

Fig. 3. Schéma des liaisons hydrogène pour chacun des atomes H des groupements $\text{Te}(\text{OH})_6$ et NH_4^+ , représenté sur le plan (a,b) .

Références

- AVERBUCH-POUCHOT, M. T. & DURIF, A. (1981). *Mater. Res. Bull.* **16**, 71–76.
 AVERBUCH-POUCHOT, M. T. & DURIF, A. (1982a). *J. Solid State Chem.* A paraître.
 AVERBUCH-POUCHOT, M. T. & DURIF, A. (1982b). *J. Solid State Chem.* A paraître.
 AVERBUCH-POUCHOT, M. T., DURIF, A. & GUITEL, J. C. (1980). *Mater. Res. Bull.* **15**, 387–395.
 BOUDJADA, N., AVERBUCH-POUCHOT, M. T. & DURIF, A. (1981a). *Acta Cryst.* **B37**, 645–647.
 BOUDJADA, N., AVERBUCH-POUCHOT, M. T. & DURIF, A. (1981b). *Acta Cryst.* **B37**, 647–649.
 BOUDJADA, N. & DURIF, A. (1982). *Acta Cryst.* **B38**, 595–597.
 Enraf-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft.
International Tables for X-ray Crystallography (1974). Tome IV. Birmingham: Kynoch Press.

Acta Cryst. (1983). **C39**, 658–661

Preparation and Structure of Sodium Octatungstotetraphosphate(12–) Icosahydrate, $\text{Na}_{12}\text{P}_4\text{W}_8\text{O}_{40}\cdot 20\text{H}_2\text{O}$, a 1:2 ($X:M$) Heteropolyanion

BY B. M. GATEHOUSE* AND A. J. JOZSA

Chemistry Department, Monash University, Clayton, Victoria 3168, Australia

(Received 22 October 1982; accepted 15 December 1982)

Abstract. $M_r = 2870.9$, monoclinic, $I2/a$, $a = 19.636(3)$, $b = 18.346(3)$, $c = 16.187(8)$ Å, $\beta = 94.80(1)^\circ$, $U = 5810.8$ Å³, $Z = 4$, D_m (measured by flotation in $\text{CH}_2\text{I}_2/\text{CCl}_4$) = $3.29(3)$, $D_x = 3.28$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 16.39$ mm⁻¹, $F(000) = 5214$, $T = 293$ K. Final $R = 0.051$ for 2687 counter reflections. The structure consists of isolated heteropolyanions $[\text{P}_4\text{W}_8\text{O}_{40}]^{12-}$ in the form of a shell of WO_6 octahedra and PO_4 tetrahedra (four blocks of $[\text{PW}_2\text{O}_{13}]$ linked by corner-sharing of the polyhedra). There is a large cavity in the centre of the anion that is occupied by a sodium ion. The heteropolyanions are embedded in a matrix of sodium ions and water molecules.

Introduction. Heteropolyanions have been of considerable interest from as long ago as the first structure report by Keggin (1934) on the anion that became known as the 'Keggin anion', $[\text{X}^{n+}\text{M}_{12}\text{O}_{40}]^{(8-n)-}$. Two excellent recent reviews dealing with the heteropoly-molybdates and tungstates are available by Weakley (1974) and Kazanskii, Torchenkova & Spitsyn (1974).

The first structural reports on heteropolyanions with an $X:M$ ratio (heteroatom to Mo/W) of 1:3 appeared only recently for the 1:3 arsenomolybdate polyanions

$[\text{As}_2\text{Mo}_6\text{O}_{26}]^{6-}$ and $[(\text{PhAs})_2\text{Mo}_6\text{O}_{24}]^{4-}$ (Filowitz & Klemperer, 1976), $[(\text{PhAs})_4\text{Mo}_{12}\text{O}_{46}]^{4-}$ (Filowitz & Klemperer, 1977), $[(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}]^{4-}$ (Kwak, Rajkovic, Stalick, Pope & Quicksall, 1976) and $[\text{H}_4\text{As}_4\text{Mo}_{12}\text{O}_{50}]^{4-}$ (Nishikawa & Sasaki, 1975), using ¹⁷O NMR studies in solution, and X-ray studies in the last two cases.

