

A Heteropolyanion with Fivefold Molecular Symmetry That Contains a Nonlabile Encapsulated Sodium Ion. The Structure and Chemistry of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$

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Contribution from the Laboratoire de Chimie des Métaux de Transition, CNRS-ERA 608, France, Université Pierre et Marie Curie, 4, Place Jussieu, 75230 Paris Cedex 05, France, and the Department of Chemistry, Georgetown University, Washington, DC 20057.
Received November 7, 1984

Abstract: The title anion is formed as a byproduct in the synthesis of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and was first recognized by C. Preysslér [Bull. Soc. Chim. Fr. 1970, 30], who assigned it the formula $[\text{HP}_3\text{W}_{18}\text{O}_{66}]^{8-}$. Unit cell dimensions and densities of the potassium, ammonium, and barium salts now reveal a P_5W_{30} stoichiometry. A crystallographic investigation of $(\text{NH}_4)_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}\cdot 31\text{H}_2\text{O}$ (triclinic, $P\bar{1}$; $a = 23.570$ (7) Å, $b = 17.821$ (5) Å, $c = 17.593$ (9) Å; $\alpha = 112.17$ (3)°, $\beta = 98.10$ (3)°, $\gamma = 96.84$ (3)°; $V = 6654$ Å³; $Z = 2$; density 3.97 (obsd), 4.11 g cm⁻³ (calcd)) has been carried out by using 6341 reflections (Mo K α radiation) and refined to a conventional R of 0.055. The anion structure has approximate D_{5h} symmetry and consists of a cyclic assembly of five PW_6O_{22} units, each derived from the Keggin anion, $[\text{PW}_{12}\text{O}_{40}]^{3-}$, by removal of two sets of three corner-shared WO_6 octahedra. A sodium ion is located within the polyanion on the fivefold axis and 1.25 Å above the pseudomirror plane that contains the five phosphorus atoms. The reduction in symmetry caused by the sodium ion accounts for the previously reported four-line ¹⁸³W NMR spectrum. A further reduction in symmetry to a chiral C_5 structure may be considered from systematic W atom displacements. Exchange of internal and external (cationic) sodium is very slow, and separate ²³Na NMR resonances are observed in aqueous (D_2O) solutions for the cation (0 ppm, $\Delta\nu_{1/2}$ 30 Hz) and heteropolyanion (-21 ppm, 460 Hz). The internal sodium cannot be removed by conventional ion-exchange techniques, and the heteropolyanion could not be synthesized in the absence of Na^+ . Under extreme conditions (several hours at 120 °C, pH 8-9) the internal Na^+ could be displaced by Ca^{2+} and (partly) by Mg^{2+} . The heteropolyanion is hydrolytically stable at room temperature from pH 0-11 and is reducible to heteropoly blue species. Solutions of the four- and eight-electron reduced species each show a single unbroadened ³¹P NMR line, which implies that cyclic valence delocalization is rapid on the NMR time scale. Two isomers of the vanadium-substituted anion, $[\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{15-}$, have been prepared and separated by chromatography on modified Sephadex. The isomers are distinguishable by the ESR parameters of the vanadium(IV) derivatives: A— $g_{\parallel} = 1.904$, $g_{\perp} = 1.928$, $A_{\parallel} = 191$ G, $A_{\perp} = 50$ G; B— $g_{\parallel} = 1.889$, $g_{\perp} = 1.936$, $A_{\parallel} = 185$ G, $A_{\perp} = 52$ G. Provisional structural assignments are given on the basis of these data and ³¹P NMR.

Interest in the chemistry of large polytungstates has recently increased, and some examples of species containing more than 18 tungsten atoms have been prepared.³ In the course of preparing ammonium octadecatungstodiphosphate by Wu's method,⁴ Preysslér⁵ observed white crystals, which formed before the desired yellow $(\text{NH}_4)_6\text{P}_2\text{W}_{18}\text{O}_{62}$ and which contained phosphorus and tungsten. From chemical analysis of several salts, potentiometric titration curves, and cryoscopic measurements in saturated sodium sulfate, it was inferred that these crystals were ammonium 18-tungsto-3-phosphate, $(\text{WO}_3)_{18}(\text{PO}_4)_3\text{H}(\text{NH}_4)_8\cdot 30\text{H}_2\text{O}$. Massart et al.⁶ later showed from ³¹P NMR measurements that all the phosphorus atoms of this polytungstate were equivalent. The ¹⁸³W NMR spectrum, which was recorded independently by Acerete⁷ and Doppelt,⁸ consists of four lines (intensities 2:2:1:1) and was interpreted as indicating a different stoichiometry than that proposed by Preysslér. A crystallographic investigation of the potassium salt was begun at Georgetown University in 1979 in conjunction with work involving vanadium-substituted derivatives, the analyses of which also suggested a larger anion. The data

set collected at that time would not yield a satisfactory refinement, although as it now turns out the main features of the structure could be discerned.⁹ During the search for a more suitable crystal prior to collecting a fresh data set, work began on the ammonium salt at the Université Pierre et Marie Curie in Paris and the present collaboration was initiated.

Experimental Section

Preparation of Compounds. (a) **Preysslér's Anion.** The ammonium and potassium salts were prepared following Preysslér's method, or a slight variation thereof. Yields could be increased from ca. 10% to ca. 30% by heating the reaction mixture in a sealed container at 120 °C (see Results section). A barium salt was isolated by adding 5 mL of saturated BaCl_2 to a solution of 6.3 g of the potassium salt in ca. 10 mL of water. The white precipitate was filtered off, washed, and recrystallized from hot water. The free acid was prepared by passage of a solution of 11.4 g of the potassium salt in 20 mL of water through a column (50 × 1 cm) of Dowex 50W×8 in the H^+ form and evaporation of the eluate to dryness in vacuo.

The analytical results are presented in terms of the P_5W_{30} stoichiometry revealed by the crystallographic measurements. Anal. Calcd (Found) for $(\text{NH}_4)_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}\cdot 31\text{H}_2\text{O}$: N, 2.37 (2.22); Na, 0.28 (0.29); P, 1.87 (1.77); W, 66.74 (65.72). For $\text{K}_{12.5}\text{Na}_{2.5}\text{P}_5\text{W}_{30}\text{O}_{110}\cdot 15\text{H}_2\text{O}$: K, 5.92 (5.75); Na, 0.70 (0.45); P, 1.88 (1.93); W, 66.90 (66.90); H, 0.36 (0.60). For $\text{Ba}_{6.5}\text{KNaP}_5\text{W}_{30}\text{O}_{110}\cdot 56\text{H}_2\text{O}$: Ba, 9.54 (9.60); K, 0.41 (0.19); Na, 0.24 (0.16); P, 1.66 (1.70); W, 58.96 (58.83); H, 1.19 (1.10). For $\text{H}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}\cdot 58\text{H}_2\text{O}$: H, 1.57 (1.74); Na, 0.27 (0.21); P, 1.82 (1.86); W, 64.80 (64.82). Unit cell and density measurements were made on crystals of the ammonium salt (triclinic, see below), the potassium salt (orthorhombic, $P2_12_12_1$; $V = 11900$ Å³; $Z = 4$) and the barium salt (monoclinic, $C2/m$; $V = 14430$ Å³; $Z = 4$).

(b) **Vanadium-Substituted Anions.** A solution of 5 g of the potassium salt of Preysslér's anion in 25 mL of water at 60 °C was treated dropwise with 0.3 M NaOH until a drop of the reaction mixture gave a purple

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color when tested with a solution of $VOSO_4$. The pH of the solution at this stage was about 12. Addition of alkali was continued at such a rate that the pH did not exceed 12 over a period of 4–5 h at 60–70 °C. The total volume of alkali added was ca. 25 mL. After the solution had been cooled, addition of saturated KCl yielded a white precipitate that was filtered off, washed with 1 M KCl and air dried. About 2 g of this material was added to a solution of 0.1 g of $VOSO_4$ in 25 mL of acetate buffer (pH 4.7) whereupon it dissolved to give a purple solution. Addition of saturated KCl precipitated a purple solid that was separated, washed, and recrystallized from hot water to give dark rectangular blocks. Anal. Calcd (Found) for $K_2Na_{11}P_5W_{29}VO_{110} \cdot 40H_2O$: K, 2.76 (2.7); Na, 2.97 (3.2); P, 1.88 (1.82); W, 62.74 (62.3); V, 0.60 (0.78). Further characterization of this material is described in the Results section.

Analyses. Unless otherwise indicated, elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN, or by the Centre de Microanalyse de CNRS, Lyon, France. Sodium ion activities were measured with a sodium electrode (Orion Model 94-11). All such measurements were made in an ammonia buffer (20 g of NH_4Cl and 5 mL of 18 M NH_3 in 100 mL, pH 8.5) contained in a teflon beaker. The electrode response was found to be linear up to $[Na^+] = 0.01 M$, and all unknown concentrations were confirmed by repeat measurements on standard solutions.

Physical Measurements. Electrochemical and electron spin resonance measurements were made as described previously.¹⁰ All ESR parameters were confirmed by simulation of the experimental spectra. Nuclear magnetic resonance spectra were recorded on 90-, 400-, and 500-MHz Bruker spectrometers. Experimental details are given below.

