Aquanonadecatungstodiphosphate(14−) Polyanion, $[P_2W_{19}O_{69}(OH_2)]^{14-}$:*X*-Ray Crystallographic Structure* of its Potassium Salt, Chemical Relationships in the Tungstophosphate System, and Conversion into the Diaquaicosatungstodiphosphate $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$

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The crystal structure of $K_{14}[P_2W_{19}O_{69}(OH_2)]\cdot 24H_2O$ has been determined [space group *Fddd*, a = 28.800(3), b = 38.143(8), c = 32.005(7) Å, Z = 16, R = 0.048 for 3 108 reflections with $I > 3\sigma(I)$]. The anion has crystallographic symmetry 2, very close to a C_{2v} point group symmetry. Two α-A-$PW_9O_{34}{}^{9-}$ units are linked through one $WO(OH_2)^{4+}$ unit. Two interior and one exterior water molecules are hydrogen bonded to anionic oxygens; two K^+ cations are complexed by the anion as a double cryptate to give the polyanion a compact close form. The behaviour of the salt in aqueous solution is discussed and studied by ^{183}W and ^{31}P n.m.r. spectroscopy which reveals a reversible transformation and the influence of K^+ cations on its stability. Divalent polarizing cations such as Zn^{2+} transform it into $[PZn_2W_{10}O_{38}(OH_2)_2]^{7-}$ as mixtures of isomers. Other chemical aspects on the polyanion are shown including its relationships with $[PW_9O_{34}]^{9-}$ $[P_2W_{17}O_{61}]^{10-}$, $[KP_2W_{20}O_{72}]^{13-}$, and the first reported quantitative preparation of the salt $K_{10}[P_2W_{20}O_{70}(OH_2)_2]\cdot 22H_2O$, at pH 2.5—3.5. The last is obtained also by slight acidification of $K_7[PW_{11}O_{39}]$ (aq).

The Keggin-type polyanions $[XW_{12}O_{40}]^{x-8}$ are degraded by aqueous bases affording, as a first step, the corresponding so-called 'lacunary' derivatives $[XW_{11}O_{39}]^{x-12}$ by removal of one WO group (x is the oxidation state of the central atom X).[1] The pentadentate site so created may be occupied by a metallic cation of lower oxidation state than the tungsten, and even with an alkaline or alkaline-earth cation.[2] In more basic medium, three octahedra are degraded leading to anions of general formula $[XW_9O_{34}]^{x-14}$ which result from the loss of three adjacent WO_2 groups.[3] Only few monomers XW_{10} have been prepared up to now.[4,5] Several isomers exist for each composition.[1] In addition to these general types, the polytungsto-phosphate(V) and -arsenate(V) systems contain two series of specific dimerized complexes. One is represented by the Dawson-type $[X_2W_{18}O_{62}]^{6-}$,[1,6] the other by the earlier reported $[P_2W_{21}O_{71}]^{6-}$ whose actual formula is $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ as deduced from a recent structural study.[7] The latter is obtained by acidification of the potassium salt of the monomer $[PW_{11}O_{39}]^{7-}$. The reverse process, a moderate reaction of potassium carbonate or hydroxide on this salt, also affords a dimer, formulated as $[P_2W_{19}O_{69}]^{14-}$. The preparation of adducts such as $[P_2Co_2W_{19}O_{69}(OH_2)]^{10-}$ suggests that it belongs to the P_2W_{21} family.[8] The present paper reports the structure exhibited by the nonadecatungstodiphosphate anion in its potassium salt, the only one which may be prepared with a good crystallinity. A complementary chemical study brings new aspects on its formation from various tungstophosphates, confirms the very specific influence of the K^+ cation on its stability, and shows its lability in the presence of weakly charged polarizing cations. An example of this behaviour is the formation of disubstituted Keggin-type polyanions of composition $[PZ^{II}{}_2W_{10}O_{38}OH_2)_2]^{7-}$ (Z^{II} = Zn, Co, or Ni). In particular, in weak acidic media it transforms into the intermediate $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ polyanion on the route towards $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$.

Results and Discussion

Structure of the Potassium Salt of the Nonadecatungstodiphosphate.—The molecular view of the polyanion (Figure 1) leads to its formulation as $[P_2W_{19}O_{69}(OH_2)]^{14-}$ and shows clearly how it derives from $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$.[7] The anion contains two α-A-$PW_9O_{34}{}^{9-}$ moieties [W(1)—W(9)]. (See ref. 3 for the notation designating isomer type.) The short interatomic distances between the three tungsten atoms W(1)—W(3) (mean 3.42 Å, Table 1) characterize well a complete Keggin subgroup of three adjacent edge-sharing octahedra. The 'belt' of six tungsten octahedra is formed with the three corner-bonded pairs of edge-sharing octahedra W(4,5), W(6,7), and W(8,9) as parts of three degraded Keggin subgroups W_3O_{10}. In each pair the interatomic distances W $\cdots$ W are slightly shorter (mean 3.35 Å) than those of the complete subgroup W(1)—W(3) as observed also in $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ (ref. 7) and $[P_2W_{18}O_{62}]^{6-}$ (ref. 6). The two PW_9 moieties are bridged by a tungsten atom, W(10), *via* four oxygen atoms [O(4,10), O(5,10), O(4,10^i), O(5,10^i)] of the octahedra pairs W(4,5) and W(4^i,5^i). The superscript 'i' denotes homologous atoms by the C_2 axis symmetry (Table 1, symmetry code). Two oxygenated ligands complete the W(10) octahedron. The exterior one, O(10), is interpreted as being an oxo ligand according to the short W $\cdots$ O distance of 1.67(3) Å. The other, inside the space between the PW_9 units is considered to be an aqua ligand, $H_2O(10)$, consistent with the long W–O bond length of 2.31(3) Å and the observed 14− charge (16− for 70 non-protonated oxygens). Clearly W(10) corresponds to the exterior W(3e) of the $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ polyanion; both interior W(3i) are missing here.[7] As a consequence, the non-bridged octahedra pairs W(6,7), W(8,9), W(6^i,7^i), and W(8^i,9^i) have two unshared oxo ligands [W $\cdots$ O *ca.* 1.75(3) Å] instead of one as usually

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Selected interatomic distances (Å) for $K_{14}[P_2W_{19}O_{69}(OH_2)]$*

W(1)–W(2)	3.431	W(3)–O(3)	1.73	K(3)–W(10)	3.84
W(1)–W(3)	3.425	W(3)–O(13)	2.04	K(2)–W(10)	3.90
W(1)–W(4)	3.691	W(3)–O(38)	1.84	K(2)–W(4)	3.90
W(1)–W(9)	3.820	W(3)–O(37)	1.81	K(2)–W(9)	3.90
W(2)–W(3)	3.412	W(3)–O(23)	2.02	K(2)–W(6$^{\mathrm{i}}$)	3.87
W(2)–W(5)	3.682	W(3)–O(123P)	2.39	K(2)–W(5$^{\mathrm{i}}$)	3.93
W(2)–W(6)	3.823	W(4)–O(4)	1.70	Mean	σ(K–W) = 0.01
W(3)–W(7)	3.759	W(4)–O(14)	1.90		
W(3)–W(8)	3.751	W(4)–O(45)	1.94	K(1)–O(12)	2.77
W(4)–W(5)	3.376	W(4)–O(4,10)	1.92	K(1)–O(14)	2.75
W(4)–W(9)	3.709	W(4)–O(49)	1.89	K(1)–O(45)	2.88
W(4)–W(10)	3.658	W(4)–O(45P)	2.43	K(1)–O(25)	2.78
W(5)–W(6)	3.708	W(5)–O(5)	1.74	K(2)–O(49)	3.01
W(5)–W(10)	3.661	W(5)–O(25)	1.84	K(2)–O(4,10)	2.85
W(6)–W(7)	3.347	W(5)–O(45)	1.90	K(2)–O(5,10$^{\mathrm{i}}$)	2.90
W(7)–W(8)	3.744	W(5)–O(5,10)	1.94	K(2)–O(56$^{\mathrm{i}}$)	2.98
W(8)–W(9)	3.351	W(5)–O(56)	1.87	K(2)–O(60$^{\mathrm{i}}$)	2.88
Mean	σ(W–W) = 0.002	W(5)–O(45P)	2.43	K(2)–O(90)	2.88
		W(6)–O(6)	1.71	K(2)–H$_2$O(4$^{\mathrm{ii}}$)	2.96
W(1)–P	3.511	W(6)–O(26)	2.10	K(2)–O(3$^{\mathrm{ii}}$)	2.77
W(2)–P	3.516	W(6)–O(56)	1.96	K(2)–H$_2$O(5)	2.90
W(3)–P	3.468	W(6)–O(60)	1.73	K(3)–O(13$^{\mathrm{ii}}$)	2.76
W(4)–P	3.551	W(6)–O(67)	1.92	K(3)–O(10)	2.82
W(5)–P	3.560	W(6)–O(67P)	2.40	K(3)–O(5,10$^{\mathrm{i}}$)	3.32
W(6)–P	3.549	W(7)–O(7)	1.72	K(3)–O(5$^{\mathrm{i}}$)	2.84
W(7)–P	3.545	W(7)–O(67)	1.95	K(3)–O(3$^{\mathrm{ii}}$)	2.96
W(8)–P	3.544	W(7)–O(37)	2.10	K(3)–H$_2$O(2$^{\mathrm{v}}$)	2.74
W(9)–P	3.526	W(7)–O(78)	1.90	K(3)–H$_2$O(6)	2.87
Mean	σ(W–P) = 0.01	W(7)–O(70)	1.77	K(4)–O(13)	2.90
		W(7)–O(67P)	2.38	K(4)–O(19)	2.82
P–O(89P)	1.52	W(8)–O(89P)	2.41	K(4)–O(89)	2.83
P–O(45P)	1.51	W(8)–O(8)	1.70	K(4)–O(38)	2.81
P–O(67P)	1.53	W(8)–O(38)	2.11	K(4)–O(5$^{\mathrm{iii}}$)	2.67
P–O(123P)	1.54	W(8)–O(89)	1.95	K(4)–O(1$^{\mathrm{iv}}$)	2.76
Mean	σ(P–O) = 0.026	W(8)–O(80)	1.74	K(4)–H$_2$O(3)	2.80
		W(8)–O(78)	1.90	K(4)–H$_2$O(3$^{\mathrm{iii}}$)	2.76
W(1)–O(19)	1.80	W(9)–O(9)	1.73	Mean	σ(K–O) = 0.026
W(1)–O(1)	1.70	W(9)–O(89)	1.92		
W(1)–O(13)	1.88	W(9)–O(19)	2.12	H$_2$O(1)–H$_2$O(1$^{\mathrm{i}}$)	3.02
W(1)–O(12)	1.92	W(9)–O(49)	1.93	H$_2$O(1)–O(80)	2.72
W(1)–O(14)	1.95	W(9)–O(90)	1.75	H$_2$O(1)–O(90)	2.84
W(1)–O(123P)	2.42	W(9)–O(89P)	2.39	H$_2$O(1$^{\mathrm{i}}$)–O(60)	2.76
W(2)–O(2)	1.72	W(10)–O(10)	1.67	H$_2$O(1$^{\mathrm{i}}$)–O(70)	2.68
W(2)–O(26)	1.80	W(10)–O(5,10)	1.89	H$_2$O(1)–H$_2$O(10)	2.96
W(2)–O(23)	1.88	W(10)–O(4,10)	1.93	Mean	σ(H$_2$O–O) = 0.04
W(2)–O(12)	2.00	W(10)–H$_2$O(10)	2.31		
W(2)–O(25)	2.01	Mean	σ(W–O) = 0.026		
W(2)–O(123P)	2.36				