The preparation of sodium tritungstophosphate $\text{Na}_3\text{PW}_3\text{O}_{13}\cdot 16\text{H}_2\text{O}$, with an $X:M$ ratio of 1:3, was reported by Kehrmann & Mellett (1923), and as structural data on the 1:3 anion series were lacking at the time this study was commenced, its structure determination was of interest. Soon after commencement of the solution, however, it became clear that the heteropolyanion prepared belonged to a new series with an $X:M$ ratio of 1:2.

The structure determination of $\text{Na}_{12}\text{P}_4\text{W}_8\text{O}_{40}\cdot 20\text{H}_2\text{O}$ is reported here. A brief preliminary communication has been published elsewhere (Gatehouse & Jozsa, 1977).

Experimental. Crystals of $\text{Na}_{12}[\text{P}_4\text{W}_8\text{O}_{40}]\cdot \text{aq}$ were obtained during an attempt to prepare $\text{Na}_3\text{PW}_3\text{O}_{13}\cdot 3\text{H}_2\text{O}$ using the method suggested by Kehrmann & Mellett (1923), whereby the complex anion should be formed following acidification of an aqueous solution containing the basic oxoanions. Thus,

* To whom correspondence should be addressed.

slow crystallization of a concentrated aqueous solution, containing sodium tungstate and disodium hydrogen phosphate in a 3:1 mole ratio, that had been neutralized with glacial acetic acid, yielded a white powder. Initial attempts at recrystallization yielded an oil, but colourless prismatic crystals were eventually obtained.

Atomic-absorption analysis for sodium indicated 10.1 (5)% Na, and differential thermal analysis showed a mass loss of 13.2 (2)% for two runs over about 3h to 653 K. These results together with the unit-cell and density data, when considered with the knowledge of the nature of the heteropolyanion, indicated that the compound was $\text{Na}_{12}[\text{P}_4\text{W}_8\text{O}_{40}]\cdot 20\text{H}_2\text{O}$.

Space group $I2/a$ or Ia (equivalent to $C2/c$, No. 15 or Cc , No. 9) from systematic absences: hkl , $h+k+l$ odd and $h0l$, h odd and l odd; $I2/a$ was confirmed from reflection statistics and successful refinement; Philips PW1100 automatic four-circle diffractometer, graphite monochromator; cell dimensions quoted are the means of 11 refinements of 25 reflections used to monitor crystal stability during data collection; intensities collected from a single crystal, $0.075 \times 0.05 \times 0.05$ mm; three standard reflections monitored at 2h intervals showed no significant variation in intensity; data collected by ω scans, scan width 1.2° with an allowance for dispersion, scan rate $0.05^\circ \text{ s}^{-1}$; no reflection sufficiently intense to warrant insertion of an attenuation filter; data processed with a program written for the PW1100 diffractometer (Hornstra & Stubbe, 1972); absorption correction applied based on the indexed crystal faces (100), $(\bar{1}00)$, (011), $(0\bar{1}\bar{1})$, $(0\bar{1}1)$ and (011), and direction cosines calculated for the PW1100 data, maximum and minimum values of the transmission factors 0.5148 and 0.4477 respectively; 5277 total reflections measured to $2\theta = 50^\circ$ excluding systematic absences: 162 were multiple observations [measure of agreement 0.0507 (Sheldrick, 1976)]; 2687 unique reflections with $I > 3\sigma(I)$ used in subsequent refinement. Structure solved by Patterson and Fourier techniques; the four W-atom positional parameters were refined using full-matrix least squares, following which P and anion O atoms were located in a difference Fourier synthesis. A model then revealed that the heteropolyanion was $[\text{P}_4\text{W}_8\text{O}_{40}]^{n-}$, the charge depending on the number of any anionic water and/or hydroxyl groups. Refinement of anisotropic thermal parameters for W, isotropic thermal parameters for P and all positional parameters (U for O atoms was fixed at 0.02 \AA^2) with the data weighted [$w = \sigma^2(F_o)^{-1}$] and minimizing the function $\sum w(|F_o| - |F_c|)^2$ resulted in $R = 0.129$. At this stage, following the difficulty in distinguishing Na^+ ions from water molecules, the differential thermal analysis was carried out and the Na^+ -ion concentration determined. By carefully examining the coordination spheres of the regions of electron density corresponding to Na^+ ions and/or water molecules a distribution of these species was decided upon.

