

Sodium Paradodecatungstate 20-Hydrate

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(Received 3 October 1975; accepted 6 January 1976)

Abstract. $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\cdot 20\text{H}_2\text{O}$, $M=3470.4$. Triclinic, $P\bar{1}$, $a=12.195$ (1), $b=12.637$ (2), $c=10.558$ (2) Å, $\alpha=108.11$ (1), $\beta=98.67$ (2), $\gamma=111.63$ (1)°. For $Z=1$, $D_x=4.21$; D_m (Berman balance)=4.13 (1) g cm⁻³. Structure analysis based on diffractometer data converged to $R=0.066$. The structure contains the paradodecatungstate isopolyion, with dimensions conforming closely to previous determinations.

Experimental. In an attempt to prepare a heteropolytungstoaluminate complex, a solution of 50 g $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and 5.16 g $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ in 20 ml of water was adjusted to $\text{pH}=7.0$ with 6M HNO_3 . The solution cleared after 10–15 min at boiling temperature, and was then filtered and evaporated to crystallization on a steam bath. The product was twice recrystallized, dried in air, and analyzed for Na by flame photometry, W by the gravimetric cinchonine method and H_2O by igniting at 500° and 800°C (Rollins, 1966). The absence of Al was subsequently verified by atomic absorption spectrophotometry. Calculated for $\text{Na}_{10}\text{W}_{12}\text{O}_{41}\cdot 20\text{H}_2\text{O}$: Na, 6.62; W, 63.6; H_2O , 10.4%. Found (average of 5 analyses): Na, 6.47; W, 61.5; H_2O , 12.8%.

Preliminary unit-cell data obtained from Buerger precession photographs were refined by least-squares analysis of 2θ angle measurements for 25 reflections made with the Picker four-circle single-crystal diffractometer. The assumed centrosymmetric space group $P\bar{1}$ was confirmed by the structure refinement. Intensities were measured with Mo $K\alpha$ radiation by means of the automated Picker instrument using a crystal of approximately rectangular shape having dimensions $0.025 \times 0.019 \times 0.008$ cm. Within the range of measurement of $2\theta=50^\circ$, 4399 independent reflections were recorded, of which 3822 registered intensity greater than 3σ according to counting statistics, and were used for the structure analysis. Absorption corrections (calculated on a linear grid containing 36 points within the crystal, using the program *ACACA* written by C. T. Prewitt) were applied based on a calculated linear absorption coefficient of $\mu=247.3$ cm⁻¹ (Cromer & Liberman, 1970). Dispersion corrections were used in the final stages of structure refinement, but no extinction corrections were applied.

The structure was solved by means of the symbolic addition procedure applied to the normalized structure factors (Karle & Karle, 1966). This process led to

Table 1. Structural and thermal parameters for the crystal structure of $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\cdot 20\text{H}_2\text{O}$

