IR spectrum of  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  dispersed in nujol. The peak at  $3167\text{ cm}^{-1}$  indicates water in the structure.

## EXPERIMENTAL SECTION

TABLE 2  
Crystallographic Data for  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ *Synthesis*

Crystals of  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  were obtained in an experiment where the objective was to grow Hg-doped  $\text{CdWO}_4$  by spontaneous crystallization in a sealed gold tube, under high pressure and temperature.  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (Johnson Matthey, xtl., 95%),  $\text{HgCl}_2$  (Merck, min. 99.5%) and  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  (Riedel-de-Haën, min. 99%) with a molar ratio of 2:1:1 were ground in an agate mortar. The resultant mixture was put in a gold tube and sealed by welding. The gold tube was then placed in a cylindrical alumina crucible (1.5 cm  $\times$  15 cm), which was inserted in a three-zone Kanthal furnace. The furnace is part of a high-pressure system also consisting of a 1.5 GPa gas compressor (Unipress GCA 30T) and a water-cooled pressure chamber (23). The crystal growth experiment took place at 900°C under 1.0 GPa argon pressure during 10 h. The temperature was then decreased to room temperature within a few hours, before the pressure was released.

When the gold tube was opened, white elongated prismatic crystals with lengths up to 1 mm were found. These crystals were analyzed by energy-dispersive environmental scanning electron microscopy (ESEM<sup>®</sup>-EDX) which verified the compositions Na:W:O = 2:2:~7. The presence of water in the  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  crystals was confirmed by infrared spectroscopy (IR), see Fig. 1. The mercury had partly amalgamated with the gold tube but was also found in elemental form and as red HgO. Cadmium had formed crystals of  $\text{CdWO}_4$  which were not easily distinguished from  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ . It is likely that some NaCl was present but dissolved when the crystals were washed with water. No other sodium- or tungsten-containing phases were found.

*Crystallography*

The structure of  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  was determined by single-crystal X-ray diffraction. Pertinent crystallographic data are reported in Table 2. Intensity data was measured at room temperature on a  $\kappa$  geometry Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Unit-cell parameters were refined using LATCON (24). Data reduction including absorption correction was made within the WinGX program suite (25). The tungsten atoms were located from Patterson maps while the rest of the atoms were found from successive electron density difference maps. The hydrogen atoms in the water molecule could not be found. All non-hydrogen atoms were refined with anisotropic displacement parameters, using SHELXL-97 (26). The fairly high residual electron density is located about 0.8 Å from the W atoms. The

|  |  |
|--|--|
| Formula weight                                   | 534.69   |
| Crystal system                                   | Triclinic  |
| Space group                                      | $P\bar{1}$ (No. 2)   |
| <i>a</i> (Å)                                     | 8.4902(6)  |
| <i>b</i> (Å)                                     | 7.6636(6)  |
| <i>c</i> (Å)                                     | 5.1501(3)  |
| $\alpha$ (°)                                     | 91.959(7)  |
| $\beta$ (°)                                      | 96.521(8)  |
| $\gamma$ (°)                                     | 111.678(7)   |
| Volume (Å <sup>3</sup> )                         | 308.33(4)  |
| <i>Z</i>   | 2  |
| Density (calc.) (g cm <sup>-3</sup> )            | 5.759  |
| Radiation  | MoK $\alpha$ , $\lambda = 0.71073$ Å                               |
| Cell parameters refined from                     | 20 reflections, $22.2^\circ \leq \theta \leq 29.8^\circ$           |
| $\mu$ (mm <sup>-1</sup> )                        | 37.41  |
| Absorption correction                            | Gaussian   |
| <i>T</i> <sub>min</sub>                          | 0.1538   |
| <i>T</i> <sub>max</sub>                          | 0.5216   |
| Crystal form                                     | Prismatic  |
| Crystal color                                    | Colorless  |
| Crystal size (mm)                                | 0.08 $\times$ 0.03 $\times$ 0.02                                   |
| Type of data collection                          | $\omega$ - $2\theta$ scans   |
| $2\theta$ range(°)                               | 6.12–59.70   |
| Index ranges                                     | $-11 \leq h \leq 11, -10 \leq k \leq 10, -7 \leq l \leq 7$         |
| No. of reflections measured                      | 3550   |
| No. of independent reflections                   | 1776   |
| No. of observed reflections                      | 1456   |
| Criterion for observed reflections               | $I > 2\sigma(I)$   |
| <i>R</i> <sub>int</sub>                          | 0.020  |
| No. of standard reflections                      | 3  |
| Frequency of standard reflections (min)          | 120  |
| Intensity decay                                  | None   |
| Refinement on                                    | <i>F</i> <sup>2</sup>  |
| <i>R</i> ( <i>F</i> )                            | 0.044  |
| w <i>R</i> ( <i>F</i> <sup>2</sup> )             | 0.087  |
| <i>S</i>   | 1.05   |
| No. of reflections used in refinement            | 1776   |
| No. of parameters                                | 107  |
| Weighting scheme                                 | $1/[\sigma^2(F_o^2) + (0.0683P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| ( $\Delta/\sigma$ ) <sub>max</sub>               | 0.001  |
| $\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> ) | 6.056  |
| $\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> ) | -5.150   |
| Extinction method                                | SHELXL97 (26)  |
| Extinction coefficient                           | 0.0024(6)  |
| Source of atomic scattering factors              | International Tables for Crystallography (Vol. C) (44)             |

hydrogen position could not be located from the electron density difference maps. There is, however, one short O–O distance of 2.99(2) Å, indicating a hydrogen bond. The presence of hydrogens was also confirmed indirectly by the bond valence sum calculations (27), as shown in Table 3.