Crystallography. Preliminary precession photographs of the ammonium salt showed a triclinic unit cell. A crystal shaped approximately as a parallelepiped ($0.25 \times 0.08 \times 0.08$ mm) sealed into a Lindemann capillary was set on a Philips PW 1100 diffractometer. Lattice constants calculated by least squares-refinement from 25 reflections are as follows: $a = 23.570$ (7) Å, $b = 17.821$ (5) Å, $c = 17.593$ (9) Å, $\alpha = 112.17$ (3)°, $\beta = 98.10$ (3)°, $\gamma = 96.84$ (3)°, and $V = 6654$ Å³. The density, measured in cyclohexane by pycnometry, was 3.97 g cm⁻³. The calculated value, assuming two molecules of $[P_5W_{30}O_{110}]^{15-}$ per cell, is 4.11 g cm⁻³.

A total of 9173 independent reflections were collected at room temperature: Mo $K\alpha$ radiation; scan type θ - 2θ ; scan speed 0.01 deg s⁻¹; scan length $(0.90 + 0.30 \tan \theta)$ deg; background measurements in fixed position before and after every scan for a time equal to half of the scan time; maximum recording angle $\theta = 18^\circ$; standard reflections 3,0,9, 12,1,1, and 3,0,9, measured every 2 h. No decrease of standards was observed. For every observed structure factor, F_o , a standard deviation was computed as $\sigma = F_o \Delta I / 2I$ (I is the integrated intensity and ΔI its statistical error). Only 6341 reflections with an observed structure factor greater than 6σ were kept for refinement. Lorentz and polarization corrections were applied. For Mo $K\alpha$ radiation the absorption coefficient is $\mu = 249$ cm⁻¹. Since the crystal used for recording data was set in a Lindemann capillary glass, its faces were not easily seen. An empirical correction was therefore applied for absorption.¹¹

Statistical tests¹² were computed with the whole set of collected reflections and showed centrosymmetry. The asymmetric unit is therefore P_5W_{30} , and the space group is PI .

From the Patterson map, 20 peaks corresponding to two parallel planar decagons were found and attributed to tungsten atoms. A Fourier synthesis phased on F_o 's computed on the preceding basis showed all the tungsten and phosphorus atoms. The oxygen atoms were then located from a difference Fourier synthesis. At this stage of the structure resolution two peaks of weak but equal intensity were observed inside the polyanion on its internal symmetry axis. From the analytical results the peaks were assigned to one sodium atom with a statistical distribution between those two observed positions. Nineteen other peaks were attributed to the nitrogen atoms of the ammonium cations and to the oxygen atoms of the water molecules. However, it was not possible to distinguish between N and O. Such a difficulty is often encountered in structure determinations of this type.¹³

Refinements were made with the SHELX program.¹⁴ Because of the large number of parameters, the refinement was first made by dividing the anion into ten blocks. Cations and water molecules were refined afterwards, keeping the atomic parameters of the anion atoms fixed. The

Table I. Atomic Coordinates of W Atoms

atom	X/A	Y/B	Z/C
W(1)	-0.3021 (1)	-0.0861 (2)	0.0744 (2)
W(2)	-0.3274 (1)	0.0406 (2)	0.2910 (2)
W(3)	-0.3498 (1)	0.2458 (2)	0.4371 (2)
W(4)	-0.3616 (1)	0.4619 (2)	0.4519 (2)
W(5)	-0.3571 (1)	0.6044 (2)	0.3400 (2)
W(6)	-0.3380 (1)	0.6115 (2)	0.1322 (2)
W(7)	-0.3134 (1)	0.4939 (2)	-0.0842 (2)
W(8)	-0.2910 (1)	0.2829 (2)	-0.2262 (2)
W(9)	-0.2796 (1)	0.0676 (2)	-0.2476 (2)
W(10)	-0.2834 (1)	-0.0708 (2)	-0.1285 (2)
W(11)	-0.1614 (1)	-0.0193 (2)	0.1633 (2)
W(12)	-0.1870 (1)	0.1108 (2)	0.3783 (2)
W(13)	-0.2091 (1)	0.3229 (2)	0.5107 (2)
W(14)	-0.2199 (1)	0.5381 (2)	0.5221 (2)
W(15)	-0.2133 (1)	0.6661 (2)	0.3946 (2)
W(16)	-0.1937 (1)	0.6685 (2)	0.1846 (2)
W(17)	-0.1691 (1)	0.5350 (2)	-0.0261 (2)
W(18)	-0.1470 (1)	0.3233 (2)	-0.1658 (2)
W(19)	-0.1371 (1)	0.1133 (2)	-0.1695 (2)
W(20)	-0.1417 (1)	-0.0221 (2)	-0.0458 (2)
W(21)	-0.4053 (1)	0.1741 (2)	0.2125 (2)
W(22)	-0.4162 (1)	0.3853 (2)	0.2229 (2)
W(23)	-0.3977 (1)	0.3880 (2)	0.0162 (2)
W(24)	-0.3755 (1)	0.1795 (2)	-0.1192 (2)
W(25)	-0.3803 (1)	0.0463 (2)	0.0010 (2)
W(26)	-0.0885 (1)	0.1665 (2)	0.1430 (2)
W(27)	-0.1131 (1)	0.2911 (2)	0.3557 (2)
W(28)	-0.1249 (1)	0.5027 (2)	0.3700 (2)
W(29)	-0.1060 (1)	0.5088 (2)	0.1653 (2)
W(30)	-0.0838 (1)	0.3016 (2)	0.0246 (2)

Table II. Anisotropic Thermal Parameters of W Atoms^a

atom	B(11)	B(22)	B(33)	B(12)	B(13)	B(23)
W(1)	3.3 (2)	1.0 (2)	2.8 (2)	0.7 (1)	0.9 (1)	1.6 (2)
W(2)	3.4 (2)	1.6 (2)	2.9 (2)	0.8 (1)	0.8 (1)	2.1 (2)
W(3)	3.1 (2)	2.3 (2)	2.0 (2)	0.9 (1)	0.9 (1)	1.7 (2)
W(4)	2.9 (2)	1.8 (2)	1.8 (2)	0.9 (1)	0.8 (1)	1.1 (2)
W(5)	2.7 (2)	1.1 (2)	2.5 (2)	1.0 (1)	0.6 (1)	1.0 (2)
W(6)	2.2 (2)	1.0 (2)	2.7 (2)	0.8 (1)	0.4 (1)	1.3 (2)
W(7)	2.4 (2)	1.9 (2)	2.5 (2)	0.8 (1)	0.5 (1)	1.9 (2)
W(8)	2.5 (2)	2.1 (2)	2.0 (2)	0.7 (1)	0.4 (1)	1.7 (2)
W(9)	3.0 (2)	1.3 (2)	1.6 (2)	0.6 (1)	0.4 (1)	0.8 (1)
W(10)	3.2 (2)	0.8 (2)	1.9 (2)	0.5 (1)	0.6 (1)	0.5 (1)
W(11)	3.1 (2)	1.5 (2)	2.7 (2)	1.2 (1)	0.7 (1)	1.8 (2)
W(12)	3.5 (2)	2.4 (2)	2.5 (2)	1.4 (1)	0.6 (1)	2.2 (2)
W(13)	3.2 (2)	2.4 (2)	1.4 (2)	1.0 (1)	0.4 (1)	1.2 (2)
W(14)	3.3 (2)	1.0 (2)	1.4 (2)	0.8 (1)	0.3 (1)	0.7 (2)
W(15)	2.9 (2)	0.8 (2)	2.3 (2)	0.4 (1)	0.3 (1)	0.4 (1)
W(16)	2.4 (2)	0.6 (2)	3.0 (2)	0.4 (1)	0.5 (1)	1.1 (1)
W(17)	2.3 (2)	1.5 (2)	2.6 (2)	0.6 (1)	0.8 (1)	1.6 (2)
W(18)	2.3 (2)	1.8 (2)	2.3 (2)	0.8 (1)	0.9 (1)	1.7 (2)
W(19)	2.5 (2)	1.4 (2)	2.2 (2)	1.0 (1)	0.9 (1)	1.1 (1)
W(20)	2.8 (2)	1.5 (2)	2.4 (2)	1.3 (1)	0.9 (1)	1.3 (2)
W(21)	2.1 (2)	1.1 (2)	2.0 (2)	0.4 (1)	0.4 (1)	1.3 (1)
W(22)	1.7 (1)	1.3 (2)	2.0 (2)	0.5 (1)	0.3 (1)	1.2 (1)
W(23)	1.7 (1)	1.4 (2)	2.0 (2)	0.5 (1)	0.2 (1)	1.2 (1)
W(24)	1.8 (1)	1.3 (2)	1.8 (2)	0.3 (1)	0.1 (1)	1.2 (1)
W(25)	2.3 (2)	1.0 (2)	1.9 (2)	0.3 (1)	0.3 (1)	1.1 (1)
W(26)	2.1 (1)	1.4 (2)	2.2 (2)	0.9 (1)	0.4 (1)	1.3 (1)
W(27)	2.3 (2)	1.9 (2)	1.9 (2)	0.8 (1)	0.1 (1)	1.3 (2)
W(28)	2.0 (2)	1.4 (2)	2.1 (2)	0.3 (1)	-0.0 (1)	0.8 (1)
W(29)	1.7 (1)	1.1 (2)	2.4 (2)	0.5 (1)	0.4 (1)	1.0 (1)
W(30)	1.9 (1)	1.2 (2)	2.2 (2)	0.7 (1)	0.5 (1)	1.2 (1)

^a The anisotropic temperature factor is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

isotropic temperature factors of structurally similar oxygen atoms were kept equal by using the constraints of the SHELX program. A final R value of 0.055 was obtained with anisotropic temperature factors for tungsten only. Atomic form factors were taken from Cromer and Waber.¹⁵ Corrections were made for the real and imaginary parts of the anomalous dispersion. Oxygen atomic form factors were arbitrarily