An absorption correction was applied to the data and following a number of cycles of refinement, allowing all permitted parameters to refine, structure converged at $R_w = 0.0545$, $R = 0.0514$; a total of 188 parameters was refined; final difference synthesis had no electron density $> 2.16 \text{ e \AA}^{-3}$, this being in the vicinity of $AQ(9)$, perhaps suggesting some disorder amongst the molecules of water of crystallization; largest shift-to-e.s.d. ratio in final cycle 0.027 for U of $AQ(7)$; scattering factors for neutral atoms taken from *International Tables for X-ray Crystallography* (1974) and corrected for anomalous dispersion; all calculations carried out on the Monash University B6700 computer; major programs used: *SHELX 76* (Sheldrick, 1976), *ORFFE* (Busing, Martin & Levy, 1964), *MEANPL* (Blow, 1960) and *ORTEP* (Johnson, 1965).

Discussion. Final atomic parameters are in Table 1* and interatomic distances in Table 2.

The novel structure of the idealized polyanion is shown in Fig. 1; Fig. 2 shows the actual anion viewed along the twofold axis that runs through the anion, atoms O(6), O(13) and Na(2) being located on this axis. Fig. 3 shows an exploded view of the anion together with the atom-numbering scheme used. The idealized $[\text{P}_4\text{W}_8\text{O}_{40}]^{12-}$ anion has $\bar{4}2m$ symmetry and consists of a shell of WO_6 octahedra and PO_4 tetrahedra made up of four $[\text{PW}_2\text{O}_{13}]$ groups linked by corner-sharing, thus closely resembling the 'shell' of the Keggin anion (Keggin, 1934) that consists of four $[\text{M}_3\text{O}_{13}]$ groups also linked by corner-sharing to form $[\text{X}^n\text{M}_{12}\text{O}_{40}]^{(8-n)-}$. In both anions the octahedra within the groups are edge-shared.

Deviations from the $\bar{4}2m$ symmetry of the idealized anion are not large (Table 2a); for example, the pair of distances W(1)–W(3) and W(2)–W(4) are identical within the errors but W(3)–W(3') and W(4)–W(4') differ by a small, but significant amount, whereas in the ideal $\bar{4}2m$ symmetry these would be identical. The angles W(4)–W(2)–W(1), $115.80(4)^\circ$, and W(3)–W(1)–W(2), $116.35(5)^\circ$, also indicate a reduction in symmetry from the ideal.

The W...W distances are typical of similar iso- and heteropolyanions. Thus the edge-shared distance is $3.342(2) \text{ \AA}$ compared with averaged edge-shared distances of 3.326 and 3.28 \AA in $\text{Mg}_5[\text{H}_5\text{W}_{12}\text{O}_{42}]\cdot 38\text{H}_2\text{O}$ (Tsay & Silvertown, 1973) and $[(\text{C}_4\text{H}_9)_4\text{N}]_2[(\text{W}_6\text{O}_{19})]$ (Henning & Hüllen, 1969), respectively. The W...W corner-shared distances range from $3.720(2)$ to $3.740(3) \text{ \AA}$ here, compared with the averaged analogous distance of 3.748 \AA in the above dodecapolytungstate anions.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38393 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ($\times 10^4$) and thermal parameters with e.s.d.'s in parentheses