**TABLE 3**  
**Fractional Atomic Coordinates, Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2$ ), and Bond Valence Sums (29),**  
 $\sum s$  (v.u.) for  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,  $U_{\text{eq}} = \left(\frac{1}{3}\right)\sum_i \sum_j U^{ij} a^i a_j \cdot a_j$

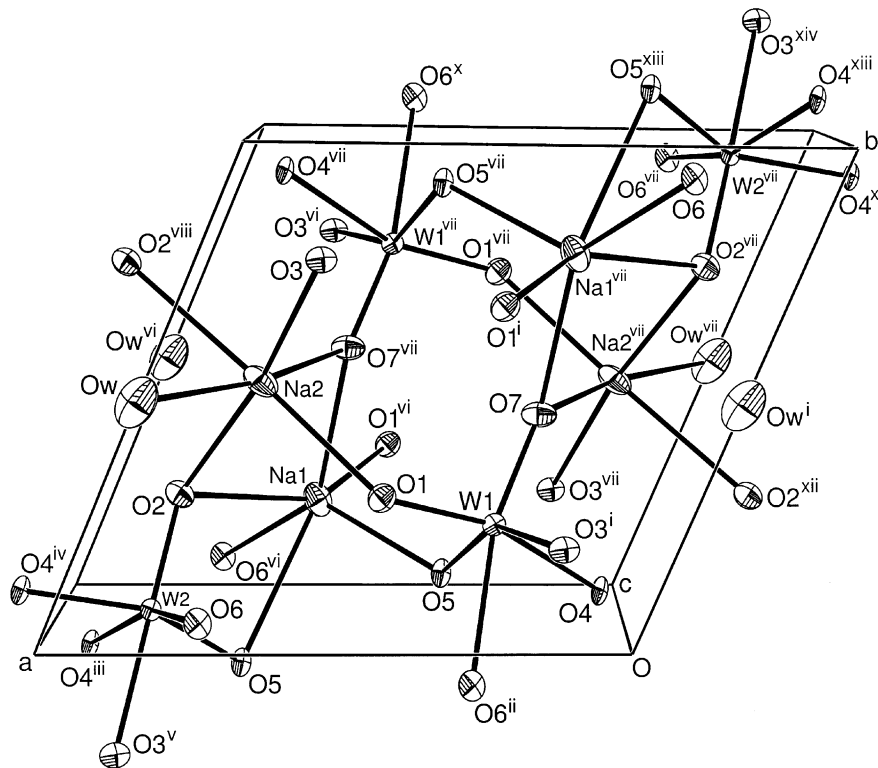
| Atom  | Site | <i>x</i>   | <i>y</i>      | <i>z</i>   | $U_{\text{eq}}$ | $\sum s$ |
|-------|------|------------|---------------|------------|-----------------|----------|
| W(1)  | 2i   | 0.31764(3) | 0.23880(4)    | 0.18610(5) | 0.00900(13)     | 5.906    |
| W(2)  | 2i   | 0.83790(3) | 0.03977(4)    | 0.34721(5) | 0.00801(12)     | 6.001    |
| Na(1) | 2i   | 0.6248(5)  | 0.2216(6)     | 0.7436(7)  | 0.0211(8)       | 1.091    |
| Na(2) | 2i   | 0.8137(6)  | 0.5133(6)     | 0.3164(8)  | 0.0213(7)       | 1.261    |
| O(w)  | 1c   | 1          | $\frac{1}{2}$ | 0          | 0.037(3)        | 0.446    |
| O(1)  | 2i   | 0.5298(8)  | 0.2992(10)    | 0.1293(13) | 0.0161(12)      | 2.027    |
| O(2)  | 2i   | 0.8729(9)  | 0.2622(10)    | 0.4919(13) | 0.0165(12)      | 2.118    |
| O(3)  | 2i   | 0.7970(8)  | 0.7692(9)     | 0.1403(11) | 0.0136(11)      | 2.167    |
| O(4)  | 2i   | 0.0753(7)  | 0.0829(8)     | 0.3264(11) | 0.0101(10)      | 2.207    |
| O(5)  | 2i   | 0.3569(7)  | 0.0959(8)     | 0.4974(11) | 0.0112(11)      | 2.231    |
| O(6)  | 2i   | 0.7508(8)  | 0.0599(9)     | 0.0211(11) | 0.0138(11)      | 2.056    |
| O(7)  | 2i   | 0.3146(9)  | 0.4484(10)    | 0.3246(13) | 0.0181(13)      | 2.085    |

Fractional atomic coordinates and anisotropic displacement parameters are listed in Tables 3 and 4. Selected geometric results concentrating on the W coordination are presented in Table 5. The graphic material was prepared using Ortep-3 (28) and Diamond (29). Complete data and structure factors in the CIF format are available on request.