* Symmetry code: i $x, \frac{3}{4} - y, \frac{3}{4} - z$; ii $-\frac{1}{4} + x, \frac{1}{4} + y, \frac{1}{2} - z$; iii $\frac{1}{4} + x, \frac{1}{2} - y, -\frac{1}{4} + z$; iv $\frac{5}{4} - x, y, \frac{1}{4} - z$; v $1 - x, \frac{1}{4} + y, \frac{1}{4} + z$.

observed in condensed tungsten polyanions. Each PW_9O_{34} unit deviates appreciably from trigonal symmetry. The 'belts' are slightly bent: W(6,9) lie 0.120(6) Å from the W(4,5,7,8) plane and are further from the 'cap' than these latter [W(1) ··· W(4) and W(2) ··· W(5) 3.682(2) Å, W(1) ··· W(9) and W(2) ··· W(6) 3.823(2) Å]. This distortion is also characterized by the difference in dihedral angle between the mean plane of the 'belts' [7.5(8)°] and the acute angle of the directions P–O(123P) and P$^{\mathrm{i}}$–O(123P$^{\mathrm{i}}$) [12(1)°]. These values also show that the PW_9 'shells' are close to a coaxial position. Three associated atomic species contribute. (*i*) Two water molecules, H$_2$O(1,1$^{\mathrm{i}}$), are inserted in the cavity and hydrogen-bonded to the unshared oxygens O(60,60$^{\mathrm{i}}$,70,70$^{\mathrm{i}}$,80,80$^{\mathrm{i}}$) and to the interior aqua ligand H$_2$O(10) (distances 2.69—2.96 Å, Table 1, bifurcated hydrogen bonds certainly). (*ii*) Two neighbouring cations, K(2,2$^{\mathrm{i}}$), interact strongly each with six oxygens lying on each side of the polyanion near the 'equatorial region' [O(4,10), O(49), O(90), O(5,10$^{\mathrm{i}}$), O(56$^{\mathrm{i}}$), O(60$^{\mathrm{i}}$) for K(2)]. (*iii*) One atom referred to as C, and interpreted preferably as a water molecule (see Experimental section) (Figure 1), is connected to terminal oxygens O(70,80,70$^{\mathrm{i}}$,80$^{\mathrm{i}}$) [distances 2.97(3) Å].

The location of the K(2) cations corresponds to those of the 'equatorial' K^+ in $K_{6-x}H_x[P_2W_{21}O_{71}(OH_2)_3]\cdot nH_2O$.[7] However in $K_{14}[P_2W_{19}O_{69}(OH_2)]\cdot 24H_2O$ the K(2) ··· O distances with the six nearest oxygens of the polyanion are distinctly shorter (2.85—3.00 Å against 3.03—3.10 Å) and similar to those observed in potassium cryptates [*cf.* for example, [K(18-crown-6)][NCS][9] and [K(18-crown-6)]$_2$[Cu(S$_2$C$_2$O$_2$)$_2$];[10] 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane}. The six oxygens exhibit an hexagonal crown configuration with a flattened boat form: O(4,10), O(5,10$^{\mathrm{i}}$), O(60$^{\mathrm{i}}$), O(90) in a plane, O(49,56$^{\mathrm{i}}$) at 0.47(6) Å and K(2) at 1.50(6) Å out of this plane. Thus $[P_2W_{19}O_{69}(OH_2)]^{14-}$ behaves as a two-fold cryptate reagent for K^+ cations (also Rb^+ certainly). Three other oxygen atoms

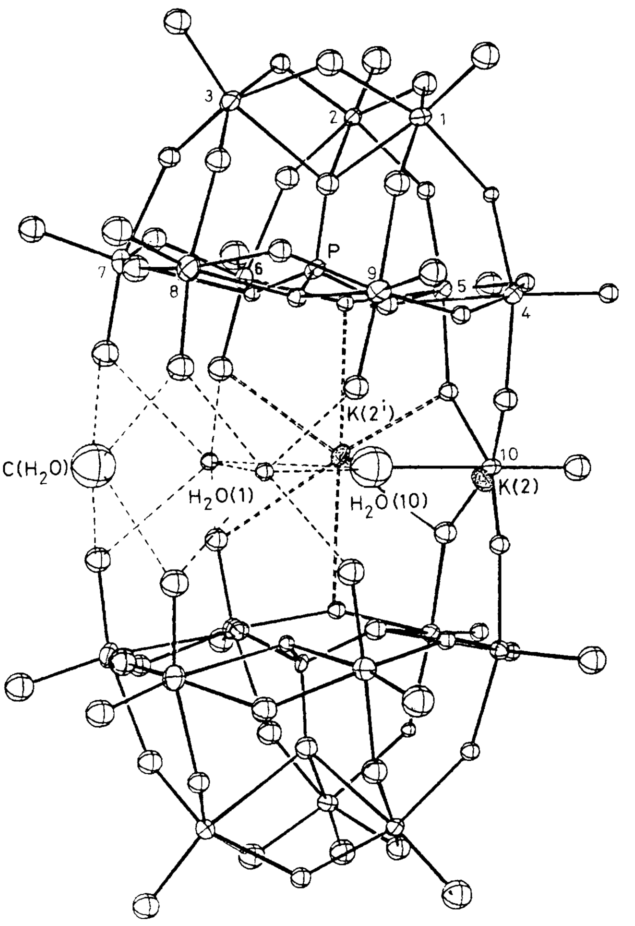

Figure 1. ORTEP drawing of the polyanion $[P_2W_{19}O_{69}(OH_2)]^{14-}$ and some important associated atoms with 40% ellipsoids. The tungsten atoms are numbered 1—10. Labelling of the oxygen atoms is omitted for clarity. Dashed lines represent hydrogen bonds, dashed double lines the connections between one K(2) atom and six near oxygens in the polyanion

of the anion are close neighbours of each K(2): O(3) of an adjacent polyanion and $H_2O(4,5)$, with similar distances.

The polyanion has crystallographic point symmetry 2 where the C_2 axis is one of the eight axes parallel to a in the cell and passes through $H_2O(10)$, W(10), O(10), and the atom C. In fact, in each anion, the atoms may be coupled in pairs, quasi symmetrical with respect to one or the other of two nearly diagonal planes parallel to a. In the atomic co-ordinates listed in Table 2 such pairs are recognizable by close values of their x co-ordinates [$\Delta x(W) < 6 \times 10^{-4}$ (0.0017 Å)]. Therefore, the polyanion exhibits in the crystal a very slightly distorted point symmetry *mm* (C_{2v}).

Three well detected potassium cations contribute to the packing of different anions in the crystal. The K(1) atoms occupy the inversion centres in quasi-prismatic arrangements of eight anionic oxygens [O(12,14,24,45) and the centrosymmetric ones] and join polyanions into 'diagonal' chains (two directions). The K(3),K(4) cations connect polyanions of chains of different directions.

