Triaquahenicosatungstodiphosphate(6−) Heteropolyanion, $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$: *X*-Ray Crystallographic† and ^{183}W Nuclear Magnetic Resonance Structural Studies

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The single-crystal *X*-ray structure of $K_4H_2[P_2W_{21}O_{71}(OH_2)_3]\cdot28H_2O$ [space group $P6_3/mmc$, a = 16.295(2), c = 19.771(5) Å, and Z = 2; Mo radiation, R = 0.037 for 1 042 unique data] has been determined and the ^{183}W n.m.r. spectrum of the anion in H_2O-D_2O has been recorded. The anion has true point symmetry C_{2v} but occupies a D_{3h} site in the crystal with orientational disorder about a crystal three-fold axis. It contains two α-A-$PW_9O_{34}^{9-}$ units, each with C_{3v} symmetry, linked through three equatorial $WO(OH_2)^{4+}$ units. Two equatorial W atoms are closer to, and the third is further from, the anion (crystal C_3) axis. The H_2O ligand on the unique W is directed towards the interior of the anion and is hydrogen-bonded to the oxo ligand, also directed internally, on each of the other equatorial W.

The partial degradation of the $[PW_{12}O_{40}]^{3-}$ heteropolyanion by aqueous base affords $[PW_{11}O_{39}]^{7-}$, from which $[PW_{12}O_{40}]^{3-}$ is regenerated on acidification together with a second heteropolyanion of partial empirical formula P_2W_{21}.[1] The latter has received little attention since it was first reported, apart from one study[2] which confirmed the P:W ratio but gave no structural information. Our interest in this anion was stimulated by the preparation[3] of what appear to be derivatives in which two W atoms have been replaced by Co^{II}, *etc.*, and by the characterization of an $As^{III}{}_2W_{21}$ heteropolyanion and its substitution products,[4] including the *X*-ray structural analysis[5] of $Rb_4H_2[As_2W_{21}O_{69}(OH_2)]\cdot34H_2O$. *X*-Ray diffraction is nowadays a routine method for determining the structures of heteropolyanions,[6] but the resolution obtainable is frequently limited by orientational disorder. In recent years[7] ^{183}W n.m.r. spectroscopy has proved to be a powerful complementary technique. The number and relative intensities of ^{183}W resonances will often directly distinguish between possible isomeric structures,[8] and further information is furnished by the analysis of W–W coupling,[9] including two-dimensional spectroscopy.[10] We have made use of both *X*-ray and n.m.r. methods in the present work.

Results and Discussion

Chemical analysis confirms that the anion is a 21-tungstodiphosphate and indicates that the charge is −6. We formulate the anion as $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ for reasons which will be set out below.

Crystallographic Results.—The anion (Figure 1) in $K_4H_2[P_2W_{21}O_{71}(OH_2)_3]\cdot28H_2O$ lies at a site of crystallographic point symmetry $\bar{6}2m$ (D_{3h}) in space group $P6_3/mmc$. Atomic coordinates are given in Table 1. The site symmetries for P, W(1), and W(3) are respectively $3m$, m, and mm; W(2) is at a general position. The anion contains two α-A-$PW_9O_{34}^{9-}$ moieties (for the notation designating isomers, see ref. 11), each of which is derived from the well known Keggin (α-$PW_{12}O_{40}^{3-}$) structure[12] by the removal of three adjacent corner-sharing WO_6