## RESULTS AND DISCUSSION

### Structure Description

The unit cell content is shown in Fig. 2 and a polyhedral drawing of the structure is shown in Fig. 3. The crystallographically independent tungsten atoms are both



**FIG. 2.** Unit-cell content of  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  showing all refined atoms, including coordination spheres for W and Na atoms. Displacement ellipsoids are drawn at 50% probability level. Symmetry codes are listed in Table 5.

**TABLE 4**  
Anisotropic Displacement Parameters (Å<sup>2</sup>) for Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub>·½H<sub>2</sub>O

| Atom  | U <sub>11</sub> | U <sub>22</sub> | U <sub>33</sub> | U <sub>23</sub> | U <sub>13</sub> | U <sub>12</sub> |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| W(1)  | 0.01098(18)     | 0.01003(18)     | 0.00551(17)     | 0.00286(11)     | 0.00051(11)     | 0.00337(12)     |
| W(2)  | 0.00961(18)     | 0.00974(17)     | 0.00517(17)     | 0.00307(12)     | 0.00001(11)     | 0.00428(12)     |
| Na(1) | 0.0242(18)      | 0.027(2)        | 0.0165(16)      | 0.0035(15)      | -0.0002(15)     | 0.0153(16)      |
| Na(2) | 0.0311(19)      | 0.0178(16)      | 0.0218(17)      | 0.0092(14)      | 0.0083(15)      | 0.0151(15)      |
| O(w)  | 0.030(6)        | 0.051(8)        | 0.025(6)        | 0.001(6)        | 0.008(5)        | 0.005(6)        |
| O(1)  | 0.015(3)        | 0.017(3)        | 0.016(3)        | 0.002(2)        | 0.003(2)        | 0.004(2)        |
| O(2)  | 0.020(3)        | 0.016(3)        | 0.015(3)        | 0.002(2)        | 0.004(2)        | 0.009(2)        |
| O(3)  | 0.019(3)        | 0.013(3)        | 0.008(2)        | 0.004(2)        | -0.002(2)       | 0.005(2)        |
| O(4)  | 0.007(2)        | 0.016(3)        | 0.008(2)        | 0.007(2)        | -0.0004(18)     | 0.004(2)        |
| O(5)  | 0.009(2)        | 0.017(3)        | 0.009(2)        | 0.006(2)        | 0.0019(18)      | 0.006(2)        |
| O(6)  | 0.017(3)        | 0.019(3)        | 0.007(2)        | 0.004(2)        | -0.003(2)       | 0.009(2)        |
| O(7)  | 0.025(3)        | 0.013(3)        | 0.015(3)        | 0.000(2)        | 0.005(3)        | 0.005(3)        |

coordinated to six oxygens forming octahedrons. The distortion of the WO<sub>6</sub> octahedra are large, which can be seen from the ranges of W–O distances, 1.750(7)–2.189(6)

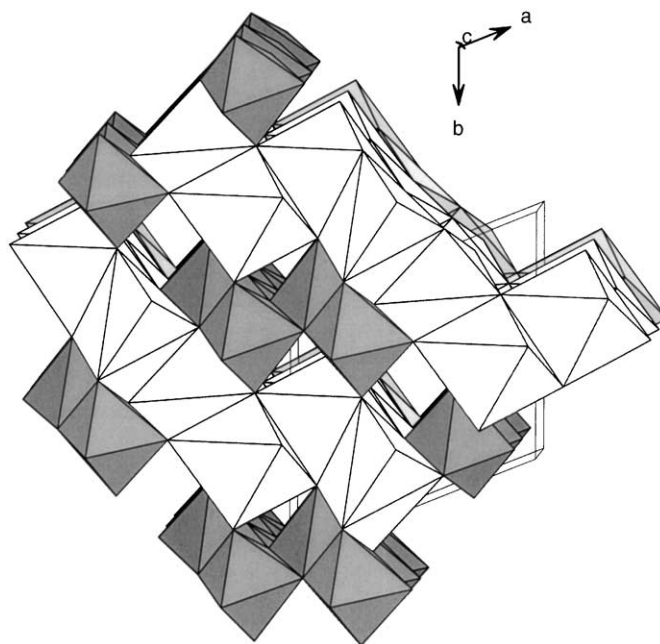
**TABLE 5**  
Selected Geometric Parameters (Å, °) for Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub>·½H<sub>2</sub>O