Chemical Properties of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ *related to its Structure.*—The crystallographic results help to understand the chemical behaviour of the $[P_2W_{19}O_{69}(OH_2)]^{14-}$ polyanion in solution. It may be expected that the associated atoms $H_2O(1)$, K(2), and $C(H_2O)$ which contribute to holding together the PW_9 units in the solid salt separate from it easily in aqueous solutions. In this case, the only remaining link, W(10), between these units is a potential cause of flexibility or breakage for the polyanion. However, the presence of templating cations such as K^+ or Rb^+ in sufficient concentration stabilizes it. Other cations also seem to provide a comparable stability. Thus cationic exchange occurs by stirring solid $K_{14}[P_2W_{19}O_{69}(OH_2)]$ in solutions of Sr^{2+} or Ba^{2+}. The resulting sparingly soluble salts (badly crystallized) retain the usual analytical character of $[P_2W_{19}O_{69}(OH_2)]^{14-}$: treated with a pink Co^{2+} solution (*ca.* 50 °C), these Sr^{2+}- or Ba^{2+}-exchanged salts turn pink then blue after 30 min. This specific reaction is similar, although slower, than that performed with the non-exchanged K^+ salt.[8] When the molar ratio Sr^{2+} (or Ba^{2+}): $K_{14}[P_2W_{19}O_{69}(OH_2)]$ is lower than 2, the filtrate does not contain any more alkaline-earth cation, showing a quantitative exchange. For higher ratios, the exchange is partial and the product is always a K–M^{2+} mixed salt of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ which does not dissolve appreciably and does not decompose even by heating at 80—90 °C. The corresponding quasi-insoluble (K^+, Sr^{2+}) or (K^+, Ba^{2+}) salts of $[P_2Co_2W_{19}O_{69}(OH_2)_2]^{10-}$ also are stable to heating, contrary to the dissolved potassium salts of the same anion.

Therefore, it is believed that Sr^{2+} and Ba^{2+} may be cryptated by the polyanion.

Similarly, K^+ cations can be replaced from the solid salt by ammonium or substituted ammonium cations (pyridinium, guanidinium, tetra-alkylammonium, lysine, arginine, pH 6.0—7.0). After exchange, even repeated, the sparingly soluble product never contains less than 2 K^+ per anion and always retains the properties characterizing $[P_2W_{19}O_{69}(OH_2)]^{14-}$.

On the other hand, the polyanion is modified in aqueous solution. Thus, freshly prepared saturated solutions of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ (*ca.* 0.01 mol dm^{-3} at 25 °C) immediately added to solutions of Co^{2+} give purple-blue solutions. On cooling and evaporating the blue potassium salt of $[P_2Co_2W_{19}O_{69}(OH_2)_2]^{10-}$ crystallizes first, leaving a red solution which contains the well known Keggin-type $[PCoW_{11}O_{39}(OH_2)]^{5-}$ polyanion. Since $[P_2Co_2W_{19}O_{69}(OH_2)_2]^{10-}$ is unstable $[PCoW_{11}O_{39}(OH_2)]^{5-}$ may arise from its rapid degradation. However, non-saturated solutions of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ aged overnight at room temperature turn red after addition of aqueous Co^{2+} and the blue complex is not formed. Moreover the final products depend on the Co^{2+} proportions and on the pH. For example, the clear red solution obtained from an aged $K_{14}[P_2W_{19}O_{69}(OH_2)]$ solution and 4 Co^{2+} per anion (pH 7.0—7.5) and evaporated affords slowly a potassium salt of a novel complex $[PCo_2W_{10}O_{38}(OH_2)_2]^{7-}$ (cubic structure observed for salts of various substituted Keggin-like polyanions such as $[CoCoW_{11}O_{39}]^{8-}$, $[SiW_{11}O_{39}]^{8-}$, see below). At lower pH, Co^{2+} in excess also involves the partial formation of $[PCoW_{11}O_{39}(OH_2)]^{5-}$. Consequently, one would consider that $K_{14}[P_2W_{19}O_{69}(OH_2)]$ breaks up in aqueous solution. However on the contrary, the polyanion is well recovered from its solutions *even* when they are *aged or heated*. The addition of moderate amounts of a potassium salt favours that, certainly stabilizing the cryptate form.

Attempts to determine the behaviour of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ in solution using n.m.r. spectroscopy are not conclusive but bring some information.

Due to the weak receptivity of ^{183}W and the too low solubility of $K_{14}[P_2W_{19}O_{69}(OH_2)]$, K^+ cations were first exchanged to obtain very soluble products {with Li^+, Na^+, $[NH_2(CH_2CH_2OH)_2]^+$, or $[NH(CH_2CH_2OH)_3]^+$ (resin exchange or reaction with the corresponding perchlorate)}. Each product gives a unique spectrum which characterizes the

Table 2. Fractional atomic co-ordinates for $K_{14}[P_2W_{19}O_{69}(OH_2)]\cdot24H_2O$ {$\times 10^5$ for W, $\times 10^4$ for others}. The oxygen numbering scheme is deduced from the neighbouring tungsten or/and phosphorus atoms (labelled P). Note that a zero indicates that the neighbouring (bridging) tungsten is missing compared to the complete $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$

Atom	*x*	*y*	*z*
W(1)	61 716(5)	27 390(4)	20 646(5)
W(2)	61 770(6)	21 692(4)	28 942(5)
W(3)	71 983(6)	24 114(4)	24 376(5)
W(4)	55 263(6)	33 821(4)	27 017(5)
W(5)	55 242(6)	28 165(4)	35 132(5)
W(6)	66 417(6)	24 956(5)	39 434(5)
W(7)	76 466(6)	27 072(5)	34 829(6)
W(8)	76 512(6)	33 264(5)	25 750(6)
W(9)	66 451(6)	36 635(4)	22 361(5)
W(10)	53 875(8)	$\frac{3}{8}$	$\frac{3}{8}$
P	6 604(3)	3 025(3)	3 032(3)
K(1)	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$
K(2)	5 942(3)	4 342(3)	2 890(3)
K(3)	4 391(4)	4 374(3)	3 466(5)
K(4)	7 197(4)	3 001(3)	1 471(3)
O(1)	5 892(10)	2 697(8)	1 599(9)
O(12)	5 923(9)	2 337(7)	2 346(8)
O(13)	6 718(9)	2 482(6)	1 976(8)
O(14)	5 680(8)	2 992(6)	2 358(7)
O(19)	6 464(9)	3 154(7)	2 028(8)
O(123P)	6 548(9)	2 705(7)	2 741(8)
O(2)	5 918(9)	1 764(7)	2 944(9)
O(23)	6 729(9)	2 047(7)	2 617(8)
O(25)	5 671(8)	2 477(6)	3 126(7)
O(26)	6 457(9)	2 229(7)	3 392(8)
O(3)	7 558(9)	2 124(7)	2 171(8)
O(37)	7 420(9)	2 412(7)	2 968(8)
O(38)	7 415(8)	2 853(6)	2 310(7)
O(4)	5 066(10)	3 541(7)	2 427(9)
O(45)	5 214(8)	3 057(6)	3 075(8)
O(45P)	6 126(8)	3 146(6)	3 156(8)
O(49)	6 037(8)	3 633(6)	2 485(7)
O(4,10)	5 508(8)	3 708(6)	3 158(7)
O(5)	5 046(8)	2 622(6)	3 752(8)
O(56)	6 018(8)	2 693(6)	3 863(7)
O(5,10)	5 500(9)	3 263(7)	3 805(8)
O(6)	6 525(9)	2 147(7)	4 264(8)
O(60)	6 768(9)	2 829(7)	4 291(8)
O(67)	7 266(9)	2 373(7)	3 791(8)
O(67P)	6 870(8)	2 917(6)	3 424(7)
O(7)	8 163(10)	2 479(8)	3 500(9)
O(78)	7 762(9)	3 032(7)	3 045(9)
O(70)	7 709(9)	3 014(7)	3 894(8)
O(8)	8 168(13)	3 320(10)	2 318(12)
O(89P)	6 865(8)	3 327(6)	2 833(7)
O(89)	7 265(9)	3 503(7)	2 121(8)
O(80)	7 704(10)	3 719(8)	2 846(9)
O(9)	6 516(10)	3 856(7)	1 760(9)
O(90)	6 770(9)	4 031(7)	2 544(8)
O(10)	4 807(14)	$\frac{3}{8}$	$\frac{3}{8}$
$H_2O(10)$	6 196(21)	$\frac{3}{8}$	$\frac{3}{8}$
$H_2O(1)$	7 080(8)	4 003(6)	3 387(7)
$H_2O(2)$	5 950(12)	1 772(9)	1 755(11)
$H_2O(3)$	6 967(12)	3 602(9)	1 011(10)
$H_2O(4)$	8 526(12)	2 541(9)	2 502(11)
$H_2O(5)$	5 700(15)	4 333(11)	2 010(14)
$H_2O(6)$	4 292(18)	3 862(13)	2 815(16)
$H_2O(7)$	$\frac{3}{8}$	$\frac{3}{8}$	1 508(21)
$H_2O(8)$	5 616(13)	1 798(10)	3 915(11)
A	7 538(11)	4 466(8)	2 725(10)
B	6 479(11)	5 272(8)	1 788(10)
C	7 997(22)	$\frac{3}{8}$	$\frac{3}{8}$
D	7 340(12)	1 662(9)	3 233(11)