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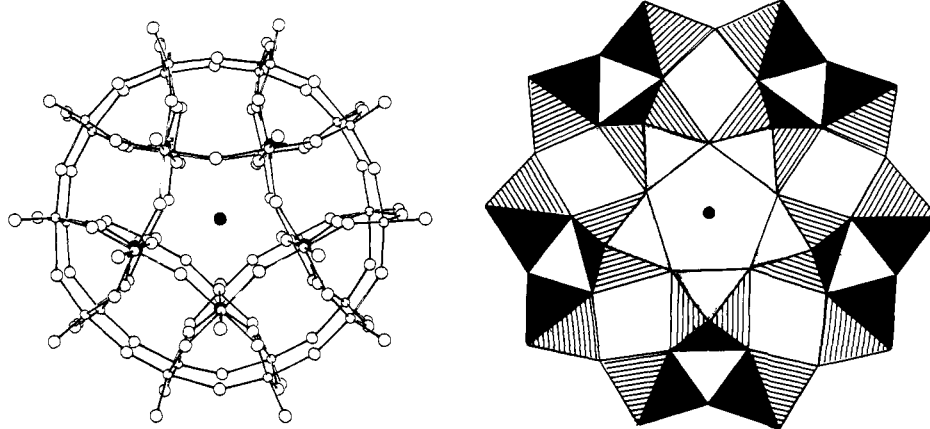


Figure 1. (a, left) An ORTEP view of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ looking approximately along the virtual C_5 symmetry axis. Oxygen and tungsten atoms are represented as large and small open circles, respectively, and the sodium ion by the central closed circle. The phosphorus atoms are shown as closed circles that are almost entirely obscured by the inner pentagon of five tungsten atoms. (b, right) An idealized view along C_5 showing the WO_6 octahedra in the upper half of the anion.

assigned to both nitrogen atoms of ammonium cations and oxygen atoms of water molecules. Only 19 of these atoms were included in the final refinement (those with temperature factors less than an arbitrary limit of 14 \AA^2), although the chemical analysis indicated 14 ammonium cations and 31 water molecules. It was assumed that higher temperature factors correspond to disordered atoms as is usually encountered in polyanion structures.

Final atomic coordinates, vibrational parameters, and corresponding standard deviations are given in Tables I-III.

Results and Discussion

Stoichiometry and Structure of the Anion. The unit cell of the ammonium salt contains two $[\text{P}_5\text{W}_{30}\text{O}_{110}]^{15-}$ anions related by the center of symmetry. The anions appear as ellipsoids (prolate spheroids) and each is built of five PW_6 units arranged in a crown so that the whole anion has an internal fivefold symmetry axis (Figure 1). Perpendicular to this axis is a mirror plane that contains the five phosphorus atoms. The tungsten atoms are distributed in four parallel planes perpendicular to the axis: each of the outer planes contains five tungsten atoms; each of the inner ones contains ten tungsten atoms. A PW_6 unit consists of two groups of three corner-shared WO_6 octahedra. Two pairs of octahedra of each group are joined together by sharing one edge located in the mirror plane. Each WO_6 octahedron shares a vertex with the central PO_4 tetrahedron as shown in Figure 2. The PW_6 unit is formally derived from the well-known Keggin structure. Removal of a corner-shared W_3O_{13} unit from the latter leads to the structure of the PW_9 moiety of the P_2W_{18} (Dawson) anion.¹⁶ Removal of a second such W_3 group leads to the PW_6 unit of P_5W_{30} (see Figure 3). Each PW_6 unit is bound to two other such units by eight oxygen atoms, making only corner-shared octahedra (Figure 2). As in the Keggin and Dawson structures, all tungsten atoms are octahedrally surrounded by oxygen atoms. Each octahedron contains only one $\text{W}=\text{O}$ double bond which is directed toward the exterior of the polyanion.

The main bond lengths and angles are listed in Table IV. These are all unexceptional, but we note systematic displacements of the tungsten atoms in the "equatorial" rings. These displacements result in alternating $\text{W}-\text{O}$ bond lengths (average values are 1.83 and 2.04 \AA) within these rings. The difference between the average values is of the order of magnitude of the statistical error (0.21 \AA for this difference and 0.26 \AA for 6σ). However, the differences are quite systematic, and similar metal atom displacements have been noted in Keggin- and Dawson-type heteropolymolybdates.¹⁷ Looking down the fivefold axis, one short $\text{W}-\text{O}$ distance in decagon 1 is seen to lie above a long one in decagon 2. Therefore this would confer a chirality to the whole structure.

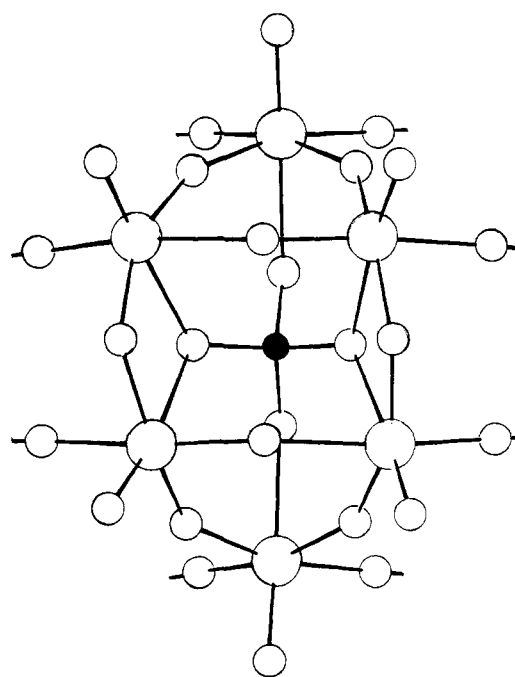


Figure 2. The PW_6O_{22} unit viewed perpendicular to the anion's virtual C_5 axis. Oxygen and tungsten atoms are represented by the large and small open circles, respectively, and the phosphorus atom by the closed circle.

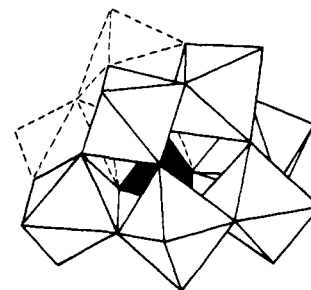


Figure 3. Polyhedral representation showing the relationship of the PW_6 unit to the PW_9 half-Dawson anion.

There are several vacancies inside the polyanion structure (excluding the sodium ion), along the fivefold axis. Three sites may be described. The first one, the central site, S_1 , lies in the mirror plane and is surrounded by ten oxygen atoms making two parallel pentagons related by the mirror plane. The mean distance between pentagons is 2.45 \AA . Two other sites, S_2 , are also located

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Table III. Atomic Coordinates and Isotropic Temperature Factors of P, O, Na, and N Atoms^a