|                            |           |   |          |
|----------------------------|-----------|---|----------|
| W(1)–O(7)                  | 1.749(7)  | O(5)–W(1)–O(4)                                | 69.8(2)  |
| W(1)–O(1)                  | 1.752(7)  | O(3) <sup>i</sup> –W(1)–O(6) <sup>ii</sup>    | 72.2(2)  |
| W(1)–O(3) <sup>i</sup>     | 1.835(6)  | O(4)–W(1)–O(6) <sup>ii</sup>                  | 78.9(2)  |
| W(1)–O(5)                  | 2.041(6)  | O(5)–W(1)–O(6) <sup>ii</sup>                  | 79.3(2)  |
| W(1)–O(4)                  | 2.187(5)  | O(1)–W(1)–O(6) <sup>ii</sup>                  | 89.7(3)  |
| W(1)–O(6) <sup>ii</sup>    | 2.334(6)  | O(7)–W(1)–O(4)                                | 89.7(3)  |
| W(2)–O(2)                  | 1.750(7)  | O(3) <sup>j</sup> –W(1)–O(4)                  | 89.9(2)  |
| W(2)–O(6)                  | 1.801(5)  | O(1)–W(1)–O(5)                                | 90.9(3)  |
| W(2)–O(5) <sup>iii</sup>   | 1.898(5)  | O(7)–W(1)–O(3) <sup>i</sup>                   | 99.5(3)  |
| W(2)–O(4) <sup>iv</sup>    | 1.923(5)  | O(1)–W(1)–O(3) <sup>i</sup>                   | 103.5(3) |
| W(2)–O(4) <sup>iii</sup>   | 2.141(6)  | O(7)–W(1)–O(1)                                | 103.6(3) |
| W(2)–O(3) <sup>v</sup>     | 2.189(6)  | O(7)–W(1)–O(5)                                | 104.9(3) |
| Na(1)–O(5)                 | 2.318(7)  | O(3) <sup>j</sup> –W(1)–O(5)                  | 147.8(3) |
| Na(1)–O(6) <sup>vi</sup>   | 2.345(7)  | O(1)–W(1)–O(4)                                | 159.0(3) |
| Na(1)–O(1) <sup>vi</sup>   | 2.369(8)  | O(7)–W(1)–O(6) <sup>ii</sup>                  | 165.8(3) |
| Na(1)–O(7) <sup>vii</sup>  | 2.439(8)  | O(5) <sup>iii</sup> –W(2)–O(4) <sup>iii</sup> | 73.4(2)  |
| Na(1)–O(2)                 | 2.530(8)  | O(4) <sup>iv</sup> –W(2)–O(4) <sup>iii</sup>  | 73.5(3)  |
| Na(1)–O(5) <sup>iii</sup>  | 2.763(7)  | O(6)–W(2)–O(3) <sup>v</sup>                   | 76.6(3)  |
| Na(2)–O(3)                 | 2.238(7)  | O(4) <sup>iv</sup> –W(2)–O(3) <sup>v</sup>    | 82.9(2)  |
| Na(2)–O(7) <sup>vii</sup>  | 2.317(7)  | O(4) <sup>iii</sup> –W(2)–O(3) <sup>v</sup>   | 83.0(2)  |
| Na(2)–O(2)                 | 2.350(8)  | O(5) <sup>iii</sup> –W(2)–O(3) <sup>v</sup>   | 85.3(2)  |
| Na(2)–O(w)                 | 2.426(4)  | O(2)–W(2)–O(5) <sup>iii</sup>                 | 96.8(3)  |
| Na(2)–O(1)                 | 2.428(8)  | O(2)–W(2)–O(4) <sup>iv</sup>                  | 97.1(3)  |
| Na(2)–O(2) <sup>viii</sup> | 2.636(9)  | O(2)–W(2)–O(6)                                | 99.7(3)  |
| W(1)–W(2) <sup>ii</sup>    | 3.2539(5) | O(2)–W(2)–O(4) <sup>iii</sup>                 | 100.7(3) |
| W(2)–W(2) <sup>ix</sup>    | 3.2587(6) | O(6)–W(2)–O(5) <sup>iii</sup>                 | 102.8(3) |
| W(1)–W(2) <sup>iii</sup>   | 3.3372(5) | O(6)–W(2)–O(4) <sup>iv</sup>                  | 105.3(2) |
| W(2)–Na(1)                 | 3.466(4)  | O(5) <sup>iii</sup> –W(2)–O(4) <sup>iv</sup>  | 145.9(3) |
| Na(1)–Na(2)                | 3.308(5)  | O(6)–W(2)–O(4) <sup>iii</sup>                 | 159.5(3) |
|                            |           | O(2)–W(2)–O(3) <sup>v</sup>                   | 176.1(3) |