$[PW_{11}O_{39}]^{7-}$ polyanion in its specific species {$[PLiW_{11}O_{39}(OH_2)]^{6-}$ $[PNaW_{11}O_{39}(OH_2)]^{6-}$, or the $[NH_2(CH_2CH_2OH)_2]^+$ or $[NH(CH_2CH_2OH_3)]^+$ exchanged salt of $K_7[PW_{11}O_{39}]$*}. Thus $[P_2W_{19}O_{69}(OH_2)]^{14-}$ transforms to $[PW_{11}O_{39}]^{7-}$ when K^+ is absent or in a minor amount. When a substantial quantity of K^+ is present, the more complex spectra give evidence of several polyanions. For a saturated solution of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ in 4 mol dm^{-3} $[NH_2(CH_2CH_2OH)_2]Cl$ with a slight excess of non-dissolved $K_{14}[P_2W_{19}O_{69}(OH_2)]$, the spectrum reveals a mixture in which the PW_{11}-$[NH_2(CH_2CH_2OH)_2]^+$ derivative is only recognizable and other polyanions belong to the P_2W_{21} family (several peaks between -150 and -212 p.p.m.). The solution shows clearly the blue cobalt(II) reaction for 3 h at least at 298 K; it certainly contains $[P_2W_{19}O_{69}(OH_2)]^{14-}$. However, we are unable to discriminate its n.m.r. spectrum. Starting from pure $K_{14}[P_2W_{19}O_{69}(OH_2)]$ heated at 330 K to increase its solubility, the ^{183}W spectrum is still complex and not interpretable but proves the transformation of the polyanion. Thus thirteen main lines are observed instead of six with relative intensities 2:4:4:4:4:1 for the probable C_{2v} symmetry. No such set of six lines is unambiguously distinguishable and neither is the spectrum of $K_7[PW_{11}O_{39}]$. Condensed polyanions are however present as shown by peaks lying between -150 and -212 p.p.m., the first peak of the spectrum appearing at -93.5 p.p.m. These anions are presently unknown. Because various mixtures exist depending strongly on the experimental conditions (cations, temperature) these spectra may be resolved only by a considerable improvement in the sensitivity. We are presently trying a novel technique for this.

Other information can be deduced from the spectra of the most sensitive ^{31}P nucleus because, generally, one signal is representative of one polyanion only.

The ^{31}P n.m.r. spectrum was recorded for a freshly prepared saturated solution of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ at 298 K (started 5—6 min after the preparation). It shows two peaks at -8.85 (**I**) and -10.25 p.p.m. (**II**). The integrated intensities give a (**II**):(**I**) ratio of *ca.* 0.8 initially which increases with the time to 3.6 after 1.46 h. Species (**I**) disappears after several days. When an excess of the solid salt is in equilibrium with the solution, the ratio of both species stabilizes at *ca.* 1.8 (1.5 h, 298 K). Species (**II**) is not identified as $K_7[PW_{11}O_{39}]$ whose chemical shift is -10.12 p.p.m. under the same conditions (well-distinguished from -10.25 p.p.m.). Thus (**I**) is attributed to the potassium cryptate form $[P_2W_{19}O_{69}(OH_2)]^{14-}$ found in the solid salt in accordance with the 'blue reaction' of Co^{2+} (aq) from freshly prepared solutions of $K_{14}[P_2W_{19}O_{69}(OH_2)]$. Species (**II**) has not been determined, but we consider it to be a rearrangement of the cryptate form (**I**). We note that the transformation is reversible and regresses strongly by slight addition of K^+. Moreover species (**II**) also transforms slowly, leading to complex and variable mixtures which depend strongly on the

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* G. Tourne, unpublished work: $K_7[PW_{11}O_{39}]$, 305 K, δ (p.p.m.), -94.38 (2 W), -98.16 (2 W), -114.32 (1 W), -114.68 (2 W), -130.48 (2 W), -152.42 (2 W); $[NH_2(CH_2CH_2OH)_2]^+$ exchanged $K_7[PW_{11}O_{39}]$, 305 K, δ (p.p.m.), -96.34 (2 W), -103.80 (2 W), -109.18 (2 W), -116.42 (1 W), -130.70 (2 W), -152.69 (2 W).

Table 3. Isotropic and anisotropic ^{31}P n.m.r. data for $[P_2W_{19}O_{69}(OH_2)]^{14-}$ and related polytungstophosphates

	Solid salts		Freshly prepared solutions at 295 K
Polyanions of K^+ salts	δ^a p.p.m. ($\Delta\nu$/Hz)	C.s.a./p.p.m.	δ^b p.p.m.
$[PKW_{11}O_{39}]^{6-}$	−10.9(40)	−32	−10.12
$[KP_2W_{20}O_{72}]^{13-}$	−11.6(25)	+38.4	−8.87, −10.32
$[P_2W_{19}O_{69}(OH_2)]^{14-}$	−9.8(41)	+31.7	−8.85, −10.25
$[P_2W_{21}O_{71}(OH_2)_3]^{6-}$	−13.5(73)	+51	*ca.* −13.20 (pH dependent)
$[PW_9O_{34}]^{9-}$(Na^+ salt)	−7.2(55)	+27.5	

[a] $\delta \pm 0.1$ p.p.m. [b] $\delta \pm 0.02$ p.p.m.

concentration (several uninterpreted weaker peaks appear progressively). This degradation is inhibited by addition of K^+.

Solutions of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ showed a relationship to the compound $K_{13}[KP_2W_{20}O_{72}]$ discovered by Fuchs and Palm.[11] From a clear saturated solution of $K_{14}[P_2W_{19}O_{69}(OH_2)]$, a few crystals appear *without evaporation*. They are identified as those of the less soluble salt $K_{12}[KP_2W_{20}O_{72}]$ by their space group ($P2_1/c$) and parameters $a = 13.55$, $b = 22.27$, $c = 15.07$ Å, and $\beta = 96°$. Preparing the salt $K_{13}[KP_2W_{20}O_{72}]$ from the procedure of Fuchs and Palm,[11] we verified that it was unique in the crystalline product by means of its *X*-ray powder diffraction diagram and its solid-state ^{31}P magic angle spinning n.m.r. spectrum. It was therefore surprising that the ^{31}P n.m.r. spectrum of its freshly prepared aqueous solution exhibits two peaks at −8.87 and −10.32 p.p.m. The former (the least intense) corresponds certainly to the species (**I**) discussed above, although the 'blue reaction' with Co^{2+} was not observed. Its relative intensity increases slowly. The latter is assumed to characterize $[KP_2W_{20}O_{72}]^{13-}$. Because its resonance line (−10.32 p.p.m.) is very close to that of species (**II**) (−10.25 p.p.m.), one might conclude that both species are identical (both may superimpose in the spectra). But this slight difference is always found independently of the experiments and is not attributable to experimental error. At present, it is believed that (**II**) and $[KP_2W_{20}O_{72}]^{13-}$ have very close but different structures.

In the salts $K_{14}[P_2W_{19}O_{69}(OH_2)]$ and $K_{13}[KP_2W_{20}O_{72}]$ the polyanions are built from the same type of fragments and differ by the bridging mode of PW_9O_{34} units: one bridging octahedron *via* four *trans* oxygens in the former, two octahedra, each *via* four *cis* oxygens in the latter. Therefore, it is not surprising that they may transform into each other. However attempts to convert directly $K_{13}[KP_2W_{20}O_{72}]$ into $K_{14}[P_2W_{19}O_{69}(OH_2)]$ or conversely always leads to poor yields. Indirectly, various reactions of potassium bases on $K_7[PW_{11}O_{39}]$ result only either in $K_{14}[P_2W_{19}O_{69}(OH_2)]$ or in other unknown products and never in $K_{13}[KP_2W_{20}O_{72}]$. The procedure reported by Fuchs and Palm[11] suggests that $K_{13}[KP_2W_{20}O_{72}]$ is probably a metastable compound. In their work the final solution is described as cloudy, showing the presence of unreacted $K_3[PW_{12}O_{40}]$ and *six products* are detected (excluding the paratungstate) as against *only one* from a clear final solution in our preparation of $K_{14}[P_2W_{19}O_{69}(OH_2)]$. Hence different chemical states are reached in both works. The identification of the various unknown compounds obtained as by- or intermediate-products by Fuchs and Palm[11] and ourselves would clarify the tungstophosphate system in this composition range. We assume that free monomeric fragments PW_{10} may be formed which associate in various ways. In particular, dissolved $K_{14}[P_2W_{19}O_{69}(OH_2)]$ affords such fragments which recombine partially in $[KP_2W_{20}O_{72}]^{13-}$.

The solid-state thermal stability of the salt $K_{14}[P_2W_{19}O_{69}(OH_2)]$ has been examined. After dehydration (130 °C, 6 h, residual $4.5H_2O$; 160 °C, 8 h, $0.8H_2O$) the product redissolves in water and the pure hydrated salt recrystallizes. Upon addition of a non-aqueous solvent (MeOH, EtOH, or acetone) its aqueous solution gives an amorphous precipitate. Redissolved in water, crystalline $K_{14}[P_2W_{19}O_{69}(OH_2)]$ is regenerated. This polyanion is very stable in K^+ media.