Polyanion	<i>x</i>	<i>y</i>	<i>z</i>	\bar{u} (Å)
W(1)	0.2828 (1)	0.0355 (1)	0.2158 (1)	0.098 (1)
W(2)	0.0071 (1)	0.1893 (1)	-0.0939 (1)	0.096 (1)
W(3)	0.0555 (1)	0.1042 (1)	0.2955 (1)	0.097 (1)
W(4)	0.0812 (1)	0.4015 (1)	0.2712 (1)	0.108 (1)
W(5)	0.3012 (1)	0.3278 (1)	0.1898 (1)	0.104 (1)
W(6)	0.1983 (1)	-0.1742 (1)	-0.1512 (1)	0.104 (1)
O(1)	0.005 (2)	-0.063 (2)	0.261 (3)	0.14 (2)
O(2)	0.181 (2)	-0.122 (2)	0.200 (2)	0.13 (2)
O(3)	0.224 (2)	0.111 (2)	0.357 (2)	0.14 (2)
O(4)	0.056 (2)	0.319 (2)	-0.129 (3)	0.16 (2)
O(5)	0.039 (2)	0.150 (2)	0.462 (2)	0.13 (2)
O(6)	0.426 (2)	0.062 (2)	0.308 (2)	0.13 (2)
O(7)	0.099 (2)	0.008 (2)	0.104 (2)	0.13 (2)
O(8)	0.147 (2)	0.194 (2)	0.000 (2)	0.11 (2)
O(9)	0.092 (2)	-0.067 (2)	-0.187 (2)	0.10 (2)
O(10)	0.047 (2)	-0.236 (2)	-0.065 (2)	0.09 (2)
O(11)	0.148 (2)	0.253 (2)	0.274 (2)	0.12 (2)
O(12)	0.280 (2)	-0.032 (2)	0.020 (2)	0.12 (2)
O(13)	0.326 (2)	0.186 (2)	0.176 (2)	0.11 (2)
O(14)	0.204 (2)	0.418 (2)	0.178 (2)	0.12 (2)
O(15)	0.054 (2)	-0.301 (2)	-0.316 (2)	0.12 (2)
O(16)	0.392 (2)	0.374 (2)	0.084 (2)	0.15 (2)
O(17)	0.288 (2)	-0.108 (2)	-0.244 (2)	0.13 (2)
O(18)	0.025 (2)	0.497 (2)	0.220 (2)	0.14 (2)
O(19)	0.175 (2)	0.491 (2)	0.442 (2)	0.16 (2)
O(20)	0.260 (2)	-0.273 (2)	-0.119 (3)	0.15 (2)
O(21)	0.399 (2)	0.428 (2)	0.359 (2)	0.14 (2)
Water				
O(22)	0.200 (2)	0.649 (2)	0.126 (2)	0.17 (2)
O(23)	0.500 (3)	0.833 (3)	0.136 (4)	0.25 (4)
O(24)	0.385 (3)	0.688 (3)	0.357 (3)	0.19 (2)
O(25)	0.135 (2)	0.736 (2)	0.454 (3)	0.16 (2)
O(26)	0.377 (3)	0.996 (3)	0.543 (3)	0.19 (2)
O(27)	0.387 (3)	0.562 (3)	0.989 (3)	0.20 (2)
O(28)	0.226 (3)	0.127 (3)	0.687 (3)	0.18 (2)
O(29)	0.403 (2)	0.685 (2)	0.702 (3)	0.16 (2)
O(30)	0.379 (2)	0.304 (2)	0.607 (3)	0.18 (2)
O(31)	0.184 (3)	0.423 (3)	0.662 (3)	0.18 (2)
Cations				
Na(1)	0.1535 (15)	0.9323 (15)	0.4693 (17)	0.19 (1)
Na(2)	0.3518 (15)	0.7994 (15)	0.5671 (16)	0.18 (1)
Na(3)	0.3717 (15)	0.4809 (15)	0.5838 (17)	0.18 (1)
Na(4)	0.3011 (15)	0.1159 (15)	0.9017 (17)	0.19 (1)
Na(5)	0.1972 (15)	0.5252 (15)	0.8922 (17)	0.17 (1)

4 separate phase groups among 252 reflections having $|E| > 2.00$. Within these groups the phases were well determined, but many trials using various computational parameters failed to reveal any reliable relationship between different groups. Therefore, 16 Fourier syntheses of 556 E terms with $|E| > 1.50$ were computed on the basis of phases calculated with the reflections 544; 499; and 098 set positive to determine the origin, and the phases of the four reflections 533;

742; 842; and 244 permuted in sequence. The 16th synthesis (phases + + + - - - -, respectively) showed the least number of peaks, and when a model plot was made of this map, the characteristic configuration of the 12 W atoms in the paradodecatungstate isopolyion was immediately recognized. When these W positions were used for phasing, the first electron-density synthesis revealed most of the non-hydrogen atoms, and refinement proceeded from this point in a routine

Table 2. Comparison of reported bond lengths in the paradodecatungstate polyion

Typical standard deviation of measurement (in Å) is 0.025 for W-O, 0.003 for W-W. Atom designations as in Fig. 1; L and R denote left and right side of molecule.