AQ denotes water O atoms.

	x	y	z	$U(\text{\AA}^2 \times 10^3)$
W(1)	2139 (1)	-345 (1)	2295 (1)	•
W(2)	3593 (1)	932 (1)	2088 (1)	•
W(3)	1896 (1)	-1628 (1)	834 (1)	•
W(4)	3344 (1)	2203 (1)	614 (1)	•
P(1)	1927 (4)	1234 (4)	1174 (5)	12 (2)
P(2)	3443 (4)	-668 (4)	974 (5)	10 (2)
O(1)	1834 (9)	414 (10)	1355 (11)	15 (5)
O(2)	2724 (10)	1353 (10)	1209 (12)	17 (5)
O(3)	1167 (9)	1329 (10)	250 (11)	15 (5)
O(4)	1612 (9)	1716 (10)	1745 (11)	16 (5)
O(5)	2922 (10)	293 (11)	2457 (12)	23 (5)
O(6)	$\frac{1}{2}$	2461 (13)	0	6 (6)
O(7)	3621 (9)	120 (10)	1112 (11)	15 (5)
O(8)	4355 (10)	571 (11)	2566 (13)	25 (5)
O(9)	3963 (8)	1573 (9)	1268 (10)	8 (4)
O(10)	3421 (10)	1638 (11)	2776 (12)	19 (5)
O(11)	3213 (9)	2821 (11)	1412 (12)	19 (5)
O(12)	3927 (9)	2681 (10)	61 (12)	15 (5)
O(13)	$\frac{1}{2}$	-1853 (13)	0	9 (6)
O(14)	1508 (9)	-968 (10)	1619 (11)	14 (4)
O(15)	2301 (10)	-2216 (11)	1587 (12)	21 (5)
O(16)	1172 (9)	-2132 (10)	522 (12)	18 (5)
O(17)	1578 (10)	-760 (10)	-23 (12)	18 (5)
O(18)	2674 (9)	-759 (9)	1202 (11)	12 (4)
O(19)	2511 (10)	-1045 (10)	2912 (12)	18 (5)
O(20)	1589 (11)	32 (11)	2933 (13)	28 (6)
O(21)	3902 (10)	-1187 (11)	1489 (12)	23 (5)
Na(1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	22 (4)
Na(2)	$\frac{1}{2}$	259 (9)	0	27 (4)
Na(3)	8300 (7)	1929 (7)	2468 (8)	34 (3)
Na(4)	1026 (6)	1259 (6)	2832 (7)	23 (3)
Na(5)	775 (6)	2588 (7)	1320 (8)	30 (3)
Na(6)	4449 (11)	725 (11)	165 (13)	89 (6)
Na(7)	1720 (12)	245 (12)	4598 (13)	101 (7)
AQ(1)	268 (11)	2391 (12)	2682 (14)	32 (6)
AQ(2)	9147 (13)	1624 (14)	3584 (15)	50 (7)
AQ(3)	6015 (12)	2050 (12)	2743 (14)	39 (6)
AQ(4)	700 (12)	1002 (13)	4216 (14)	42 (7)
AQ(5)	9927 (16)	1749 (17)	625 (19)	78 (10)
AQ(6)	55 (16)	620 (17)	2206 (20)	76 (10)
AQ(7)	6829 (28)	1736 (29)	4240 (32)	190 (23)
AQ(8)	2762 (13)	927 (14)	4212 (15)	50 (7)
AQ(9)	5486 (15)	116 (17)	858 (18)	72 (9)
AQ(10)	4925 (17)	1334 (18)	3956 (21)	87 (11)

* Anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

$$\text{where } T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W(1)	134 (7)	133 (7)	122 (7)	17 (6)	7 (5)	9 (6)
W(2)	125 (7)	127 (6)	106 (7)	-23 (5)	-26 (5)	9 (5)
W(3)	150 (7)	119 (7)	129 (7)	31 (5)	-3 (5)	-16 (5)
W(4)	110 (6)	127 (6)	110 (6)	-24 (6)	1 (5)	-22 (5)