atom	X/A	Y/B	Z/C	B(iso)	atom	X/A	Y/B	Z/C	B(iso)
P(1)	-0.2326 (7)	0.090 (1)	0.067 (1)	1.5 (4)	O(17,18)	-0.164 (2)	0.442 (3)	-0.103 (2)	2.140 (8)
P(2)	-0.2596 (7)	0.227 (1)	0.298 (1)	1.5 (4)	O(17,29)	-0.119 (1)	0.520 (2)	0.060 (2)	1.598 (6)
P(3)	-0.2726 (7)	0.457 (1)	0.311 (1)	1.5 (4)	O(18,19)	-0.143 (2)	0.216 (3)	-0.204 (2)	2.342 (8)
P(4)	-0.2531 (7)	0.462 (1)	0.085 (1)	1.5 (4)	O(18,30)	-0.104 (1)	0.347 (2)	-0.058 (2)	1.598 (6)
P(5)	-0.2275 (7)	0.236 (1)	-0.063 (1)	1.3 (4)	O(19,20)	-0.145 (2)	0.031 (3)	-0.133 (2)	2.140 (8)
O(1,11,P(1))	-0.238 (1)	0.031 (3)	0.115 (2)	1.815 (7)	O(19,30)	-0.100 (1)	0.199 (2)	-0.066 (2)	1.598 (6)
O(10,20,P(1))	-0.223 (1)	0.032 (3)	-0.025 (2)	1.815 (7)	O(20,26)	-0.102 (1)	0.078 (2)	0.035 (2)	1.598 (6)
O(2,12,P(2))	-0.256 (2)	0.138 (3)	0.293 (2)	1.815 (7)	O(21,22)	-0.412 (1)	0.273 (3)	0.199 (2)	1.641 (8)
O(3,13,P(2))	-0.271 (1)	0.275 (3)	0.385 (2)	1.815 (7)	O(21,25)	-0.397 (1)	0.119 (3)	0.098 (2)	1.641 (8)
O(4,14,P(3))	-0.279 (2)	0.458 (3)	0.399 (2)	1.815 (7)	O(22,23)	-0.409 (1)	0.370 (2)	0.115 (2)	1.641 (8)
O(5,15,P(3))	-0.276 (1)	0.546 (3)	0.318 (2)	1.815 (7)	O(23,24)	-0.388 (1)	0.276 (2)	-0.042 (2)	1.641 (8)
O(6,16,P(4))	-0.260 (1)	0.548 (3)	0.143 (2)	1.815 (7)	O(24,25)	-0.384 (1)	0.130 (2)	-0.044 (2)	1.641 (8)
O(7,17,P(4))	-0.244 (1)	0.465 (3)	0.001 (2)	1.815 (7)	O(26,27)	-0.095 (1)	0.245 (3)	0.245 (2)	1.641 (8)
O(8,18,P(5))	-0.225 (1)	0.296 (3)	-0.109 (2)	1.815 (7)	O(26,30)	-0.087 (1)	0.253 (2)	0.103 (2)	1.641 (8)
O(9,19,P(5))	-0.220 (1)	0.152 (3)	-0.126 (2)	1.815 (7)	O(27,28)	-0.112 (1)	0.392 (2)	0.340 (2)	1.641 (8)
O(25,P(1))	-0.291 (1)	0.115 (2)	0.059 (2)	0.954 (7)	O(28,29)	-0.112 (1)	0.489 (2)	0.266 (2)	1.641 (8)
O(26,P(1))	-0.183 (1)	0.159 (2)	0.111 (2)	0.954 (7)	O(29,30)	-0.093 (1)	0.398 (3)	0.106 (2)	1.641 (8)
O(21,P(2))	-0.309 (1)	0.223 (2)	0.234 (2)	0.954 (7)	O(1)	-0.348 (2)	-0.178 (3)	0.059 (3)	2.760 (7)
O(27,P(2))	-0.204 (1)	0.262 (2)	0.287 (2)	0.954 (7)	O(2)	-0.379 (2)	-0.031 (3)	0.308 (3)	2.760 (7)
O(22,P(3))	-0.320 (1)	0.397 (2)	0.243 (2)	0.954 (7)	O(3)	-0.403 (2)	0.232 (3)	0.486 (3)	2.760 (7)
O(28,P(3))	-0.214 (1)	0.441 (2)	0.298 (2)	0.954 (7)	O(4)	-0.418 (2)	0.485 (3)	0.505 (3)	2.760 (7)
O(23,P(4))	-0.305 (1)	0.402 (2)	0.073 (2)	0.954 (7)	O(5)	-0.410 (2)	0.662 (3)	0.359 (3)	2.760 (7)
O(29,P(4))	-0.199 (1)	0.442 (2)	0.123 (2)	0.954 (7)	O(6)	-0.391 (2)	0.666 (3)	0.115 (3)	2.760 (7)
O(24,P(5))	-0.285 (1)	0.228 (2)	-0.043 (2)	0.954 (7)	O(7)	-0.361 (2)	0.513 (3)	-0.161 (3)	2.760 (7)
O(30,P(5))	-0.179 (1)	0.273 (2)	0.008 (2)	0.954 (7)	O(8)	-0.334 (2)	0.260 (3)	-0.324 (3)	2.760 (7)
O(1,2)	-0.309 (2)	-0.029 (3)	0.196 (2)	2.140 (8)	O(9)	-0.314 (2)	-0.005 (3)	-0.340 (3)	2.760 (7)
O(1,10)	-0.288 (2)	-0.107 (3)	-0.029 (2)	2.342 (8)	O(10)	-0.320 (2)	-0.161 (3)	-0.203 (3)	2.760 (7)
O(1,11)	-0.226 (2)	-0.101 (3)	0.121 (2)	1.930 (8)	O(11)	-0.110 (2)	-0.075 (3)	0.177 (3)	2.760 (7)
O(1,25)	-0.359 (1)	-0.023 (2)	0.063 (2)	1.598 (6)	O(12)	-0.140 (2)	0.076 (3)	0.437 (3)	2.760 (7)
O(2,3)	-0.336 (2)	0.143 (3)	0.388 (3)	2.342 (8)	O(13)	-0.165 (2)	0.344 (3)	0.610 (3)	2.760 (7)
O(2,12)	-0.257 (2)	0.045 (3)	0.362 (2)	1.930 (8)	O(14)	-0.184 (2)	0.594 (3)	0.622 (3)	2.760 (7)
O(2,21)	-0.378 (1)	0.080 (3)	0.228 (2)	1.598 (6)	O(15)	-0.176 (2)	0.754 (3)	0.469 (3)	2.760 (7)
O(3,4)	-0.351 (2)	0.366 (3)	0.468 (2)	2.140 (8)	O(16)	-0.150 (2)	0.765 (3)	0.222 (3)	2.760 (7)
O(3,13)	-0.284 (2)	0.285 (3)	0.524 (2)	1.930 (8)	O(17)	-0.120 (2)	0.605 (3)	-0.045 (3)	2.760 (7)
O(3,21)	-0.393 (1)	0.231 (2)	0.325 (2)	1.598 (6)	O(18)	-0.096 (2)	0.349 (3)	-0.214 (3)	2.760 (7)
O(4,5)	-0.361 (2)	0.565 (3)	0.420 (2)	2.342 (8)	O(19)	-0.082 (2)	0.090 (3)	-0.223 (3)	2.760 (7)
O(4,14)	-0.297 (2)	0.530 (3)	0.543 (2)	1.930 (8)	O(20)	-0.088 (2)	-0.074 (3)	-0.080 (3)	2.760 (7)
O(4,22)	-0.404 (1)	0.407 (2)	0.339 (2)	1.598 (6)	O(21)	-0.477 (1)	0.139 (2)	0.199 (2)	1.607 (8)
O(5,6)	-0.345 (2)	0.627 (3)	0.240 (2)	2.140 (8)	O(22)	-0.490 (1)	0.374 (2)	0.209 (2)	1.607 (8)
O(5,15)	-0.290 (2)	0.691 (3)	0.401 (2)	1.930 (8)	O(23)	-0.468 (1)	0.381 (2)	-0.023 (2)	1.607 (8)
O(5,22)	-0.396 (1)	0.506 (2)	0.259 (2)	1.598 (6)	O(24)	-0.443 (1)	0.144 (2)	-0.181 (2)	1.607 (8)
O(6,7)	-0.321 (2)	0.574 (3)	0.012 (2)	2.342 (8)	O(25)	-0.448 (1)	-0.002 (2)	-0.042 (2)	1.607 (8)
O(6,16)	-0.270 (2)	0.691 (3)	0.163 (2)	1.930 (8)	O(26)	-0.018 (1)	0.172 (2)	0.171 (2)	1.607 (8)
O(6,23)	-0.384 (1)	0.502 (2)	0.085 (2)	1.598 (6)	O(27)	-0.043 (1)	0.311 (2)	0.410 (2)	1.607 (8)
O(7,8)	-0.295 (2)	0.391 (3)	-0.167 (2)	2.140 (8)	O(28)	-0.056 (1)	0.552 (2)	0.424 (2)	1.607 (8)
O(7,17)	-0.241 (2)	0.543 (3)	-0.088 (2)	1.930 (8)	O(29)	-0.033 (1)	0.557 (2)	0.192 (2)	1.607 (8)
O(7,23)	-0.365 (1)	0.416 (2)	-0.061 (2)	1.598 (6)	O(30)	-0.009 (1)	0.322 (2)	0.034 (2)	1.607 (8)
O(8,9)	-0.277 (2)	0.171 (3)	-0.268 (2)	2.342 (8)	NA(1)	-0.298 (2)	0.274 (3)	0.114 (2)	1.3 (6)
O(8,18)	-0.215 (1)	0.306 (3)	-0.246 (2)	1.930 (8)	NA(2)	-0.191 (2)	0.319 (3)	0.171 (2)	1.3 (6)
O(8,24)	-0.344 (1)	0.247 (2)	-0.173 (2)	1.598 (6)	X(1)	0	0.5	0	6 (2)
O(9,10)	-0.271 (2)	-0.019 (3)	-0.196 (2)	2.140 (8)	X(2)	0.465 (2)	0.063 (3)	-0.113 (3)	4 (1)
O(9,19)	-0.202 (2)	0.055 (3)	-0.259 (2)	1.930 (8)	X(3)	0.009 (2)	0.110 (3)	-0.033 (3)	3 (1)
O(9,24)	-0.342 (1)	0.097 (2)	-0.189 (2)	1.598 (6)	X(4)	-0.498 (2)	0.470 (3)	-0.132 (3)	6 (1)
O(10,20)	-0.205 (1)	-0.101 (3)	-0.127 (2)	1.930 (8)	X(5)	0.428 (2)	0.352 (3)	0.056 (3)	6 (1)
O(10,25)	-0.343 (1)	-0.020 (2)	-0.087 (2)	1.598 (6)	X(6)	0.491 (2)	0.207 (4)	0.028 (3)	7 (1)
O(11,12)	-0.179 (2)	0.029 (3)	0.267 (2)	2.140 (8)	X(7)	0.020 (2)	0.034 (4)	0.206 (4)	9 (2)
O(11,20)	-0.153 (2)	-0.049 (3)	0.043 (2)	2.342 (8)	X(8)	0.334 (2)	0.289 (4)	0.129 (4)	8 (2)
O(11,26)	-0.113 (1)	0.077 (2)	0.173 (2)	1.598 (6)	X(9)	0.437 (2)	0.067 (4)	0.262 (4)	9 (2)
O(12,13)	-0.200 (2)	0.198 (3)	0.460 (2)	2.342 (8)	X(10)	0.263 (3)	0.146 (4)	-0.281 (4)	9 (2)
O(12,27)	-0.134 (1)	0.183 (2)	0.352 (2)	1.598 (6)	X(11)	0.223 (3)	0.262 (5)	0.006 (4)	11 (2)
O(13,14)	-0.225 (2)	0.427 (3)	0.532 (2)	2.140 (8)	X(12)	0.068 (3)	0.229 (4)	-0.085 (4)	10 (2)
O(13,27)	-0.151 (1)	0.326 (2)	0.446 (2)	1.598 (6)	X(13)	-0.184 (3)	0.476 (5)	-0.263 (5)	13 (2)
O(14,15)	-0.222 (2)	0.625 (3)	0.487 (2)	2.342 (8)	X(14)	0.059 (3)	0.470 (5)	0.181 (4)	12 (2)
O(14,28)	-0.161 (1)	0.508 (2)	0.464 (2)	1.598 (6)	X(15)	-0.056 (3)	0.507 (5)	-0.407 (4)	12 (2)
O(15,16)	-0.211 (2)	0.684 (3)	0.295 (2)	2.140 (8)	X(16)	0.443 (3)	0.198 (4)	-0.182 (4)	10 (2)
O(15,28)	-0.154 (1)	0.606 (2)	0.383 (2)	1.598 (6)	X(17)	-0.463 (3)	0.309 (5)	-0.243 (4)	12 (2)
O(16,17)	-0.185 (2)	0.627 (3)	0.073 (2)	2.342 (8)	X(18)	0.060 (3)	0.258 (5)	-0.364 (5)	14 (3)
O(16,29)	-0.139 (1)	0.607 (2)	0.207 (2)	1.598 (6)	X(19)	0.429 (3)	0.201 (5)	0.149 (5)	13 (3)