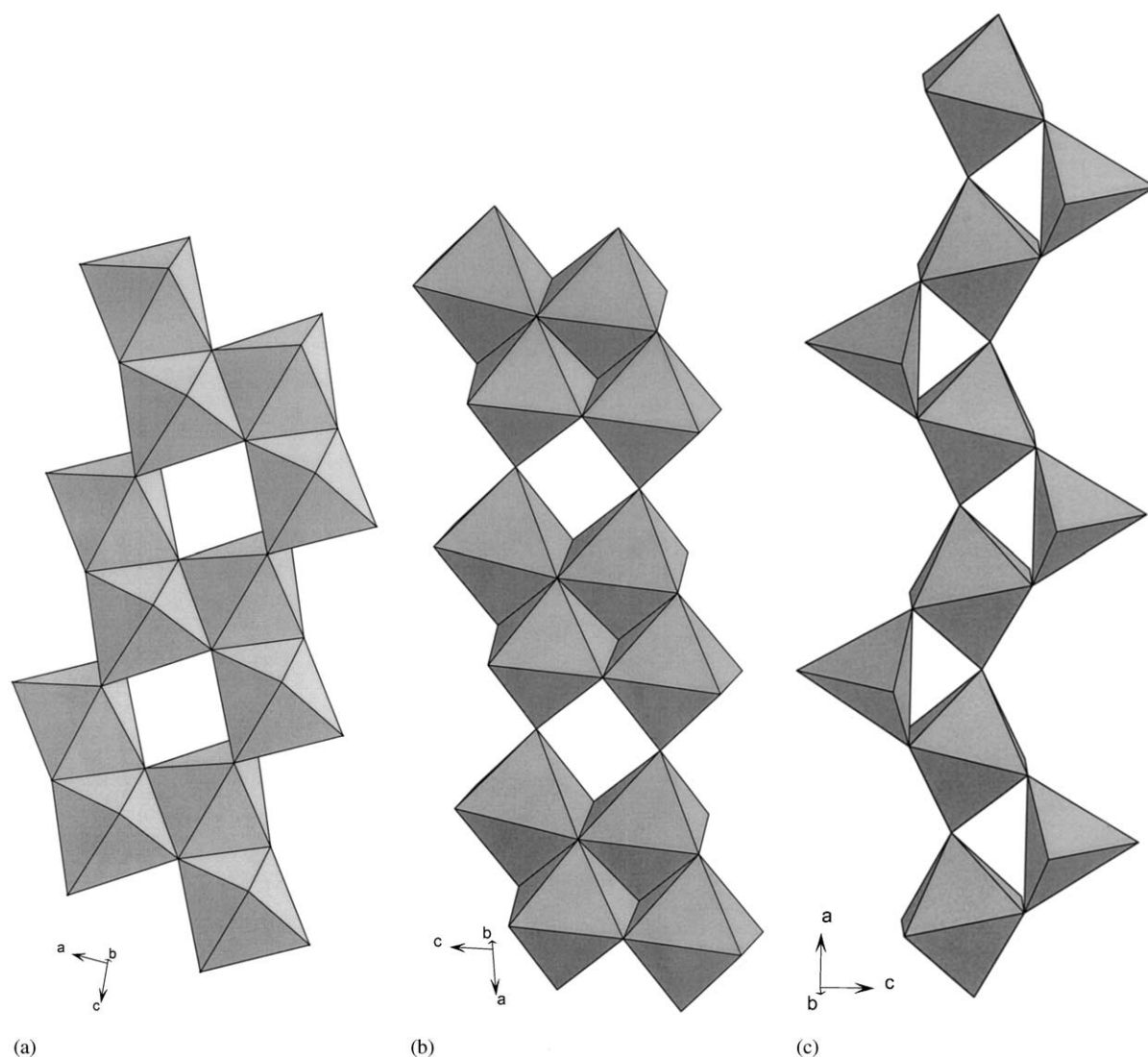
Note. Symmetry codes: (i) 1 - x, 1 - y, -z; (ii) 1 - x, -y, -z; (iii) -x, -y, 1 - z; (iv) 1 + x, y, z; (v) x, y - 1, z; (vi) x, y, 1 + z; (vii) 1 - x, 1 - y, 1 - z; (viii) 2 - x, 1 - y, 1 - z; (ix) 2 - x, -y, 1 - z; (x) x, 1 + y, 1 + z; (xi) -x, 1 - y, 1 - z; (xii) x - 1, y, z; (xiii) x, 1 + y, z; (xiv) 1 - x, 2 - y, 1 - z.

and 1.749(7)–2.334(6) Å for W(1) and W(2), respectively, see also Table 5. The two sodium atoms are six-coordinated to oxygens, although forming two different coordination polyhedra. For Na(1) a trigonal prismatic coordination is formed while Na(2) is octahedrally coordinated, see Fig 3. Both polyhedra are distorted with Na–O bond lengths in the range 2.318(7)–2.763(7) Å for Na(1) and 2.238(7)–2.636(9) Å for Na(2), see Table 5.

The WO<sub>6</sub> octahedra form infinite double chains, running along the c-axis, as shown in Fig. 4a. Four octahedra form a planar group by edge-sharing. The infinite chains are then formed by connecting such groups by edge-sharing. This



**FIG. 3.** Perspective polyhedral representation of Na<sub>2</sub>W<sub>2</sub>O<sub>7</sub>·½H<sub>2</sub>O. The WO<sub>6</sub> octahedra are gray, and the NaO<sub>6</sub> polyhedra are white.



**FIG. 4.** Perspective drawing of the polymeric ring-chain structure built of W–O polyhedra for (a)  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ , (b)  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$  and (c)  $\text{Na}_2\text{W}_2\text{O}_7$ .

linkage of the  $\text{WO}_6$  octahedra gives much shorter O–O distances for the shared edges, range 2.422(7)–2.491(5) Å, compared with those of the unshared, range 2.711(12)–3.011(6) Å. The W–W distances between neighboring octahedra in the double-chain range from 3.2539(5) to 3.3372(5) Å. This double-chain of  $\text{WO}_6$  octahedra (Fig. 4a) has also been found in, e.g.,  $\text{Li}_2\text{W}_2\text{O}_7$  (30, 31).

The  $\text{WO}_6$  double-chains are connected by two-dimensional nets of  $\text{NaO}_6$  polyhedra, in the 110 plane, see Fig. 5. These nets are built from two types of  $\text{NaO}_6$ -polyhedra, octahedra and trigonal prisms. Edge-sharing is the most common connection building up these nets. However, the water oxygen is at the corner in an  $\text{NaO}_6$  octahedron which is connected to another  $\text{NaO}_6$  octahedron by corner-sharing. Octahedrally coordinated Na atoms can be found

in  $\text{Na}_2\text{W}_2\text{O}_7$  (9) and the trigonal prismatic coordination of Na is similar to that of K and Rb found in  $\text{K}_2\text{W}_2\text{O}_7$  (32) and  $\text{Rb}_2\text{W}_2\text{O}_7$  (33), respectively. (K and Rb are seven-coordinated but with the six shortest M–O distances forming a trigonal prism.)