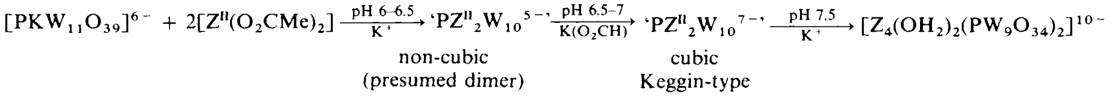
To be sure that the solid salts used were pure and free of the parent compounds observed in solution, *X*-ray powder diffraction diagrams were obtained together with a solid-state ^{31}P n.m.r. spectrum (magic angle spinning and non-spinning techniques). The results are reported in Table 3. Each compound showed a unique peak and a positive chemical shift anisotropy (c.s.a.) (local axial symmetry C_{3v}, cylindrical tensor) consistent with the structural type A of the $[PW_9O_{34}]^{9-}$ units. We note that the resonance moves towards lower frequencies (increased shielding) and the c.s.a. increases when the number of bridging atoms between both PW_9 groups increases.

Chemical Relationships of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ *with other Polytungstophosphates.*—(*a*) *Nonatungstophosphate.* α-A-$PW_9O_{34}^{9-}$ is prepared in Na^+ media by two routes: the direct acidification of HPO_4^{2-} and WO_4^{2-} (HPO_4^{2-}: WO_4^{2-}: H^+ = 1:9:11) or the reaction of $Na_7[PW_{11}O_{39}]\cdot nH_2O$ with sodium hydrogencarbonate.[12] Previously reported as a β-B isomer,[3] recent papers provide evidence for a A-type structure and a strong presumption for the α-isomeric form.[13] Cold solutions of the pure PW_9 sodium salt $Na_8[HPW_9O_{34}]$ (aq) give precipitates by addition of an excess of solid potassium acetate. At a pH higher than 8.0, the product is the body-centred cubic $K_9[PW_9O_{34}]\cdot nH_2O$ (microcrystalline powder) reported earlier,[14] but at a pH lower than 7.0, $K_{14}[P_2W_{19}O_{69}(OH_2)]$ is only formed and a mixture of both between these pH values.

Of the most interest is the rapid quantitative synthesis of pure $[P_2W_{19}O_{69}(OH_2)]^{14-}$ by combining $K_7[PW_{11}O_{39}]$ (aq) and $Na_8[HPW_9O_{34}]$ (aq) (PW_{11}:PW_9 = 1:3, pH 6.5, *ca.* 45 °C) followed by precipitation with a potassium salt.

All these fast reactions strongly suggest that $Na_8[HPW_9O_{34}]$ used as a starting reactant is an α-isomer like the groups found in $K_{14}[P_2W_{19}O_{69}(OH_2)]$, a rapid β to α isomerization by rotating the complete W_3O_{10} subgroup being very improbable.

(*b*) *Octadecatungstophosphate* (*Dawson series*). The most surprising new synthesis of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ is carried out from $[P_2W_{18}O_{62}]^{6-}$. It is known that the reaction of tungstate with an excess of phosphoric acid leads to a mixture of two P_2W_{18} isomers.[15] Dawson[6] determined the structure of the most abundant isomer which consists of two α-A-PW_9 units sharing six oxygens of the six-octahedra 'belts'. Contant[16] has described several derivatives of $[P_2W_{18}O_{62}]^{6-}$ as members of a 'close family'. We have now found a route from the Dawson compound $[P_2W_{18}O_{62}]^{6-}$ towards the Keggin polytungstophosphates through $[P_2W_{19}O_{69}(OH_2)]^{14-}$. The P_2W_{18} polyanion is degraded by moderate alkaline attack into $[P_2W_{17}O_{61}]^{10-}$. Two isomers α_1- and α_2-$[P_2W_{17}O_{61}]^{10-}$ are



$$[PKW_{11}O_{39}]^{6-} + 2[Z^{II}(O_2CMe)_2] \xrightarrow[K^+]{pH\ 6\text{—}6.5} \underset{\substack{\text{non-cubic}\\ \text{(presumed dimer)}}}{\text{‘}PZ^{II}{}_2W_{10}{}^{5-}\text{’}} \xrightarrow[K(O_2CH)]{pH\ 6.5\text{—}7} \underset{\substack{\text{cubic}\\ \text{Keggin-type}}}{\text{‘}PZ^{II}{}_2W_{10}{}^{7-}\text{’}} \xrightarrow[K^+]{pH\ 7.5} [Z_4(OH_2)_2(PW_9O_{34})_2]^{10-}$$

Scheme 1.

obtained.[17] The latter is the most stable and results on the removal of one tungsten atom from a terminal W_3O_{10} subgroup. Usually it is prepared by slow addition of $KHCO_3$ to $K_6[P_2W_{18}O_{62}]$ (50—60 °C, pH *ca.* 6.5).[18] After separation of the potassium salt of α_2-$[P_2W_{17}O_{61}]^{10-}$, slightly soluble at room temperature, evaporation of the filtrate and the recovery of successive fractions of solid salt ultimately gave pure $[P_2W_{19}O_{69}(OH_2)]^{14-}$ (*X*-ray powder diffraction pattern and Co^{2+} addition). No trace of paradodecatungstate $K_{10}[H_2W_{12}O_{42}]$ is detected. The yield of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ increases by faster addition of the base, a longer heating time, and a higher temperature (80 °C to boiling). This unexpected reaction suggested that the P_2W_{18} and P_2W_{17} polyanions may open up when the alkaline hydrolysis is carried out in the presence of free $WO_4{}^{2-}$. In fact, a pure potassium salt of $[P_2W_{19}O_{69}(OH_2)]^{14-}$ is obtained quantitatively by heating to reflux an aqueous solution of $K_{10}[P_2W_{17}O_{61}]$ with potassium tungstate as a base according to the stoicheiometry $[P_2W_{17}\text{-}O_{61}]^{10-} + 2WO_4{}^{2-} + H_2O \longrightarrow [P_2W_{19}O_{69}(OH_2)]^{14-}$.

Thus, it is possible to pass from the Dawson to the Keggin series *via* the P_2W_{19} polyanion and its transformation in $[PW_{11}O_{39}]^{7-}$. Curiously, a similar reaction with $[As_2W_{17}O_{61}]^{10-}$ does not occur even by heating the solution for several days.

(*c*) *Basic hydrolysis of* $[PZ^{II}W_{11}O_{39}(OH_2)]^{5-}$ *in* K^+ *media: identification of* $PZ^{II}{}_2W_{10}$ *polyanions as precursors of* $[Z^{II}{}_4(OH_2)_2(PW_9O_{34})_2]^{10-}$. As observed above, the reaction of aged solutions of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ with polarizing bivalent cations Z^{II} such as Co^{2+}(aq) leads to Keggin-type polyanions whereas the solid salt or freshly prepared solutions afford a $P_2Z^{II}{}_2W_{19}$ derivative. We wanted to explore the basic degradations of $PZ^{II}W_{11}$ polyanions in K^+ medium compared to $K_7[PW_{11}O_{39}]$ {considered as $K_6[PKW_{11}O_{39}(OH_2)]$}.

First, we have noted that the result of the reaction between $[PKW_{11}O_{39}]^{6-}$ and a Z^{II} salt differs according to whether the counter anion of Z derives from a strong or weak acid. In the latter case, the anion acts as a weak base. In particular, reaction of $[PKW_{11}O_{39}]^{6-}$ with a Z^{II} acetate ($Z^{II} = Mn^{2+}, Co^{2+}, Ni^{2+}$, or Zn^{2+}) gives a sparingly soluble complex and not the very soluble tetragonal potassium salt of $[PZ^{II}W_{11}O_{39}(OH_2)]^{5-}$. *X*-Ray powder diffraction reveals that the product is a mixture of two species. One component exhibits the well identified cubic structure of potassium salts of Keggin-type anions (*i.e.* $[Zn_2W_{11}O_{39}]^{8-}$). The other has an unknown non-cubic structure, but is recognized by its *X*-ray powder diffraction diagram. The bulk composition is always close to $[PZ_2W_{10}O_{38}(OH_2)_2]^{7-}$ even with an initial equimolar $Z:PW_{11}$ ratio. The separation of both components is almost impossible because they have weak solubility (even after heating). They transform by heating or dissolution in Na^+ or Li^+ media (cationic exchange or salt addition). However, a systematic study on reactions of $[PKW_{11}O_{39}]^{6-}$ with acetates of bivalent elements and a $Z^{2+} : PKW_{11}$ molar ratio of 2 (no noticeable difference appears with higher values) allows them to be obtained separately.

The non-cubic complex is prepared from cold solutions after successive evaporations to dryness (see Experimental section). An almost pure compound (the trace impurity is the cubic compound) is obtained with a yield higher than 85%. No single crystal can be prepared at present. The non-cubic salt clearly behaves as an unstable precursor of the cubic one.