^aO atoms indexed (*i,j*,P(*n*)) are bonded to W(*i*), W(*j*) and P(*n*). O atoms indexed (*i*,P(*n*)) are bonded to W(*i*) and P(*n*). O atoms indexed (*i,j*) are bonded to W(*i*) and W(*j*). O atoms indexed (*i*) are bonded to W(*i*). The cation N atoms and the water O atoms which are not distinguished are noted as X.

on the fivefold axis and related by the mirror plane. They are surrounded by ten oxygen atoms, five of which belong to one of the previously mentioned pentagons with the other five in an outer parallel plane. The distance between the two planes is 2.22 Å.

The ten oxygen atoms surrounding S₂ are arranged in an antiprism fashion. In the inner basal plane of the antiprism, oxygen–oxygen distances range from 3.06 to 3.19 Å with a mean value of 3.12 Å; in the outer basal plane they range from 2.53 to 2.79 Å with

Table IV. Selected Bond Distances (Å)

P(1)–O(25,P(1))	1.49 (4)	P(2)–O(21,P(2))	1.47 (4)	W(15)–O(5,15,P(3))	2.26 (3)	W(16)–O(6,16,P(4))	2.29 (4)
–O(26,P(1))	1.47 (3)	–O(27,P(2))	1.46 (4)	–O(15)	1.66 (4)	–O(16)	1.72 (4)
–O(1,11,P(1))	1.58 (6)	–O(2,12,P(2))	1.58 (5)	–O(15,16)	1.90 (5)	–O(16,17)	1.87 (4)
–O(10,20,P(1))	1.62 (4)	–O(3,13,P(2))	1.53 (4)	–O(14,15)	2.03 (5)	–O(15,16)	1.97 (4)
P(3)–O(22,P(3))	1.49 (3)	P(4)–O(23,P(4))	1.45 (4)	–O(15,28)	1.85 (4)	–O(16,29)	1.88 (4)
–O(28,P(3))	1.47 (4)	–O(29,P(4))	1.50 (4)	–O(5,15)	1.91 (4)	–O(6,16)	1.91 (4)
–O(4,14,P(3))	1.58 (5)	–O(6,16,P(4))	1.53 (4)	W(17)–O(7,17,P(4))	2.25 (4)	W(18)–O(8,18,P(5))	2.30 (4)
–O(5,15,P(3))	1.56 (5)	–O(7,17,P(4))	1.55 (5)	–O(17)	1.75 (5)	–O(18)	1.69 (5)
P(5)–O(24,P(5))	1.46 (4)			–O(17,18)	1.73 (4)	–O(18,19)	1.78 (4)
–O(30,P(5))	1.46 (3)			–O(16,17)	2.01 (4)	–O(17,18)	2.11 (4)
–O(8,18,P(5))	1.57 (6)			–O(17,29)	1.91 (4)	–O(18,30)	1.88 (4)
–O(9,19,P(5))	1.54 (4)			–O(7,17)	1.93 (4)	–O(8,18)	1.90 (4)
W(1)–O(1,11,P(1))	2.23 (4)	W(2)–O(2,12,P(2))	2.25 (4)	W(19)–O(9,19,P(5))	2.28 (4)	W(20)–O(10,20,P(1))	2.56 (4)
–O(1)	1.76 (4)	–O(2)	1.78 (5)	–O(19)	1.71 (4)	–O(20)	1.70 (4)
–O(1,2)	2.04 (4)	–O(2,3)	2.02 (4)	–O(19,20)	1.81 (5)	–O(11,20)	1.84 (5)
–O(1,10)	1.81 (4)	–O(1,2)	1.81 (4)	–O(18,19)	2.15 (5)	–O(19,20)	2.08 (5)
–O(1,25)	1.89 (4)	–O(2,21)	1.89 (5)	–O(19,30)	1.88 (3)	–O(20,26)	1.85 (3)
–O(1,11)	1.95 (4)	–O(2,12)	1.91 (4)	–O(9,19)	1.90 (3)	–O(10,20)	1.91 (3)
W(3)–O(3,13,P(2))	2.27 (4)	W(4)–O(4,14,P(3))	2.26 (4)	W(21)–O(21,P(2))	2.25 (3)	W(22)–O(22,P(3))	2.21 (3)
–O(3)	1.65 (5)	–O(4)	1.72 (4)	–O(21)	1.67 (4)	–O(22)	1.70 (3)
–O(3,4)	2.01 (5)	–O(4,5)	2.11 (5)	–O(2,21)	1.96 (5)	–O(4,22)	1.90 (4)
–O(2,3)	1.81 (4)	–O(3,4)	1.87 (5)	–O(3,21)	1.82 (4)	–O(5,22)	1.97 (4)
–O(3,21)	1.99 (4)	–O(4,22)	1.92 (3)	–O(21,22)	1.89 (5)	–O(22,23)	1.85 (4)
–O(3,13)	1.88 (3)	–O(4,14)	1.94 (3)	–O(21,25)	1.93 (4)	–O(21,22)	1.90 (4)
W(5)–O(5,15,P(3))	2.28 (4)	W(6)–O(6,16,P(4))	2.29 (4)	W(23)–O(23,P(4))	2.22 (3)	W(24)–O(24,P(5))	2.22 (3)
–O(5)	1.70 (4)	–O(6)	1.74 (5)	–O(23)	1.68 (4)	–O(24)	1.69 (3)
–O(5,6)	1.99 (5)	–O(6,7)	2.07 (4)	–O(6,23)	1.89 (4)	–O(8,24)	1.92 (5)
–O(4,5)	1.81 (5)	–O(5,6)	1.85 (4)	–O(7,23)	1.85 (5)	–O(9,24)	1.88 (4)
–O(5,22)	1.82 (3)	–O(6,23)	1.92 (4)	–O(23,24)	1.93 (4)	–O(24,25)	1.87 (5)
–O(5,15)	1.93 (3)	–O(6,16)	1.87 (14)	–O(22,23)	1.93 (5)	–O(23,24)	1.83 (4)
W(7)–O(7,17,P(4))	2.29 (4)	W(8)–O(8,18,P(5))	2.31 (4)	W(25)–O(25,P(1))	2.20 (3)	W(26)–O(26,P(1))	2.20 (3)
–O(7)	1.80 (5)	–O(8)	1.74 (4)	–O(25)	1.65 (3)	–O(26)	1.64 (3)
–O(7,8)	2.01 (4)	–O(8,9)	1.94 (4)	–O(10,25)	1.95 (4)	–O(20,26)	1.91 (3)
–O(6,7)	1.80 (4)	–O(7,8)	1.83 (4)	–O(1,25)	2.00 (5)	–O(11,26)	1.92 (5)
–O(7,23)	1.92 (4)	–O(8,24)	1.86 (4)	–O(21,25)	1.84 (4)	–O(26,27)	1.85 (4)
–O(7,17)	1.84 (4)	–O(8,18)	1.90 (4)	–O(24,25)	1.94 (5)	–O(26,30)	1.91 (5)
W(9)–O(9,19,P(5))	2.24 (3)	W(10)–O(10,20,P(1))	2.20 (3)	W(27)–O(27,P(2))	2.20 (3)	W(28)–O(28,P(3))	2.21 (3)
–O(9)	1.66 (3)	–O(10)	1.68 (4)	–O(27)	1.72 (3)	–O(28)	1.70 (3)
–O(9,10)	2.09 (5)	–O(1,10)	2.08 (5)	–O(12,27)	1.91 (5)	–O(14,28)	1.95 (4)
–O(8,9)	2.00 (5)	–O(9,10)	1.79 (5)	–O(13,27)	1.87 (4)	–O(15,28)	1.98 (4)
–O(9,24)	1.92 (4)	–O(10,25)	1.85 (4)	–O(26,27)	1.94 (4)	–O(27,28)	1.91 (4)
–O(9,19)	1.89 (4)	–O(10,20)	1.99 (4)	–O(27,28)	1.92 (5)	–O(28,29)	1.83 (4)
W(11)–O(1,11,P(1))	2.29 (4)	W(12)–O(2,12,P(2))	2.28 (4)	W(29)–O(29,P(4))	2.24 (3)	W(30)–O(30,P(5))	2.19 (3)
–O(11)	1.70 (5)	–O(12)	1.74 (5)	–O(29)	1.74 (3)	–O(30)	1.73 (3)
–O(11,12)	1.83 (3)	–O(12,13)	1.77 (4)	–O(16,29)	1.93 (4)	–O(18,30)	1.95 (5)
–O(11,20)	2.03 (4)	–O(11,12)	2.00 (4)	–O(17,29)	1.92 (5)	–O(19,30)	1.87 (3)
–O(11,26)	1.88 (4)	–O(12,27)	1.91 (4)	–O(28,29)	1.95 (5)	–O(29,30)	1.84 (4)
–O(1,11)	1.83 (3)	–O(2,12)	1.82 (4)	–O(29,30)	1.93 (4)	–O(26,30)	1.90 (5)
W(13)–O(3,13,P(2))	2.26 (4)	W(14)–O(4,14,P(3))	2.24 (3)	Na(1)–O(21,P(2))	2.64 (7)	Na(2)–O(26,P(1))	2.67 (6)
–O(13)	1.78 (4)	–O(14)	1.70 (4)	–O(22,P(3))	2.65 (5)	–O(27,P(2))	2.63 (7)
–O(13,14)	1.84 (5)	–O(14,15)	1.88 (5)	–O(23,P(4))	2.65 (7)	–O(28,P(3))	2.65 (5)
–O(12,13)	2.11 (4)	–O(13,14)	2.04 (5)	–O(24,P(5))	2.65 (6)	–O(29,P(4))	2.65 (7)
–O(13,27)	1.91 (4)	–O(14,28)	1.84 (4)	–O(25,P(1))	2.67 (6)	–O(30,P(5))	2.73 (6)
–O(3,13)	1.88 (4)	–O(4,14)	1.91 (4)				