The connection between the  $\text{WO}_6$  double-chains and  $\text{NaO}_6$  nets is by edge- and corner-sharing. The  $\text{NaO}_6$  trigonal prisms share edges with  $\text{WO}_6$ -octahedra while the  $\text{NaO}_6$ -octahedra share corners with  $\text{WO}_6$ -octahedra in the double chains.

#### Structural Discussion

$\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$  is the fourth compound in the  $\text{Na}_2\text{W}_2\text{O}_7 \cdot x\text{H}_2\text{O}$  system which have been structurally

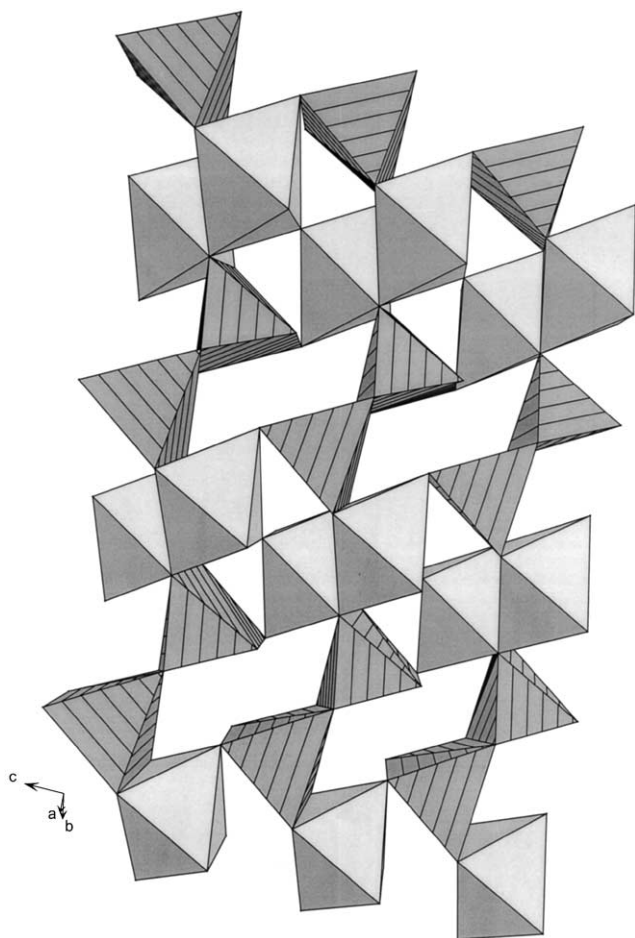


FIG. 5. Perspective drawing of the two-dimensional net of  $\text{NaO}_6$  polyhedra in  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

characterized, and the second that contains water. The others are; the mono-hydrate,  $\text{Na}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$  (6), and two different phases of the anhydrous  $\text{Na}_2\text{W}_2\text{O}_7$ , one prepared at normal pressure (9) and one at high pressure (10). The title compound, the mono-hydrate, and the anhydrous phase prepared at normal pressure can all be described as being built of double chains of tungsten oxide connected by two-dimensional nets of sodium oxide. The different double chains are shown in Fig. 4.

The mono-hydrate is polymeric with a cluster of four edge-sharing  $\text{WO}_6$  octahedra linked by corner-sharing (Fig. 4b). The W chains are linked by five- and six-coordinated Na atoms, also arranged in isometric chains, parallel to the polytungstate chains. This W coordination is also found in  $\text{Ag}_2\text{W}_2\text{O}_7$  (34).

The anhydrous  $\text{Na}_2\text{W}_2\text{O}_7$  prepared at normal pressure (9) is built of chains of  $\text{WO}_6$  octahedra and  $\text{WO}_4$  tetrahedra. Na coordinates to oxygen forming two different polyhedra, a distorted octahedron and a pentagonal pyramid.  $\text{Na}_2\text{W}_2\text{O}_7$  is isostructural to  $\text{Na}_2\text{Mo}_2\text{O}_7$  (35–37).

The high-pressure phase of  $\text{Na}_2\text{W}_2\text{O}_7$  (10) consists of perovskite-type slabs of tilted and distorted  $\text{WO}_6$  octahedra. Na is 12-coordinated in the perovskite slabs and seven-coordinated when connecting the slab.  $\text{Na}_2\text{W}_2\text{O}_7(\text{II})$  is isostructural to  $\text{Sr}_2\text{Nb}_2\text{O}_7$  (38).