The more stable cubic salt is prepared from a moderately heated solution (*ca.* 50—55 °C) in which the pH is maintained in the range 6.5—7 by addition of potassium formate (preferable to the acetate which is slightly more basic). Cubic microcrystals grow slowly. The fractions recovered (*ca.* 50%) are very pure (specially with Zn) the only impurity being the paratungstate $K_{10}[H_2W_{12}O_{42}]$ in the final fraction. Recrystallisation fails. These cubic PZ_2W_{10} polyanions are also unstable in aqueous solution. They transform slowly into the previously reported $[Z_4(OH_2)_2(PW_9O_{34})_2]^{10-}$ polyanions in which the PW_9 groups have the B-type structure.[19] The transformation rate is strongly dependent on the temperature and the counter cations (2 d at 50 °C, several months at 25 °C for 0.008 mol dm^{-3} solutions of potassium salts). It also increases when the pH is raised to 7.5 or more. Therefore, the acetate medium is not suitable for the preparation of cubic complexes. These results elucidate the mechanism of formation of the $[Z_4(OH_2)_2(PW_9O_{34})_2]^{10-}$ polyanions by direct synthesis (after formation of the PW_{11} polyanion) according to Scheme 1. Both precursors are also obtained by the reaction of aged solutions of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ with acetates. We note that the non-cubic precursor is also obtained in similar reactions carried out with $K_7[AsW_{11}O_{39}]$.

As for the study of $K_{14}[P_2W_{19}O_{69}(OH_2)]$, n.m.r. spectroscopy brings interesting information. The ^{31}P n.m.r. spectrum of the cubic precursor containing $[PZn_2W_{10}O_{38}(OH_2)_2]^{7-}$ in aqueous solution shows an intense narrow peak at −7.08 p.p.m. After *ca.* 10—15 min, other peaks appear, the first at −7.01, then −11.44 {$[PZW_{11}O_{39}(OH_2)]^{5-}$}, −4.08 {$[Zn_4(OH_2)_2(PW_9O_{34})_2]^{10-}$}, and −4.80 p.p.m. (unknown). This confirms the instability of the PZn_2W_{10} anion. The ^{31}P n.m.r. spectra of the various solid fractions of the cubic zinc-containing precursor were also recorded. The magic angle spinning spectra show a broad, non-symmetrical peak (*ca.* −7.5 p.p.m., $\Delta\nu$ = 105—140 p.p.m., a shoulder at −8.2 p.p.m.) whose outline varies owing the sample. Clearly it is composite. On the best resolved one, two near peaks at −7.41 and −7.66 p.p.m. are distinguished. The non-spinning spectra confirm the presence of two species at least. The *X*-ray powder diffraction diagrams of the various fractions give evidence of one very pure structural phase; this is explained by the fact that each of them is really a variable mixture of Keggin-type isomers {five α-isomers are expected for $[PZ_2W_{10}O_{38}(OH_2)_2]^{7-}$}.[1] Their very close chemical shifts make resolution of the individual resonances difficult. The non-spinning spectra show that both major components exhibit a negative c.s.a. consistent with a B-type PW_9 or $PZnW_8$ fragment in the polyanion {$[PZnW_{11}O_{39}(OH_2)]^{5-}$ has also a negative c.s.a.}. Thus, one of them would be a 1,4 Zn_2-substituted Keggin-type isomer[20a] (one heterometallic subgroup WZn_2 and B-PW_9). This has the most favourable molecular structure to be transformed into the dimer $[Zn_4(OH_2)_2(PW_9O_{34})_2]^{10-}$. The shoulder at −8.2 p.p.m. observed in the isotropic resonance spectrum of the first cubic samples is also assigned to a third isomer but its corresponding anisotropic signal is masked.

For the last cubic fraction isolated in each preparation, the analytical Zn:W molar ratio is clearly lower than 2:10 (see Experimental section). The *X*-ray powder diffraction diagram also reveals a pure cubic product. This may be interpreted by the presence in the cubic solid solution of a polyanion having a low Zn:W ratio. The latter may be either the polyanion $[PZnW_{11}O_{39}(OH_2)]^{5-}$ which enters in solid solutions with

$[PZn_2W_{10}O_{38}(OH_2)_2]^{7-}$ or the hypothetical $[PKZnW_{10}O_{38}(OH_2)_2]^{8-}$, isomorphous with polyanions such as $[PKZ^{III}W_{10}O_{38}OH_2)_2]^{7-}$ which we have isolated with certain trivalent elements.[20b]

For the non-cubic precursor, one peak is observed at −7.45 p.p.m. with the usual width of 40 Hz (evidence for a unique compound). A small shoulder at −8.2 p.p.m. is due to the cubic impurity as described above. The non-spinning spectrum shows a negative c.s.a. (−49.7 p.p.m.) characterizing B-type PW_9 groups.

(*d*) $K_{14}[P_2W_{19}O_{69}(OH_2)]$ (aq) *in acidic media: preparation of the* $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ *polyanion.* Although $K_{14}[P_2W_{19}O_{69}(OH_2)]$ results on the treatment of $[PW_{11}O_{39}]^{7-}$ with potassium bases, the opposite reaction does not regenerate the latter, except when free tungstate is added. When solid $K_{14}[P_2W_{19}O_{69}(OH_2)]$ is added to a diluted strong acid solution with $H^+:P_2W_{19} = 4$, a novel polyanion is produced quantitatively from the resulting clear solution. The pH rises from 2.0—2.2 for the initial solution to *ca.* 4.0 after 1 h. The crystals differ morphologically from those of the potassium salts of $[PW_{11}O_{39}]^{7-}$ and $[P_2W_{19}O_{69}(OH_2)]^{14-}$ and exhibit a specific *X*-ray powder diffraction pattern. The product does not give the 'blue reaction' with aqueous Co^{2+} solutions but a specific 'red reaction' with a temperature-dependent reversible colour change (red to purple by heating). The analyses agree well with a salt $K_{10}P_2W_{20}O_{70}{\cdot}24H_2O$. The novel P_2W_{20} anion is clearly different from that of $[KP_2W_{20}O_{72}]^{13-}$.[11] It is presumed to be the intermediate polyanion between $[P_2W_{19}O_{69}(OH_2)]^{14-}$ and $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ for which we propose logically the formula $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ (structure will be reported elsewhere). The same product is obtained by reacting a cold aqueous solution of $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ with solid $K_{14}[P_2W_{19}O_{69}(OH)_2]$ in an equimolar ratio. This P_2W_{20} polyanion is evidently the same as that Knoth *et al.*[13] discovered among others in the acid treatment of $[Zn_3(PW_9O_{34})_2]^{12-}$. However, we consider that these authors assigned an incorrect formulation to, for example, $K_{14}(WO_2)_2(PW_9O_{34})_2$ for the potassium salt precipitated at pH 7. Indeed, at this pH $K_{10}[P_2W_{20}O_{70}(OH_2)_2]$ converts to $[P_2W_{19}O_{69}(OH_2)]^{14-}$ whose less soluble potassium salt precipitates and characterizes easily by our usual tests. Note that analysis does not allow discrimination unambiguously between the formulae $K_{14}(WO)(PW_9O_{34})_2$ (Calc. K, 10.50; P, 1.20; W, 67.10%) and $K_{14}(WO_2)_2(PW_9O_{34})_2$ (Calc. K, 10.05; P, 1.15; W, 67.60%). In contrast, their[13] lithium salt prepared from an acidic solution contained the P_2W_{20} polyanion as shown by ^{183}W n.m.r. spectroscopy. Comparatively, Figure 2 shows the ^{183}W n.m.r. spectra obtained from $K_{10}[P_2W_{20}O_{70}(OH_2)_2]$ in which K^+ was almost entirely exchanged by Na^+ (*a*) or Li^+ (*b*). A set of six lines (with intensity ratio 2:4:4:4:4:2) is found. However the chemical shifts are noticeably dependent on the counter cation and the pH. This explains the differences in the positions of certain peaks between both works. In addition, the spectra recorded 3 d after the cationic exchange show that $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ transforms slowly in Li^+ or Na^+ media at pH 4. One resulting product is clearly the corresponding $[PMW_{11}O_{39}(OH_2)]^{6-}$ species (M = Li or Na); the other, which exhibits 8 or 9 peaks with equivalent intensities, is presently unknown {an isomer of $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ with two non-equivalent bridging atoms, we think}. These views are confirmed by the ^{31}P n.m.r. spectra: −12.32 (73), −10.92 (18), −11.20 p.p.m. (9%) for the Li^+ salt; −13.32 (80), −10.02 (8), −10.77 p.p.m. (12%) for the Na^+ salt; assignments respectively to $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$, $[PMW_{11}O_{39}(OH_2)]^{6-}$, and the unidentified polyanion.

Surprisingly, when the well known salt $K_7PW_{11}O_{39}$ is treated with a slightly acid solution ($H^+:PW_{11} = 1.5$), the resulting clear solution (pH 2.5—3.5) also affords the P_2W_{20} polyanion. We verify that a similar reaction occurs from $K_7AsW_{11}O_{39}$.