Atoms		(i)		(ii)		(iii)		(iv)		(v)		Average	σ
L	R	L	R	L	R	L	R	L	R	L	R		
$W_{I}-O_c$	$W_{I}-O_b$	1.88	1.95	1.86	1.95	1.86	1.92	1.88	1.97	1.85	1.89	1.90	0.04
$-O_f$		1.76		1.70		1.71		1.77		1.73		1.73	0.03
$-O_g$		2.28		2.28		2.27		2.24		2.20		2.25	0.03
$-O_h$	$-O_i$	1.98	2.08	2.01	1.98	1.93	2.06	1.98	1.91	1.98	1.98	1.98	0.05
$W_{III}-O_a$	$W_{III}-O_a$	1.92	2.03	1.84	2.04	1.90	1.98	1.96	1.96	1.93	1.86	1.94	0.06
$-O_c$	$-O_b$	2.09	2.02	2.05	2.17	2.06	2.01	2.08	2.07	2.10	2.02	2.07	0.05
$-O_e$	$-O_d$	1.81	1.79	1.78	1.65	1.74	1.76	1.74	1.71	1.72	1.77	1.75	0.04
$-O_g$	$-O_g$	2.26	2.33	2.22	2.29	2.27	2.32	2.26	2.27	2.31	2.27	2.28	0.03
$-O_i$	$-O_h$	1.83	1.87	1.82	1.78	1.83	1.83	1.77	1.79	1.82	1.77	1.81	0.03
$-O_k$	$-O_j$	1.95	1.90	1.94	1.91	1.92	1.91	1.93	1.90	1.92	1.90	1.92	0.02
$W_{IV}-O'_k$	$W_{IV}-O_j$	2.20	2.38	2.18	2.27	2.21	2.33	2.26	2.33	2.29	2.32	2.28	0.06
$-O_s$	$-O_n$	1.93	1.91	1.95	1.95	1.89	1.90	1.90	1.87	1.90	1.92	1.91	0.03
$-O_s$	$-O_r$	1.80	1.74	1.73	1.69	1.80	1.74	1.76	1.73	1.76	1.73	1.75	0.03
$W_{VI}-O_i$	$W_{VI}-O_h$	2.22	2.18	2.12	2.24	2.18	2.19	2.18	2.19	2.17	2.27	2.19	0.04
$-O_o$	$-O_n$	1.93	2.02	2.04	1.92	1.96	2.00	1.96	1.96	1.93	1.98	1.97	0.04
$-O_q$	$-O_p$	1.80	1.70	1.72	1.78	1.75	1.70	1.76	1.73	1.74	1.76	1.75	0.03
$-O_j$	$-O_k$	2.18	2.32	2.22	2.23	2.17	2.28	2.19	2.20	2.22	2.17	2.22	0.05
$-O_i$	$-O_m$	1.82	1.88	1.87	1.77	1.81	1.90	1.90	1.83	1.89	1.88	1.85	0.04
$-O_t$	$-O_u$	1.81	1.80	1.71	1.78	1.82	1.80	1.77	1.79	1.75	1.76	1.78	0.03
$W_{II}-W'_{II}$		5.665		5.760		5.630		5.680		5.676		5.69	0.04
$W_{III}-W'_{III}$		5.701		5.639		5.751		5.662		5.685			
$W_{V}-W'_{V}$		8.003		8.009		8.086		7.884		8.017			
$W_{VI}-W'_{VI}$		8.073		8.004		8.015		7.963		8.037		8.01	0.04

(i) $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 4H_2O$: D'Amour & Allmann (1972). (ii) $Na_2(NH_4)_8[H_2W_{12}O_{42}] \cdot 12H_2O$: D'Amour & Allmann (1973). (iii) $(NH_4)_{10}[H_2W_{12}O_{42}] \cdot 10H_2O$: Allmann (1971). (iv) $Mg_3[H_2W_{12}O_{42}] \cdot 12H_2O$: Tsay & Silverton (1973). (v) $Na_{10}[H_2W_{12}O_{42}] \cdot 20H_2O$: This paper.