Table 2. Interatomic distances

(a) Selected interatomic distances (\AA) with e.s.d.'s in parentheses

W(1)—W(3)	3.342 (2)	Edge-shared WO_6 octahedra	
W(2)—W(4)	3.342 (2)		
W(4)—W(4')	3.720 (2)		
W(1)—W(2)	3.730 (2)	Corner-shared WO_6 octahedra	
W(3)—W(3')	3.740 (3)		
W(1)—W(4')	6.647 (2)		
W(2)—W(3')	6.679 (2)		
P(1)—W(4')	3.400 (8)	P(2)—W(3')	3.433 (7)
W(1)	3.426 (7)	W(2)	3.445 (7)
W(4)	3.486 (8)	W(3)	3.501 (7)
W(2)	3.520 (7)	W(1)	3.521 (8)
P(1')	4.58 (2)	P(2')	4.66 (1)
P(2)	4.62 (1)	P(1')	4.94 (1)
W(1)—O(20)	1.70 (2)	W(2)—O(8)	1.76 (2)
O(19)	1.75 (2)	O(10)	1.76 (2)
O(5)	1.93 (2)	O(5)	1.90 (2)
O(14)	1.95 (2)	O(9)	1.96 (2)
O(1)	2.11 (2)	O(7)	2.18 (2)
O(18)	2.26 (2)	O(2)	2.26 (2)

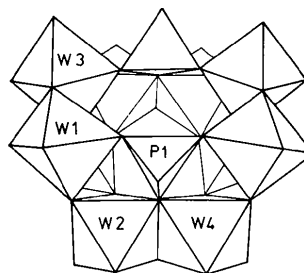
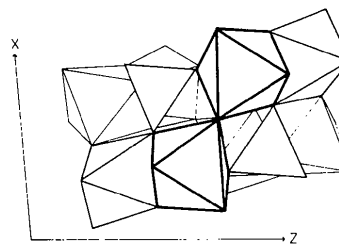
Table 2 (cont.)

W(3)—O(16)	1.74 (2)	W(4)—O(12)	1.75 (2)
O(15)	1.77 (2)	O(11)	1.75 (2)
O(13)	1.92 (1)	O(6)	1.92 (1)
O(14)	1.95 (2)	O(9)	1.93 (2)
O(17)	2.17 (2)	O(3')	2.13 (2)
O(18)	2.25 (2)	O(2)	2.25 (2)
P(1)—O(4)	1.45 (2)	P(2)—O(7)	1.50 (2)
O(1)	1.55 (2)	O(21)	1.52 (2)
O(3)	1.55 (2)	O(17')	1.55 (2)
O(2)	1.58 (2)	O(18)	1.59 (2)
Na(1)—O(11)	2.41 (2) \times 2	Na(2)—O(17)	2.60 (2) \times 2
O(10)	2.42 (2) \times 2	O(3)	2.61 (2) \times 2
O(4)	2.50 (2) \times 2	O(1)	2.66 (2) \times 2
O(2)	3.02 (2) \times 2	O(18)	2.70 (2) \times 2
		O(7)	2.74 (2) \times 2
		O(2)	2.81 (2) \times 2
Na(3)—AQ(3 ^{II})	2.35 (3)	Na(4)—O(4)	2.34 (2)
O(15 ^{III})	2.39 (2)	AQ(6)	2.39 (3)
O(19 ^{III})	2.40 (2)	AQ(4)	2.43 (3)
AQ(2)	2.42 (3)	O(11')	2.50 (2)
O(21 ^{III})	2.47 (2)	O(20)	2.51 (2)
O(15')	2.55 (2)	AQ(1)	2.56 (2)
O(18 ^{III})	3.15 (2)	Na(6)—AQ(9 ^{III})	2.27 (4)
Na(5)—O(4)	2.36 (2)	O(3')	2.50 (3)
O(12')	2.36 (2)	AQ(9)	2.50 (4)
AQ(10')	2.43 (3)	O(7)	2.58 (3)
AQ(5')	2.47 (3)	O(9)	2.61 (3)
O(10')	2.50 (2)	AQ(5 ^{III})	2.63 (4)
AQ(1)	2.52 (3)		
Na(7)—AQ(8 ^{II})	2.45 (3)		
AQ(4)	2.47 (3)		
AQ(8)	2.52 (4)		
O(20)	2.71 (3)		