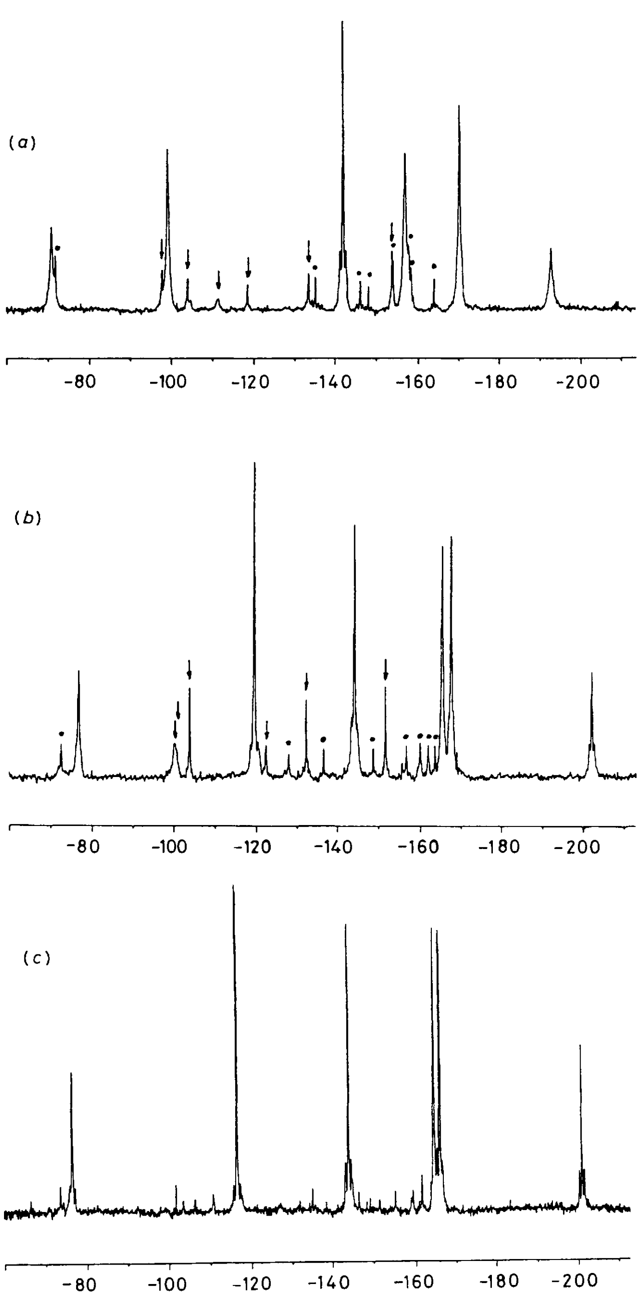
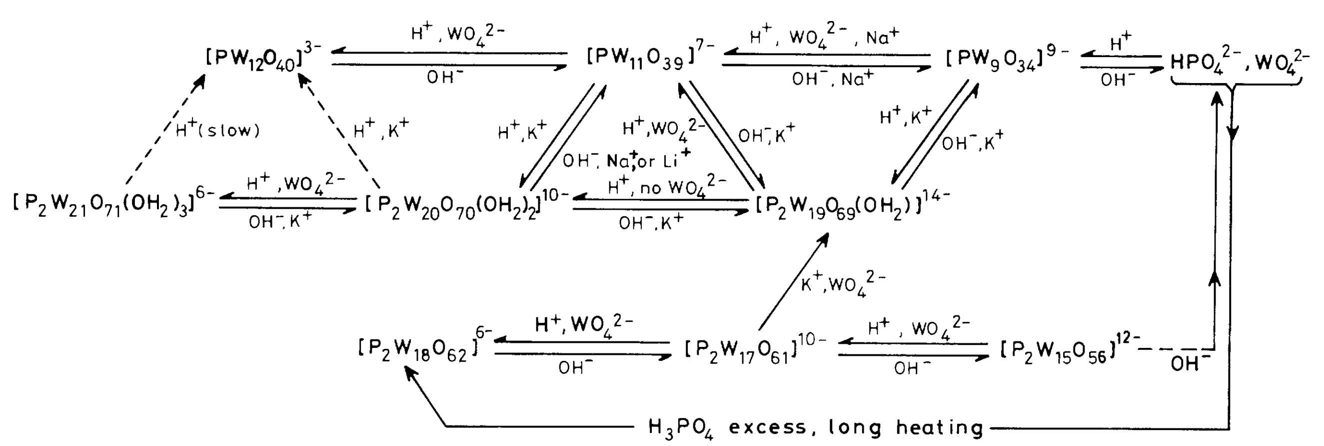


Figure 2. ^{183}W N.m.r. spectra of lithium and sodium salts of the polyanion $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$. (*a*) Sodium salt, pH 4, and (*b*) lithium salt, pH 4; both obtained by resin exchange. (*c*) Lithium salt, pH 3.5, formed by $LiClO_4$ treatment of K^+ salt. Arrows and points indicate the $[PMW_{11}O_{39}(OH_2)]^{6-}$ and unknown species, respectively (M = Li or Na)

Preliminary crystallographic data support the theory that $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ is the parent polyanion between $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ and $[P_2W_{19}O_{69}(OH_2)]^{14-}$. The structure of its salts is dependent on the counter cations. They often exhibit a rhombohedral symmetry $R\bar{3}$ by reason of a rotational trigonal disorder of the anion (Rb, Cs, or mixed salts Na–Rb, K–Rb, *etc.*). Moreover the crystals grow as interpenetrant rhombohedra twinned about the triad axis. They are iso-



Scheme 2.

morphous with K^+ salts of the $P_2Z^{III}{}_2W_{19}$ series (Z^{III} = Mn or Ga) which show the same characteristics. The structure of the polyanion will be reported separately from more suitable non-disordered salts.

In conclusion, the present study of the salt $K_{14}[P_2W_{19}O_{69}(OH_2)]$ shows that it occupies an important position in polytungstophosphate chemistry. First, the anion belongs to the family in which α-A-$PW_9O_{34}{}^{9-}$ units are linked through bridging tungsten atoms and obey the general formula $[WO(OH_2)]_n[PW_9O_{34}]_2$ (each bridging tungsten bears one oxo and one aqua ligand). The triad P_2W_{21}, P_2W_{20}, P_2W_{19} (n = 3, 2, or 1 respectively) is now synthesized and the structures of two determined. They are also the purely tungsten members of the more general series with the partial formula $(MM'M'')(PW_9)_2$ whose particular examples have been recently reported.[21] Secondly, Scheme 2 shows how $[P_2W_{19}O_{69}(OH_2)]^{14-}$ is related to the three families $[PW_{12}O_{40}]^{3-}$ (Keggin), $[P_2W_{18}O_{62}]^{6-}$ (Dawson), and $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$.

Although requiring a potassium medium, the direct synthesis of $K_{14}[P_2W_{19}O_{69}(OH_2)_2]$ is easy and rapid, starting from sodium tungstate as is usual. It may be converted so easily into $[PW_{11}O_{39}]^{7-}$, $[PW_9O_{34}]^{9-}$, and $[P_2W_{20}O_{70}(OH_2)_2]^{10-}$ and we are currently investigating a route towards $[P_2W_{18}O_{62}]^{6-}$.

An analogous compound and a similar family has been reported with the arsenate(v),[16] but we have not succeeded in obtaining $[As_2W_{19}O_{69}(OH_2)]^{14-}$ directly.

Experimental

X-Ray Structure Determination.—The salt $K_{14}[P_2W_{19}O_{69}(OH_2)]$ was prepared as previously described.[8] Previous attempts to determine its structure were unsuccessful because the single crystals always broke after a short time (from several hours to 2 d). The following thermal treatment was found necessary and efficient to stabilize well formed crystals with dimensions lower than 0.30 mm. They are collected from saturated solutions of the salt (a few mg of potassium acetate added stabilizes the pH) which are *slowly evaporated* in air at room temperature {sometimes a few prismatic crystals appeared which did not exhibit the recognizable habit of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ (see above)}. Some of the crystals were transferred into drops of paraffin oil deposited on glass plates and the adherent traces of the aqueous mother solution carefully removed. These crystal-containing drops were alternately cooled to −5 °C and warmed to room temperature twice a day for two weeks. Such crystals did not break even after one year. One was selected, glued to the end of a glass fibre and coated with a fine paraffin oil film. Further cooling and heating treatments were made after mounting the crystal on the goniometric head to remove any residual stresses.

Crystal data. $K_{14}[P_2W_{19}O_{69}(OH_2)]\cdot 24H_2O$, M = 5 655.2, orthorhombic, space group *Fddd*, a = 28.800(3), b = 38.143(8), c = 32.005(7) Å, U = 35 158.0 Å^3, Z = 16, D_c = 4.273, D_m = 4.24 g cm^{-3}, Mo-K_α radiation (λ = 0.710 69 Å), μ = 270.4 cm^{-1}, $F(000)$ = 40 064. Crystal morphology: faces and their distances from an arbitrary central origin refined with the program FACIES:[22] (110) ($\bar{1}\bar{1}0$) 0.080; ($1\bar{1}0$) ($\bar{1}10$) 0.057; (001) ($00\bar{1}$) 0.106; (111) ($\bar{1}\bar{1}\bar{1}$) 0.099; ($1\bar{1}1$) 0.075 mm.