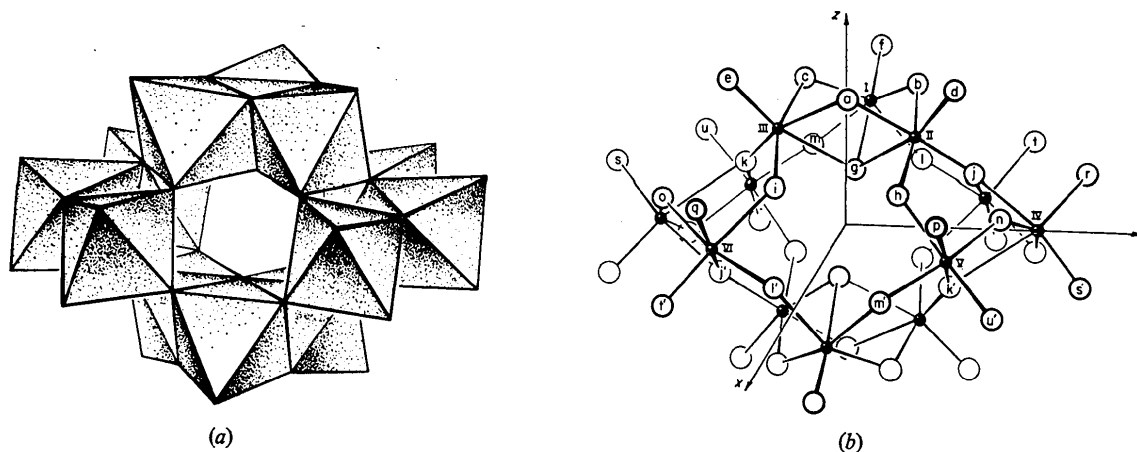


Fig. 1. The paradodecatungstate molecule ion, $[H_2W_{12}O_{42}]^{10-}$: (a) polyhedral representation; (b) bonding representation (Cartesian axes shown).

manner. After 6 cycles of least-squares analysis of 126 positional and 42 isotropic thermal parameters, convergence was achieved with a conventional $R=0.066$. The refinement was then extended in full anisotropic mode, with 246 thermal parameters (using the program *RFINE* written by L. R. Finger of the Geophysical Laboratory, Washington, D.C.). The reliability was thus reduced to $R=0.062$, but the improvement is insignificant in view of the increase in number of parameters (Hamilton, 1965). Thus, although Table 1 lists the positional parameters from this last step, only the equivalent isotropic vibration amplitude values \bar{u} are shown.*

All crystal structure calculations were executed on an IBM 360/65 computer using (except where noted) the system X-RAY 70 edited by J. R. Stewart, University of Maryland. The form factors for neutral atoms of Cromer & Mann (1968) and the dispersion parameters of Cromer & Liberman (1970) were used in the last stages of refinement.

Discussion. The chemical composition of the crystal was uncertain at the outset, but the crystal structure analysis shows conclusively that the unit cell contains $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$. The polyion, illustrated in Fig. 1, is identical with that found originally by Lindqvist (1952) (as modified by Lipscomb, 1965) in $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 27\text{H}_2\text{O}$, and described in detail by Allmann (1971) in $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 10\text{H}_2\text{O}$; by D'Amour & Allmann (1972) in $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$; by D'Amour & Allmann (1973) in $\text{Na}_2(\text{NH}_4)_8[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 12\text{H}_2\text{O}$; and by Tsay & Silverton (1973) in $\text{Mg}_5[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 12\text{H}_2\text{O}$. Both Allmann (1971) and Evans (1972) have suggested that the true symmetry of the free molecule may be $\bar{1}$ rather than $2/m$, depending on the exact disposition of the two nonlabile hydrogen atoms (shown indirectly by Allmann (1971) to be associated with O_9). Referring to the description of the polyanion structure given by Evans (1972), with the atoms designated as shown in Fig. 1(b), the provisionally equivalent W–O bond lengths in all five crystal structures are compared in Table 2. The five structure determinations have all been carried to a similar degree of refinement, and,

although the space groups differ, the environment of the molecule has $\bar{1}$ symmetry in every case. Table 2 also compares the distances found between a W atom and its centrosymmetric equivalent for W_{II} , W_{III} , W_V and W_{VI} . These distances correspond to diagonals of quadrilateral figures which would be rectangles if the molecule had monoclinic symmetry. Among all these comparisons there are no consistencies or trends that would indicate that the distortions from $2/m$ symmetry arise from any cause other than the packing effects of next-nearest neighbor groups in each crystal structure. The overall monoclinic averages are given in Table 2, which shows that the free molecule probably has $2/m$ symmetry, and that the average bond lengths shown have a standard deviation of 0.04 \AA as determined from crystal structure analysis. A neutron diffraction study is needed to determine the role of the two nonlabile hydrogen atoms and whether or not they conform to the proposed monoclinic symmetry.

Of the five types of sodium atoms, three are coordinated to 6 oxygen atoms, one to 7 oxygen atoms, and one to 8 oxygen atoms. Each sodium atom is coordinated to both polyion oxygen atoms and water molecules in varying proportions. The water molecules form an intermolecular network of hydrogen bonds. No further description of the details of intermolecular structure will be attempted in this brief report.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31604 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.