a mean value of 2.66 Å. The X-ray study showed a statistical distribution of one sodium atom between the two sites S_2 . The mean distance from the sodium atom to the five oxygen atoms of the inner plane of S_2 is 2.66 Å, whereas it is 3.16 Å to the oxygen atoms of the outer plane. It then appears that the sodium actually is located in the inner oxygen plane (Figure 1). The sodium therefore has five neighbors above it at 3.16 Å, five neighbors in the plane at 2.66 Å and five neighbors below it at 3.64 Å. (These distances are averages.) The location of the sodium in the inner plane of oxygens explains why the polyanion contains only one sodium atom. If another sodium were to be located symmetrically, one would find an interatomic (Na–Na) distance of 2.50 Å. This is too short when compared to the

observed ionic radius. Indeed, on the basis of the shortest Na–O distance of 2.66 Å, an effective ionic radius of Na^+ of 1.26 Å is found. This compares with the value of 1.32 Å given by Shannon¹⁸ for coordination number eight.

The sodium ion appears to be very tightly encrypted in the polytungstate structure and is not removed in the ion-exchange preparation of the free acid. All salts that we have prepared by metathesis contain residual sodium, and the possibility that sodium is required for the synthesis of the polyanion is discussed below. The position of the internal sodium ion reduces the symmetry of the polyanion from D_3 to C_3 and accounts for the observed ¹⁸³W

(18) Shannon, R. D. *Acta Crystallogr., Sect. A* 1976, A32, 751.

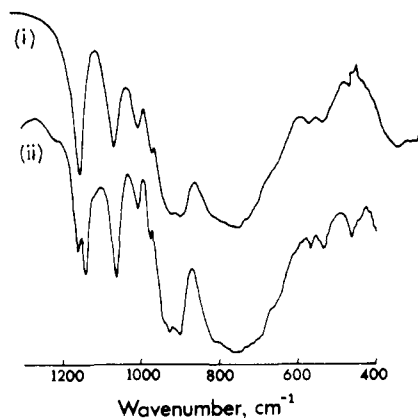


Figure 4. The IR spectra, recorded in KBr pellets, of (i) $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ and (ii) the product obtained when a solution of the heteropolyanion is heated with Ca^{2+} as described in the text.

Table V. Cathodic Peak Potentials of Cyclic Voltammograms of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$

pH	potential vs. Ag/AgCl					
0 ^a	-0.22			-0.35	-0.56	
1.5 ^b	-0.25			-0.37	-0.58	
2.5 ^b	-0.37			-0.50	-0.65	
3.5 ^c	-0.39	-0.47	-0.55	-0.60	-0.76	-0.95
4.7 ^c	-0.40	-0.51	-0.59	-0.65	-0.81	-0.97
5.9 ^c	-0.38	-0.48	-0.57	-0.69	-0.90	-1.02 -1.17
7.0 ^d	-0.37	-0.49	-0.57	-0.86	-1.10	-1.18 -1.26
8.0 ^d	-0.37	-0.50	-0.62	-0.90	-1.15	-1.20 -1.27
9.0 ^e	-0.39	-0.50	-0.64	-0.93	-1.15	-1.20 -1.28
10.0 ^e	-0.35	-0.45	-0.58	-0.70	-0.90	-1.12 -1.24 -1.29
10.8 ^e	-0.35	-0.46	-0.60	-0.70	-0.91	-1.14 -1.26 -1.32
12.0 ^f	-0.38	-0.49	-0.60	-0.69	-0.85	-1.04 -1.23

^a 1 M HCl. ^b HCl/NaCl. ^c Acetate buffer. ^d Tris/HCl. ^e Borate buffer. ^f 0.01 M NaOH.

NMR spectrum which has four lines in a 1:1:2:2 ratio.^{7,8} The IR spectrum, Figure 4, has three well-resolved bands at 1000–1150 cm^{-1} in the P–O stretching region and is consistent with a local C_s symmetry for the PO_4 groups caused by the internal sodium ion. Direct observation of sodium by ^{23}Na NMR is possible. A solution of the potassium–sodium salt in D_2O shows two peaks separated by 21 ppm. The low-field resonance ($\Delta\nu_{1/2}$ 30 \pm 5 Hz) is assigned to external cationic sodium (confirmed by spiking the solution with NaNO_3), and the broader upfield resonance (460 \pm 50 Hz) is assigned to the encrypted sodium. A solution of the free acid in the same solvent gave a spectrum with the broad –21-ppm resonance only.¹⁹ As reported by Massart et al.,⁶ the ^{31}P NMR spectrum consists of a single line at –10.35 ppm.²⁰ The electronic absorption spectrum has a broad maximum at 28 600 cm^{-1} (ϵ 700 $\text{M}^{-1}\text{cm}^{-1}$) and a shoulder at 35 900 cm^{-1} (9000 $\text{M}^{-1}\text{cm}^{-1}$).

(19) A ^{183}W NMR spectrum of the free acid, kindly recorded by Dr. P. Domaille (E. I. DuPont de Nemours, Wilmington, DE), showed the same four-line pattern as the salt. The ^{23}Na spectra were recorded at 23.81 MHz on the Bruker WH90 spectrometer (sweep width, 6000 Hz; pulse width, 15 μs ; acquisition time, 0.679 s). The number of scans for the potassium–sodium salt (0.07 M) was 68 775 and for the free acid (0.14 M) was 3271. A quantitative determination of sodium in the polyanion was attempted by using the Bruker WM 500 spectrometer. A sodium nitrate solution in D_2O was used as an external reference. In order to record spectra without any possibility of exchange, a 0.024 M polyanion solution was placed in a 10-mm NMR tube and 0.125 M NaNO_3 was placed in an inner coaxial tube of 4-mm diameter. The ^{23}Na resonance frequency was 132.29 MHz and the spectral width 10000 Hz. Other spectral parameters were the following: pulse width, 30 μs ; acquisition time, 0.82 s; no. of scans, 480. The reference sodium signal (half-width 8.5 Hz) had an integrated intensity of 0.92 units, and the polyanion signal (470 Hz, 19.3 ppm upfield) had an integrated intensity of 1.04 units, i.e., the ratio $\text{Na}(\text{in})/\text{Na}(\text{out}) = 1.13$ (calcd 1.00).

(20) Massart et al. reported a chemical shift of –9.9 ppm using an internal standard in a continuous wave spectrometer. Our chemical shifts were determined with the sample replacement method on the WH 90 spectrometer operating at 36.44 MHz.

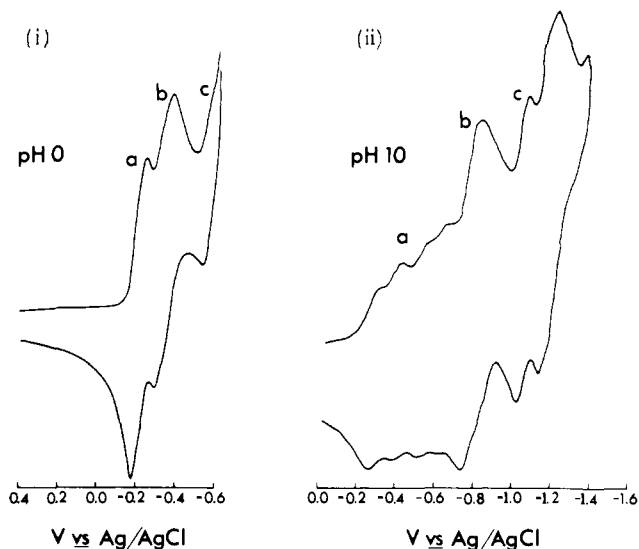


Figure 5. Cyclic voltammograms (pyrolytic graphite electrode, scan rate: 33.3 mV s^{-1}) of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ in (i) 1 M HCl and (ii) borate buffer, pH 10. In the latter solution the first four-electron reduction, a, is resolved into one-electron steps.