In addition to these compounds, the tetrahydrate has been reported twice (6, 15), characterized with IR and Raman spectroscopy, but without any structural information. Also, the pentahydrate has been reported (5) and characterized by X-ray powder diffraction and

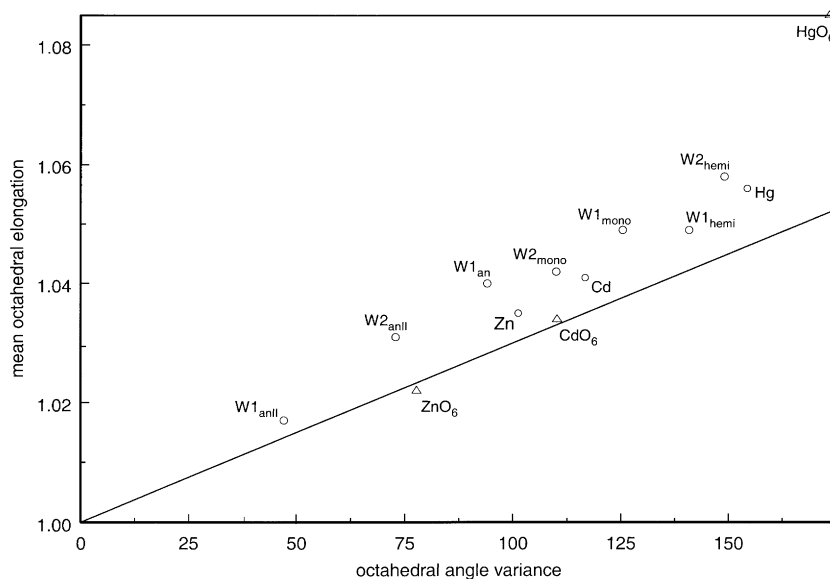


FIG. 6. 'Mean octahedral elongation vs octahedral variance' for  $\text{WO}_6$  octahedra in the  $\text{Na}_2\text{W}_2\text{O}_7\text{--H}_2\text{O}$  system together with  $\text{WO}_6$  and  $\text{MO}_6$  octahedra for  $\text{ZnWO}_4$  (41),  $\text{CdWO}_4$  (41) and  $\text{HgWO}_4$  (45) ( $\text{WO}_6$  labelled Zn, Cd and Hg, resp.). Other labels: an— $\text{Na}_2\text{W}_2\text{O}_7$  (9), anII— $\text{Na}_2\text{W}_2\text{O}_7(\text{II})$  (10), hemi— $\text{Na}_2\text{W}_2\text{O}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ , mono— $\text{Na}_2\text{W}_2\text{O}_7 \cdot \text{H}_2\text{O}$  (6). The line is calculated from values given by Robinson *et al.* (40). S.u.'s are about 0.01 and 6 for the 'mean octahedral elongations' and 'octahedral angle variance', respectively.

thermogravimetric measurements. By use of DICVOL (39) and the 25  $d$  values listed in Ref. (5), it was possible to find a relatively large triclinic unit cell with  $V = 1501 \text{ \AA}^3$ . With 20 single-indexed reflections and five double-indexed, the refined unit cell had  $F(25) = 7.5$  (0.0266, 126). This is an indication of a single phase for the pentahydrate, although the FOMs are not excellent.

Using the concept of 'mean octahedral elongation vs mean octahedral variance' by Robinson *et al.* (40) as a measure of the distortion of  $\text{WO}_6$  octahedra, Fig. 6, it is seen that all phases in the  $\text{Na}_2\text{W}_2\text{O}_7\text{-H}_2\text{O}$  system have strongly distorted  $\text{WO}_6$  octahedra. The highest distortion is for the hemihydrate, approximately the same as that for  $\text{WO}_6$  in  $\text{HgWO}_4$ . As found earlier (41), the  $\text{WO}_6$  octahedra deviates substantially from the trendline given in (40). Data from  $\text{ZnWO}_4$ ,  $\text{CdWO}_4$ ,  $\text{HgWO}_4$  and the phases in the  $\text{Na}_2\text{W}_2\text{O}_7\text{-H}_2\text{O}$  system gives a trendline with an inclination of  $3.8 \times 10^{-4}$  instead of  $3 \times 10^{-4}$ . However, the individual s.u.'s (given in Fig. 6) are too large for statistical significance of the different inclinations.

### CONCLUDING REMARKS

In the  $\text{Na}_2\text{O-WO}_3\text{-H}_2\text{O}$  system a great number of different phases are known, some with known crystal structures and others for which the structure is unknown. For the pentahydrate,  $\text{Na}_2\text{W}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ , a powder pattern was indexed from earlier published and indicated a single phase. For this compound and the corresponding tetrahydrate, if existent, a structure determination would be of importance in order to improve the phase diagram and compare the structures.

More work should also be done to improve preparation methods and to characterize the properties of these compounds, e.g., luminescence.