Symmetry code: (i) $\frac{1}{2}-x, y, -z$; (ii) $\frac{3}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, -y, z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (vi) $-1+x, y, z$; (vii) $1-x, -y, -z$; (viii) $\frac{3}{2}-x, y, -z$; (ix) $\frac{1}{2}-x, y, 1-z$.

(b) Summary of $d(\text{W}-\text{O})$ vs oxygen type

Oxygen type	No. of type/asymmetric unit	Range (\AA)	Mean W—O (\AA)
A	8	1.70–1.77	1.75 (2)
B	5	1.90–1.96	1.92 (2)
C	4	2.11–2.18	2.15 (3)
D	2	2.25	2.25

Fig. 1. An idealized view of the heteropolyanion $[\text{P}_4\text{W}_8\text{O}_{40}]^{12-}$.Fig. 2. A non-idealized view, approximately along the twofold axis, of the anion $[\text{P}_4\text{W}_8\text{O}_{40}]^{12-}$.

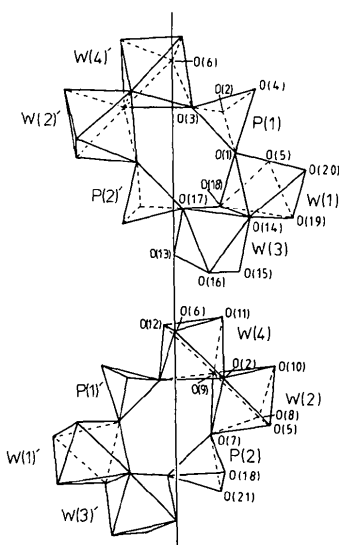


Fig. 3. An exploded view of the anion showing two layers of octahedra and tetrahedra about the common twofold axis, together with the numbering scheme used.

The anion O atoms have been classified into types according to the heavier atoms to which they are bound: type *A* O is bound to one W atom only, type *B* to two W atoms, type *C* to one P and one W atom, and type *D* to one P and two W atoms. A summary is given in Table 2(b) of the number of each type of O atom and the W—O distances. The W—O bond length increases steadily as the O atom becomes increasingly shared. Each of the WO_6 octahedra contains a pair of *cis*-unshared (type *A*) O atoms, and the angles of the 'V-shaped' O—W—O groups so formed are less than the average value, 105.2° (Evans, Gatehouse & Leverett, 1975), in iso- and heteropolymolybdates. The particular angles are O(12)—W(4)—O(11), O(15)—W(3)—O(16), O(8)—W(2)—O(10) and O(19)—W(1)—O(20) with values of $101.3(9)$, $100.7(9)$, $101.6(9)$ and $102.0(9)^\circ$, respectively.

The P—O distances do not vary greatly (range 1.45–1.59 Å, mean 1.54 Å), and the O—P—O angles in the PO_4 tetrahedra range from $104(1)$ – $116(1)^\circ$ with mean of 109° , indicating that the tetrahedral group is less sensitive to the oxygen type than are the tungsten polyhedra.