Data collection and reduction. 3 108 Independent reflections [$I > 3\sigma(I)$] were selected (among 4 100 data) on an Enraf-Nonius CAD-4F diffractometer by the ω–4θ/3 scan technique, $\theta_{max.}$ 20°. Lorentz-polarization and absorption corrections were applied, the latter by use of ψ-scans (19 planes) and the program ABSORB.[23]

Structural analysis. The sites of the heavier atoms (W,P) and consequently the framework of the polyanion were determined by direct methods (MULTAN).[24] The real and imaginary part of the anomalous dispersion were applied for W, P, and K. The complete structure was solved by alternate Fourier and difference syntheses and full-matrix least-squares refinements.[25]

A major difficulty arose in the search of the K^+ cations. Only four independent cationic sites are clearly located, in particular K(2) on a centre of symmetry. So statistically, only half the cations are found. In the final difference maps no significant intense peaks could be attributed to the missing K^+. Furthermore nine independent peaks [$H_2O(1)$—$H_2O(9)$] were interpreted unambiguously as water molecules of crystallization, $H_2O(10)$ is evidently an interior aqua ligand of W(10). Four remaining peaks, labelled A—D, have been refined as water molecules although their positions could be also consistent with K^+. However, refinement as K^+ led to very high values of their thermal parameters (B > 14Å^2), and to an increased R factor. These four sites might be occupied statistically either by K^+ or by water molecules, but the respective occupancy factors cannot be determined. Therefore, this problem has not received a deeper treatment (an identical case was also encountered with the potassium salt of the related polyanion $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$).[7] Nevertheless, the structure of the polyanion is not altered noticeably (R 0.048, R' 0.055, 3 108 data, 350 parameters; residual peaks density, max. 1.49, min. −0.98 e Å^{-3}). Additional data available from the Cambridge Crystallographic Centre comprises thermal parameters and remaining bond lengths.

N.M.R. Spectra.—The ^{183}W and ^{31}P high-resolution n.m.r. spectra were determined on a Bruker WP360 spectrometer at

15.0046 MHz with 15 mm-diameter sample tubes and at 145.742 MHz with 10 mm-diameter tubes respectively. The solvent was 25—30% D_2O-containing water as internal lock. The chemical shifts were externally referenced to a 2 mol dm^{-3} solution of $Na_2WO_4 \cdot 2H_2O$ in D_2O at 302 K for ^{183}W, to 85% H_3PO_4 at 305 K for ^{31}P. The solvent shifts due to the pH were controlled from the ^1H signal of water detected with the proton decoupling coil. Deviations were found to be <0.01 p.p.m. for W and <0.02 p.p.m. for P. The ^{31}P magic angle spinning (3.8—4.1 kHz) and non-spinning spectra were recorded on a Bruker CXP-200 spectrometer at 80.962 Hz and 291 K. The chemical shifts were referenced to an external non-spinning sample of 85% H_3PO_4. Typical experiments used proton decoupling, 30—90° pulses with a 15—90 s recycle time depending on the relaxation time T_1 (measured approximately). The chemical shift anisotropy (c.s.a.) was taken as $\delta_{\parallel} - \delta_{\perp}$ for the cylindrical tensor.

Preparation of $K_{14}[P_2W_{19}O_{69}(OH_2)] \cdot 24H_2O$ *from* $K_{10}[P_2W_{17}O_{61}]$ (aq).—The $K_{10}[P_2W_{17}O_{61}]$ (48 g, 0.01 mol) was dissolved in hot water (150 cm^3) and the solution made to boil. A solution of K_2WO_4 was prepared by dissolving $WO_3 \cdot H_2O$ (4.6 g, 0.02 mol) in a hot solution (80 °C) of potash (2.6 g of hydrated potash, 0.04 mol) and added to the former. The pH increased to 8.5—9.0 and the solution was stirred and refluxed for 1 d. The final pH was 6.8—7.1. The solution volume was reduced to half and allowed to crystallize; 51 g of $K_{14}[P_2W_{19}O_{69}(OH_2)] \cdot 24H_2O$ were recovered. The crude product free of $K_{10}[P_2W_{17}O_{61}]$ or other Dawson derivatives was controlled by *X*-ray powder diffraction and the reaction with Co^{2+} (aq).

Preparation of $K_{14}[P_2W_{19}O_{69}(OH_2)]$ *from Mixtures of* $K_7PW_{11}O_{39}$ (aq) *and* $Na_8[HPW_9O_{34}]$ (aq).—A solution of $Na_8[HPW_9O_{34}]$ (aq) (10.65g, 3.75 mmol) was added to a solution of $K_7[PW_{11}O_{39}]$ (aq) (4.0 g, 1.25 mmol), the pH reduced to *ca.* 6—6.5 and the mixture stirred and heated at 50 °C. Solid KCl was added until a fine crystalline precipitate appeared. Further KCl (3—4 g) was then added. A crystalline powder separated. Stirring was maintained until room temperature was reached. The product was then filtered off and washed with chilled water (10 cm^3). It was identified as for the previous preparation.

Preparation of the Polyanions derived from $[PZ^{II}W_{11}O_{39}(OH_2)]^{5-}$.—*Non-cubic salts.* To a cold solution of $K_7[PW_{11}O_{39}]$ (aq) (32 g, 0.01 mol) in water (100 cm^3) was added a cold solution of zinc acetate (4.4 g, 0.02 mol) in water (20 cm^3). The resulting solution was evaporated to dryness at 25 °C. The solid was slurried and stirred for 1 h with cold water (50 cm^3) and filtered. The non-dissolved product (*ca.* 4—5 g) was washed with cold water (*ca.* 5 cm^3). The filtrate was again slowly evaporated and the extraction procedure repeated until the recovery of 85—90% of solid products. Each solid fraction was controlled by *X*-ray powder diffraction. Similar reactions were performed with cobalt and nickel acetates. [Analysis. Found: H_2O, 10.1; K, 6.40; P, 1.00; W, 59.5; Zn, 4.15. Calc. for '$K_5PZn_2W_{10}O_{37} \cdot 18H_2O$': H_2O, 10.30; K, 6.20; P, 1.00; W, 59.10; Zn, 4.15%. Found: Co, 4.10; H_2O, 9.45; K, 7.05; P (not measured); W, 59.45. Calc. for '$K_5PCo_2W_{10}O_{37} \cdot 17H_2O$': Co, 3.85; H_2O, 9.40; K, 6.40; P, 1.00; W, 60.00%. Found: H_2O, 10.40; K, 6.60; Ni, 3.60; P (not measured); W, 58.50. Calc. for '$K_5PNi_2W_{10}O_{37} \cdot 18H_2O$': H_2O, 10.45; K, 6.30; Ni, 3.80; P, 1.00; W, 59.35%].

Cubic salts. $K_7PW_{11}O_{39}$ (aq) (32 g) and zinc or cobalt acetate (44 g) were dissolved, at 50 °C, in 50 and 10 cm^3 of water respectively and the solutions mixed. Solid potassium formate (15 g) was added. The clear non-stirred solution was kept at 50 °C on a hot plate. A microcrystalline solid deposited slowly on the bottom and on the wall of the beaker. This solid was recovered (3—4 g) and the remaining solution again heated at 50 °C. Fractions of the cubic salt were filtered off and the treatment was stopped when potassium paratungstate appeared as a micaceous suspension which was easily separated. 15—18 g of a well crystallized cubic solid were obtained. Each fraction was controlled by *X*-ray powder diffraction. The only impurity was traces of paratungstate. [Analysis: Found for the first fraction: H_2O, 8.95; K, 9.0; P, 1.0; W, 58.4; Zn, 3.90. Calc. for '$K_7PZn_2W_{10}O_{38} \cdot 16H_2O$': H_2O, 9.10; K, 8.65; P, 0.95; W, 58.00; Zn, 4.15%. Found for the ultimate fraction (Zn deficient): H_2O, 8.05; K, 9.40; P (not measured); W, 58.4; Zn, 3.45. Found: H_2O, 8.85; K, 8.05; Co, 3.75; W, 58.5. Calc. for '$K_7PCo_2W_{10}O_{38} \cdot 15H_2O$': H_2O, 8.60; K, 8.70; P, 1.00; Co, 3.75; W, 58.55%.]

Preparation of $K_{10}[P_2W_{20}O_{70}(OH_2)_2] \cdot 22H_2O$.—For the best procedure, the salt $K_{14}[P_2W_{19}O_{69}(OH_2)]$ (aq) must be prepared in microcrystalline form by precipitating its stirred solution, almost saturated at 40—45 °C, by adding solid KCl until precipitation began {*ca.* 4—5 g KCl for 50 g $K_{14}[P_2W_{19}O_{69}(OH_2)]$}. The solution was stirred for 10 min, kept 1—2 h at 2—5 °C and filtered. The solid was rapidly washed with chilled water (5—10 cm^3) and air dried. The salt (56 g, 0.01 mol) was poured into water (100 cm^3) acidified with HCl (0.04 mol) and stirred at room temperature. The initial pH is *ca.* 1.7—2.0 and rises finally to 3.5. The solution becomes clear after 10 min. Solid KCl (6—10 g) was added and stirring continued for 10—15 min. The crystalline product was filtered off and washed rapidly with chilled water (10 cm^3) and air dried. The crude product was very pure and contained only traces of KCl. It may be recrystallized from water (pH 2.5—3.5) [Found: H_2O, 7.5; K, 7.20; P, 1.10; W, 64.5. Calc. for $K_{10}P_2W_{20}O_{70}(OH_2)_2 \cdot 22H_2O$: H_2O, 7.6; K, 6.90; P, 1.10; W, 64.70%].

This preparation is preferred but it is possible to start from $K_7PW_{11}O_{39}$ (aq) (32 g, 0.01 mol; 60 cm^3 of water acidified with 0.015—0.02 mol HCl).

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