Redox Chemistry. The heteropolyanion is reducible to heteropoly blue species, a behavior that is consistent with the monooxo (type I) coordination environment of the tungsten atoms.²¹ Polarographic and voltammetric measurements are summarized in Table V and Figure 5. In 1 M HCl, the first two reduction steps (a and b) correspond to four electrons each as confirmed by controlled potential electrolyses at –0.31 and –0.51 V vs. SCE. The resultant heteropoly blue solutions were examined by ^{31}P and ^{23}Na NMR spectroscopy. No changes in the spectra were detected for the four-electron product. The ^{31}P spectrum of the eight-electron blue consisted of a single unbroadened line at –11.55 ppm and shows that the eight electrons are totally “delocalized”²² over one (or more) of the planes of tungsten atoms.

At pH 10 the first reduction step has split into a sequence of one-electron reductions as is observed for most heteropolytungstate systems.²³ Sequential controlled potential electrolyses at –0.39, –0.52, –0.62, and –0.73 V resulted in the quantitative addition of one, two, three, and four electrons. The electronic absorption spectra of these solutions showed a broad (ca. 5000 cm^{-1} half-width) featureless band centered at 14 300 cm^{-1} with extinction coefficients of 4 400, 11 700, 24 700, and 35 800 $\text{M}^{-1}\text{cm}^{-1}$, respectively. Although the one-electron product must be paramagnetic, no ESR spectrum could be observed at 77 K, a result of very rapid intervalence electron transfer and/or extensive delocalization, probably through the corner-shared junctions of the W_5 or W_{10} rings.²⁴ Further investigation at lower temperatures is planned. All reduced solutions could be reoxidized quantitatively to the original heteropolyanion.

Derivative Anions. (a) **Sodium Replacement.** In contrast to other polytungstate cryptates $[\text{NaSb}_9\text{W}_{21}\text{O}_{86}]^{18-}$ ²⁵ and $[\text{KAs}_4\text{W}_{40}\text{O}_{140}]^{27-}$,^{3c,26} which readily undergo alkali metal re-

(21) Pope, M. T. *Inorg. Chem.* **1972**, *11*, 1973.

(22) “Delocalization” may imply rapid electron hopping (class II mixed valence behavior), complete valence delocalization (class III), or an intermediate case.

(23) Pope, M. T. “Heteropoly and Isopoly Oxometalates”; Springer-Verlag: New York, 1983; Chapter 6.

(24) Chemseddine et al. [*Inorg. Chem.* **1984**, *23*, 2609] have shown that when the $\text{W}^{\text{V}}\text{O}-\text{W}^{\text{VI}}$ bond angle is ca. 180°, as in $(\text{W}^{\text{V}}\text{W}_3\text{O}_{32})^{5-}$, ground-state valence delocalization is complete. The $\text{W}-\text{O}-\text{W}$ bond angles (at corner-shared junctions) in $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ are (average values) 160° (W_5 rings), 155° (W_{10} rings), and 150° (between W_5 and W_{10} rings). The corresponding angles in the Keggin structure are 150°. We therefore expect there to be more valence delocalization in the Preyssler anion than in the Keggin anions, and this could account for the lack of an observable ESR signal at 77 K.

(25) Michelon, M.; Hervé, G.; Leyrie, M. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1583.

(26) Leyrie, M.; Hervé, G. *Nouv. J. Chem.* **1978**, *2*, 233.

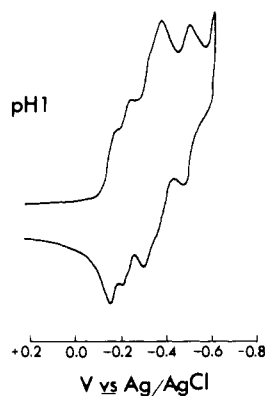


Figure 6. Cyclic voltammogram of the product obtained by heating a solution of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ with Ca^{2+} at pH 8–9 (see text).

placement reactions, the sodium ion in $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ is very tightly bound, at least in a kinetic sense. This is shown by the resolution of two ^{23}Na NMR lines in aqueous solution and the non-replacement of the internal sodium in ion-exchange experiments. Measurements with a sodium electrode confirmed that the activity of Na^+ in a millimolar solution of $\text{H}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}$ was ca. 2×10^{-5} M, a value that is close to the detectable limit. Attempts were made to displace the sodium by calcium ion, which has a similar radius (1.26 Å for coordination number 8) and which, by virtue of its higher charge, might be expected to be more strongly bound to the polytungstate. The following procedure was successful. A sample of 85 mg of $\text{H}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}$ (10 μmol) was dissolved in 9.5 mL of distilled water in an acid-washed plastic beaker, and 5 mL of an ammonia–ammonium chloride buffer (ca. 3.7 M Cl^- , pH 8.5) was added. To this mixture was added a twofold excess of Ca^{2+} (4.7 mg of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$). At this stage the sodium activity of the solution was determined to be ca. 2×10^{-5} M or 2% of the total sodium present. The solution was transferred to a Teflon-lined acid digestion bomb (Parr model 4746) and heated overnight in an oven at 120 °C. After the solution had been allowed to cool, its pH was 8.2 and its sodium ion activity was found to be 1.0 mM, or 100% of that present. Repeat experiments gave values of 0.8, 0.9, 1.1, and 1.0 mM after heating. The heated solutions were also subjected to voltammetric examination. After addition of 2 mL of this solution to 8 mL of 1 M HCl to bring the pH to ca. 1 the cyclic voltammogram (Figure 6) was similar to that of the starting material except that the first reduction step had been split into two. A sample of the potassium salt of the heated polyanion was isolated by addition of KCl. The IR spectrum is indistinguishable from that of the starting material except for a splitting of the P–O stretching band at 1145 cm^{-1} (Figure 4).

The above experiments were repeated with MgCl_2 , $\text{Ba}(\text{NO}_3)_2$, and MnCl_2 . Only in the case of MgCl_2 did the heated solution show an increase of sodium activity, corresponding to about 30% displacement of Na^+ by Mg^{2+} . Attempts to replace Na^+ by trivalent cations of similar radius, Ce^{3+} and Pr^{3+} , resulted in precipitation of the hydrous oxides.

Blank experiments in which the calcium–polyanion solution was not heated, or was heated at a lower pH, resulted in no release of sodium ion. These results suggest that sodium exchange occurs via partial hydrolysis of the polyanion structure and may involve a lacunary intermediate, cf. the $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ – $[\text{P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ and allied systems. If this is so the sodium ion should be regarded as a true heteroatom which *must* be present to ensure the formation of the polyanion. The experiments leading to the formation of vanadium-substituted polyanions (see below) support the hypothesis of the existence of lacunary structures. The following experiments demonstrate the essentiality of sodium. Sodium tungstate was converted to the lithium salt by ion exchange on a column of Dowex 50X8 and evaporation of the eluate to dryness. The product gave no sodium flame. To a solution of 6.0 g of this salt in 8 mL of water was added 5.3 mL of 85% H_3PO_4 (P/W = 3.9), and the mixture was transferred to a Teflon-lined acid

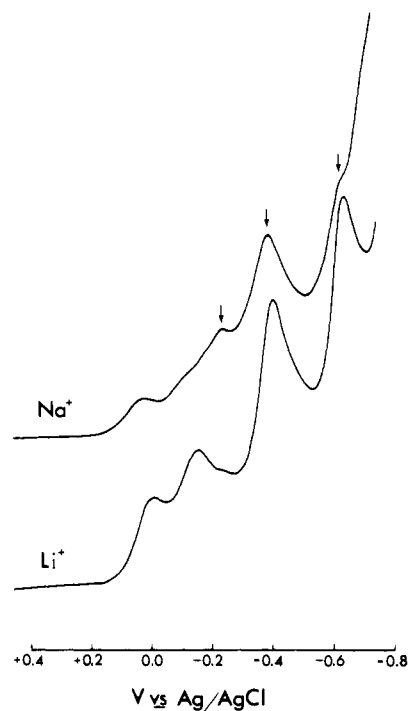


Figure 7. Cathodic sweep voltammograms of reaction mixtures resulting from the heating, in a Teflon-lined bomb at 120 °C for ca. 12 h, of (upper) 1.7 M Na_2WO_4 + 6.7 M H_3PO_4 and (lower) 1.7 M Li_2WO_4 + 6.7 M H_3PO_4 . A sample of each product solution was diluted with 1 M HCl to ca. 1.6×10^{-2} M in tungsten(VI) prior to recording the voltammogram. The upper trace shows reduction processes for $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$. Comparison with voltammograms of mixtures of the pure components shows that the molar proportion of the two anions is ca. 3:1. The arrows indicate the positions of the peak potentials for the P_5W_{30} anion, the second and third of which overlap with the third and fourth reductions of P_2W_{18} . The lower trace shows reduction peaks of the P_2W_{18} anion only, in greater yield. Close inspection of the lower voltammogram reveals a minor contamination (<3%) with P_5W_{30} , a result almost certainly of traces of adventitious Na^+ .