In common with $[H_4As_4Mo_{12}O_{50}]^{4-}$ (Nishikawa & Sasaki, 1975), $[P_4W_8O_{40}]^{12-}$ consists of a 'shell' of octahedra and tetrahedra with a large hole in the centre of the anion. The radii of these cavities are about 2.8 and 2.6 Å respectively, both too large to accommodate a central atom of the type found in the Keggin anions, $[X^nM_{12}O_{40}]^{(8-n)-}$, in which the X_t —O distances are usually in the range 1.6–1.9 Å. A remarkable feature of the $[P_4W_8O_{40}]^{12-}$ anion is the presence of a sodium ion, $Na(2)^+$, in the centre of the anion on the twofold axis and coordinated to 12 of the inner anion O atoms with coordination distances of 2.60–2.81 (2) Å, mean

2.69 Å. This cage-type inclusion of a cation has also been observed for $(NH_4)_{17}Na[NaW_{21}Sb_9O_{86}]\cdot 14H_2O$ (Fischer, Ricard & Weiss, 1976) in which the cryptate Na^+ ion is six-coordinate, the Na—O distance being 2.44 (5) Å with a further weak Na—O interaction at 2.91 (8) Å giving an overall coordination of 12.

The compound described here should perhaps be written as $Na_{11}[NaP_4W_8O_{40}]\cdot 20H_2O$ to emphasize the cryptate nature of the heteropolyanion.

The remaining Na^+ ions and water molecules are distributed between the anions in the unit cell, but special mention should be made of $Na(1)^+$. This ion is eight-coordinate linking through O(2), O(4), O(10) and O(11) of two anion units. $Na(1)^+$ is the only non-cryptate sodium ion or water molecule whose nearest neighbours are only anion O atoms, and it therefore plays an important part in the overall anion-packing scheme.

Other than the cryptate $Na(2)^+$ ion, $Na(1)^+$ has the highest coordination number, there being one seven-coordinate sodium ion, $Na(3)^+$, three six-coordinate ions, $Na(4)^+$, $Na(5)^+$ and $Na(6)^+$, and one that is four-coordinate to within the limits of this structure determination.

This work forms part of a research project supported by the Australian Research Grants Committee.

References

- BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.
 EVANS, H. T. JR, GATEHOUSE, B. M. & LEVERETT, P. (1975). *J. Chem. Soc. Dalton Trans.* pp. 505–514.
 FILOWITZ, M. & KLEMPERER, W. G. (1976). *J. Chem. Soc. Chem. Commun.* pp. 233–234.
 FILOWITZ, M. & KLEMPERER, W. G. (1977). *J. Chem. Soc. Chem. Commun.* pp. 201–202.
 FISCHER, J., RICARD, L. & WEISS, R. (1976). *J. Am. Chem. Soc.* **98**, 3050–3052.
 GATEHOUSE, B. M. & JOZSA, A. J. (1977). *J. Chem. Soc. Chem. Commun.* pp. 674–675.
 HENNING, G. & HÜLLEN, A. (1969). *Z. Kristallogr.* **130**, 162–172.
 HORNSTRA, J. & STUBBE, B. (1972). *PW1100 Data Processing Program*. Philips Research Laboratories, Eindhoven, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 148. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 KAZANSKII, L. P., TORCHENKOVA, E. A. & SPITSYN, V. I. (1974). *Russ. Chem. Rev.* **43**(7), 525–538.
 KEGGIN, J. F. (1934). *Proc. R. Soc. London Ser. A*, **144**, 75–100.
 KEHRMANN, F. & MELLET, T. (1923). *Helv. Chim. Acta*, **6**, 443–449.
 KWAK, W., RAJKOVIC, L. M., STALICK, J. K., POPE, M. L. & QUICKSALL, C. O. (1976). *Inorg. Chem.* **15**, 2778–2783.
 NISHIKAWA, T. & SASAKI, Y. (1975). *Chem. Lett.* pp. 1185–1186.
 SHELDRIK, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.
 TSAY, Y. H. & SILVERTON, J. V. (1973). *Z. Kristallogr.* **137**, 256–279.
 WEAKLEY, T. J. R. (1974). *Struct. Bonding*, **18**, 131–176.