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### REFERENCES

- G. Blasse and B. C. Grabmaier, "Luminescent Materials," Springer-Verlag, Berlin, 1994.
- S. Baccaro, B. Borgia, I. Dafinei, and E. Longo (Eds.), "Proceedings of the International Workshop on Tungstate Crystals," Università degli Studi Sapienza, Roma, 1999.
- V. Mikhailin (Ed), "SCINT'99, Proceedings of the 5th International Conference on Inorganic Scintillators and their Applications," M. V. Lomonosov Moscow State University, Moscow, 2000.
- K. H. Tytko and O. Glemser, *Adv. Inorg. Chem. RadioChem.* **19**, 239–315 (1976).
- E. L. Simons, *Inorg. Chem.* **3**, 1079–1085 (1964).
- I. Brüdgam, J. Fuchs, H. Hartl, and R. Palm, *Angew. Chem. Int. Ed.* **37**(19), 2668–2671 (1998).
- J.-M. Réau, C. Fouassier, and P. Hagenmuller, *Bull. Soc. Chim. Fr.* **1967**, 3873–3876 (1967).
- R. Hoffmann and R. Hoppe, *Z. Anorg. Allg. Chem.* **573**, 143–156 (1989).
- K. Okada, H. Morikawa, F. Marumo, and S. Iwai, *Acta Crystallogr. B* **31**, 1200–1201 (1975).
- K.-J. Range and H. Haase, *Acta Crystallogr. C* **46**, 317–318 (1990).
- K. Viswanathan, *J. C. S. Dalton* **1974**, 2170–2174 (1974).
- J.-M. Réau and C. Fouassier, *Bull. Soc. Chim. Fr.* **1971**, 398–402 (1971).
- K. P. Reis, E. Prince, and M. Stanley Wittingham, *Chem. Mater.* **4**, 307–312 (1992).
- A. Magneli, *Acta Chem. Scand.* **7**, 315–324 (1953).
- H. Hartl, R. Palm, and J. Fuchs, *Angew. Chem. Int. Ed.* **32**, 1492–1494, (1993).
- K. G. Burtseva, T. S. Chernaya, and M. I. Sirota, *Sov. Phys. Dokl.* **23**, 784–786 (1978).
- H. T. Evans Jr. and O. W. Rollins, *Acta Crystallogr. B* **32**, 1565–1567 (1976).
- J. J. Cruywagen, I. F. J. Van der Merwe, L. R. Nassimbeni, M. L. Niven, and E. A. Symonds, *J. Crystallogr. Spectrosc. Res.* **16**, 525–535 (1986).
- A. Chrissafidou, J. Fuchs, H. Hartl, and R. Palm, *Z. Naturforsch. B* **50**, 217–222 (1995).
- I. Lindqvist, *Acta Crystallogr.* **5**, 667–670 (1952).
- O. Glemser, W. Holznagel, W. Höltje, and E. Schwarzmann, *Z. Naturforsch. B* **20**, 725–746 (1965).
- J. F. Keggin, *Proc. R. Soc. (London) Ser. A* **144**, 75–100 (1934).
- K. Przybylski and A. Morawski, "2nd International Summer School on High Temperature Superconductivity," Eger, Hungary, Vol. 45, 1996.
- D. Schwarzenbach and G. King, "LATCON Xtal3.6 System." (S. R. Hall, D. J. du Boulay and R. Olthof-Hazekamp, Eds.) University of Western Australia, Perth, Australia, 1999.
- L. J. Farugia, *J. Appl. Crystallogr.* **32**, 837–838 (1999).
- G. M. Sheldrick, "SHELX Programs," University of Göttingen, Germany, 1997.
- I. D. Brown and D. Altermatt, *Acta Crystallogr. B* **41**, 244–247 (1985).
- M. N. Burnett and C. K. Johnson, "ORTEP III," Report ORNL-6895, Oak Ridge National Laboratory, TN, USA, 1996.
- K. Brandenburg, "Diamond," Version 2.1c, Crystal Impact GbR, Bonn, Germany, 1999.
- S. A. Magarill, R. F. Klevtsova, and V. V. Bakakin, *Sov. Phys. Crystallogr.* **18**(2), 166–170 (1973).
- K. Okada, H. Morikawa, F. Marumo, and S. Iwai, *Acta Crystallogr. B* **31**, 1451–1454 (1975).
- K.-J. Range, W. Hegenbart, A. M. Heyns, F. Rau, and U. Klement, *Z. Naturforsch.* **45b**, 107–110 (1990).
- K.-J. Range, U. Klement, F. Rau, and U. Schiessel, *Z. Kristallogr.* **203**, 318–319 (1993).
- B. M. Gatehouse and P. Leverett, *J. C. S. Dalton* **1976**, 1316–1320 (1976).
- I. Lindqvist, *Acta Chem. Scand.* **4**, 1066–1074 (1950).
- I. Lindqvist, *Acta Chem. Scand.* **14**, 960 (1960).
- M. Seleborg, *Acta Chem. Scand.* **21**, 499–504 (1967).
- N. Ishizawa, F. Marumo, T. Kawamura, and M. Kimura, *Acta Crystallogr. B* **31**, 1912–1915 (1975).
- A. Boulitf and D. Louer, *J. Appl. Crystallogr.* **24**, 987–993 (1991).



40. K. Robinson, G. V. Gibbs, and P. H. Ribbe, *Science* **172**, 567–570 (1971).
41. M. Åsberg Dahlborg and G. Svensson, *Acta Chem. Scand.* **53**, 1103–1109 (1999).
42. K. Okada, H. Morikawa, F. Marumo, and S. Iwai, *Acta Crystallogr. B* **30**, 1872–1873 (1974).
43. K. Okada, H. Morikawa, F. Marumo, and S. Iwai, *Bull. Tokyo Inst. Technol.* **120**, 7–11 (1974).
44. A. J. C. Wilson (Ed.), “International Tables of Crystallography,” Vol. C. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1995.
45. M. Åsberg Dahlborg and G. Svensson, *Acta Crystallogr. C* **58**, i35–i36 (2002).