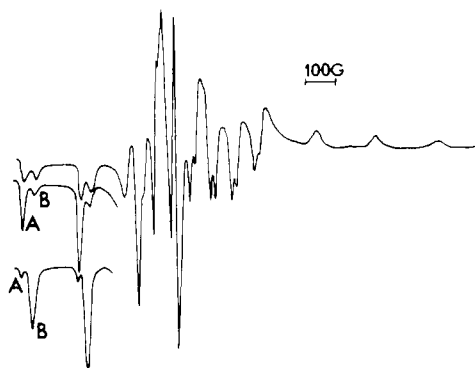


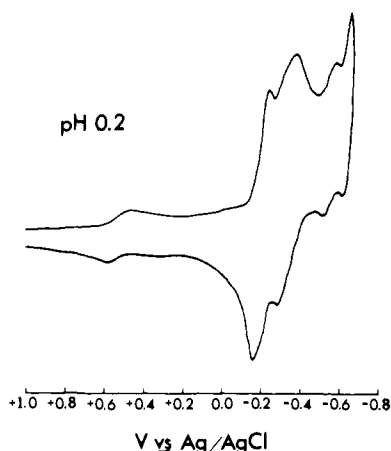
Figure 8. X-band spectra of $[\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{16-}$ isomers recorded in an aqueous–glycerol glass at 77 K. The upper trace is of the mixture of isomers A and B as produced in the synthesis. The lower traces are of solutions that have been fractionated on a Sephadex column as described in the text.

digestion bomb and heated overnight at 120 °C. After the solution had been allowed to cool, it was diluted by the addition of 1 mL of water. One-tenth of a milliliter of this solution was added to 1 M HCl to give a total volume of 10 mL. The cyclic voltammogram of this solution (Figure 7) shows it to contain $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ as the only electroactive species. A repeat experiment gave identical results, but when Na_2WO_4 was used in the same apparatus, the resulting solution contained a mixture of $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ and $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ in the molar proportion of ca. 3:1, see Figure 7.

(b) **Tungsten Replacement.** As described in the Experimental Section, treatment of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ with NaOH leads to a

Table VI. ESR Parameters of $[\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{16-}$ Isomers

	g_{\parallel}	g_{\perp}	A_{\parallel}^a	A_{\perp}^a
isomer A	1.904 (5)	1.928 (10)	191 (5)	50 (5)
isomer B	1.889 (5)	1.936 (10)	185 (5)	52 (5)

^aGauss.Figure 9. Cyclic voltammogram of $[\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{16-}$ (predominantly isomer B) in HCl.

material that reacts with VOSO_4 to yield a vanadium-containing tungstophosphate. The IR spectrum of the recrystallized purple material is indistinguishable from that of the starting polyanion, but the ESR spectrum of a frozen solution shows it to be a mixture of at least two species, A and B, see Figure 8. Separation of A and B was achieved by chromatography on modified Sephadex as described elsewhere.²⁷ Both fractions yielded solids that had IR spectra that were identical with that of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ and are considered to be isomers of $[\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{16-}$. The ESR parameters of A and B, confirmed by simulation, are given in Table VI.

The relative yields of A and B varied from one preparation to the next, and sufficient quantities only of B, which was eluted first from the Sephadex column, could be accumulated for further characterization. A cyclic voltammogram of this material, Figure 9, is similar to that of $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ except that a new one-electron redox feature is observed at $E_{pc} = +0.42$ V. That this corresponded to the vanadium oxidation-reduction was confirmed by controlled-potential electrolyses at $+0.80$ V ($\rightarrow [\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{15-}$, yellow, ESR inactive) and 0.0 V ($\rightarrow [\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{16-}$, purple, ESR active).

On the basis of the structure found for $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, there are four possible isomers for $[\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{15-}$ corresponding to the VO_6 octahedron in each of the four planes of WO_6 octahedra that constitute the anion. We denote these by I, I', II, and II', where I indicates vanadium substitution in the five-metal rings, II indicates substitution in the ten-metal rings, and the primes indicate substitution in the half of the anion that contains the sodium ion. The two isomers A and B are provisionally identified as II (and/or II') and I (and/or I'), respectively, on the basis of their ESR parameters, notably g_{\parallel} . We have elsewhere made the empirical correlation that, for tungstovanadates, g_{\parallel} decreases as the number of corner-shared (as opposed to edge-shared) connections, V-O-W, increases.²⁷ The anions $\alpha_1\text{-}[\text{P}_2\text{W}_{17}\text{VO}_{62}]^{8-}$ with three such connections and $[\text{As}_2\text{W}_{20}\text{VO}_{69}]^{8-}$ with four together with isomer B of $[\text{NaP}_5\text{W}_{29}\text{VO}_{110}]^{16-}$ are the only tungstovanadates with $g < 1.9$. Isomers I and II have four and three corner-shared connections respectively, and we therefore identify the species with the smaller g_{\parallel} as isomer I.²⁹

(27) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286.(28) Lefebvre, F.; Leyrie, M.; Hervé, G.; Sanchez, C.; Livage, J. *Inorg. Chim. Acta* **1983**, *73*, 173.

Conclusions

The unusual stoichiometry and structure of the heteropolyanion require some comment, for there are very few examples of molecular species with fivefold symmetry axes.³⁰ A space-filling model for $[\text{P}_5\text{W}_{30}\text{O}_{110}]^{15-}$, using hard spheres for the oxide ions, shows that, apart from the central core, the anion is very nearly a close-placed structure (as are the Keggin and Dawson anions). Calculations show that a cyclic hexamer ($\text{P}_6\text{W}_{36}\text{O}_{132}$) is almost as good an approximation to a close-packed structure since the hard sphere PW_6O_{22} "cake slice" subtends an angle of ca 63° . All other possibilities ($\text{P}_3\text{W}_{18}\text{O}_{66}$, $\text{P}_4\text{W}_{24}\text{O}_{88}$, etc.) are incommensurate with a cyclic structure. We suppose that the central sodium ion controls assembly of a pentameric structure, since the Preyssler anion is not formed when Na^+ is strictly excluded.³¹

We have already noted that the PW_6 units from which the anion is constructed can be obtained from the Keggin structure by removal of two triplets of corner-shared WO_6 octahedra. Each triplet has a net stoichiometry of $\text{W}_3\text{O}_6(\text{O}_{1/2})_6$ or W_3O_9 .³² The three compact (type I²¹) tungstophosphate heteropolyanions $\alpha\text{-}[\text{PW}_{12}\text{O}_{40}]^{3-}$, $\alpha\text{-}[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, and $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ have structures composed only of such corner-shared W_3 groups and may be formulated as $[(\text{PO}_4)(\text{W}_3\text{O}_9)_4]^{3-}$, $[(\text{PO}_4)_2(\text{W}_3\text{O}_9)_6]^{6-}$, and $[\text{Na}(\text{PO}_4)_5(\text{W}_3\text{O}_9)_{10}]^{14-}$. The stereochemical arrangement of W_3O_9 groups about the PO_4^{3-} anions is topologically analogous to that of hydrogen atoms about carbon in methane $[\text{CH}_4]$, ethane $[(\text{CH}_3)_2]$, and (planar) cyclopentane $[(\text{CH}_2)_5]$, respectively. In view of the existence of saturated hydrocarbons $(\text{CH})_n$ (cubane, dodecahedrane, etc.), we are moved to speculate about the possibility of a higher tungstophosphate "homologue", $[(\text{PO}_4)_n(\text{W}_3\text{O}_9)_n]^{3n-}$. Although there are reports³³ of tungstophosphates with P:W = 1:3, little is known of their true stoichiometry. It seems likely that the hypothetical homologue of Preyssler's anion would have to be formed around a template species that accommodates all of the stereochemical requirements of the $\text{PO}_4\text{W}_3\text{O}_9$ groups.

Acknowledgment. Several colleagues have contributed to this project over the past few years. We are particularly grateful to Dr. C. Knobler for valuable advice and discussion in the crystallographic study. Drs. R. L. Firor and R. J. Butcher carried the structure of the potassium salt as far as it would go. Dr. H. T. Evans, Jr., determined the space group of the barium salt. Dr. M. A. Leparulo and G. S. Chorghade recorded many of the NMR spectra. Dr. P. Domaille recorded the ^{183}W NMR spectrum of the free acid. The work at Georgetown University was supported in part by NSF Grants CHE-8019039 and 8306736.

Supplementary Material Available: A listing of structure factor amplitudes (38 pages). Ordering information is given on any current masthead page.

(29) That isomer B is probably a mixture of I and I' is shown by preliminary ^{31}P NMR spectra which have several lines, two of which are shifted significantly downfield from that of the unsubstituted anion (-7.71 and -7.90 vs. -10.35 ppm). These two lines have much shorter relaxation times than the others. On the basis of our experience with other tungstovanadates such lines can be assigned to phosphorus atoms that share an oxygen with the vanadium atom.²⁷ There is only one such phosphorus in each of the four possible isomers.

(30) Cyclopentadienide anion and certain derivatives, $[\text{B}_{12}\text{H}_{12}]^{2-}$ and $\text{C}_{20}\text{H}_2\text{O}$ (dodecahedrane).

(31) It is of course conceivable that a larger cation might act as a template for the P_6W_{36} structure. The obvious candidate, K^+ , causes solubility problems in the synthesis solutions, and we have not explored this further.

(32) A cyclic M_3O_9 group can be constructed of corner-shared MO_4 tetrahedra, and the Keggin anion, for example, can be assembled by adding such groups to the central XO_4 tetrahedron. The M-O-M bond length alternations that are so evident in the structures of $\alpha\text{-}[\text{GeMo}_{12}\text{O}_{40}]^{4-}$ [Strandberg, R. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3090] and $\alpha\text{-}[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ (ref 17), as well as in the present structure, may reflect the effects of converting a terminal $\text{M}^{\text{VI}}\text{-O}$ bond to bridging $\text{M}^{\text{VI}}\text{-O-M}$. See also Day et al. (Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 952) for a discussion of pentamolybdodiphosphate anions from a similar viewpoint.

(33) See, for example: Dubois, S.; Souchay, P. *Ann. Chim.* **1948**, *3*, 105.