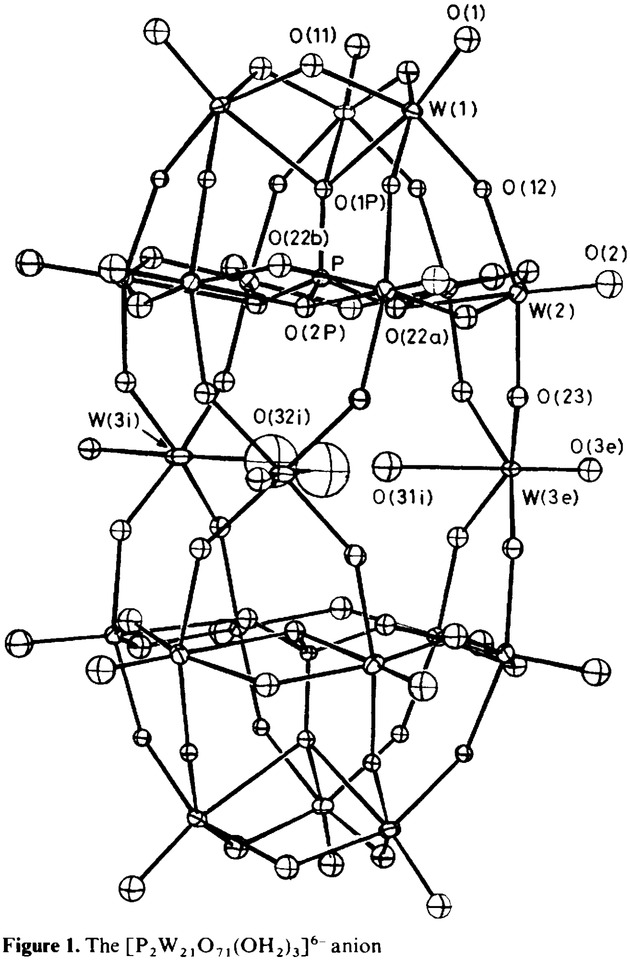

Figure 1. The $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ anion

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† *Supplementary data available.* (No. SUP 56610, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates (× 10^4) for $K_4H_2[P_2W_{21}O_{71}(OH_2)_3]\cdot 28H_2O$

Atom	*x*	*y*	*z*
W(1)	4 029.3(5)	5 970.7(5)	4 349.3(6)
W(2)	3 267.9(7)	4 477.4(6)	5 884.5(4)
W(3e)[a]	2 001.2(23)	7 998.8(23)	7 500
W(3i)[b]	2 213.9(21)	7 786.1(21)	7 500
P	3 333	6 667	5 813(7)
K	4 940(8)	5 059(8)	7 500
O(1)	4 439(8)	5 561(8)	3 698(11)
O(11)	2 790(8)	7 210(8)	3 958(10)
O(22a)	4 499(7)	5 501(7)	6 101(10)
O(22b)	1 927(8)	8 073(8)	5 701(11)
O(2P)	2 821(8)	7 179(8)	6 068(10)
O(12)	3 462(9)	4 963(9)	4 986(7)
O(2)	3 455(12)	3 561(12)	5 777(7)
O(23)	2 977(10)	8 651(11)	6 824(7)
O(1P)	3 333	6 667	5 031(15)
O(3e)	1 448(12)	8 552(12)	7 500
O(31i)[a]	3 092(104)	7 364(102)	7 500
O(32i)[a]	2 847(33)	7 153(33)	7 500
Aq(1)[c]	1 679(19)	8 321(19)	4 114(21)
Aq(2)[c]	7 265(44)	2 735(44)	7 500
Aq(3)[c]	6 882(94)	5 979(86)	6 899(46)

[a] Site occupancy factor $\frac{1}{3}$. [b] Site occupancy factor $\frac{2}{3}$. [c] Water molecule.

Table 2. Interatomic distances (Å) and interbond angles ( )

W(1)–O(1)	1.73(2)	W(3e)–O(23)	1.94(1)
W(1)–O(12)	1.90(1)	W(3e)–O(31i)	2.39(5)
W(1)–O(11)	1.95(1)	W(3i)–O(32i)	1.87(15)
W(1)–O(1P)	2.38(2)	W(3i)–O(23)	1.89(1)
W(2)–O(2)	1.68(2)	W(3i)–O(3e)	2.16(2)
W(2)–O(23$^{\text{I}}$)	1.90(1)	P–O(1P)	1.54(3)
W(2)–O(12)	1.90(1)	P–O(2P)	1.53(1)
W(2)–O(22a)	1.91(1)	K–O(1$^{\text{II}}$)	2.95(2)
W(2)–O(22b$^{\text{I}}$)	1.93(1)	K–O(22)	3.03(2)
W(2)–O(2P$^{\text{I}}$)	2.38(1)	K–O(23$^{\text{I}}$)	3.10(2)
W(3e)–O(3e)	1.56(2)		
W(1) ··· W(1$^{\text{III}}$)	3.402(1)	W(2) ··· W(3e$^{\text{III}}$)	3.669(2)
W(1) ··· W(2)	3.695(1)	W(3i) ··· W(3i$^{\text{III}}$)	5.472(6)
W(2) ··· W(2$^{\text{IV}}$)	3.354(2)	W(3e) ··· W(3i$^{\text{III}}$)	6.000(6)
W(2) ··· W(2$^{\text{V}}$)	3.674(2)	W(1) ··· P	3.497(11)
W(2) ··· W(3i$^{\text{III}}$)	3.608(2)	W(2) ··· P	3.518(1)
O(1P)–P–O(2P)	109.2(9)	O(23)–W(2)–O(22a)	88.8(7)
O(2P)–P–O(2P)	109.7(9)	O(23)–W(2)–O(22b)	88.4(8)
O(1)–W(1)–O(11)	96.6(7)	O(12)–W(1)–O(12)	84.8(8)
O(1)–W(1)–O(12)	105.9(6)	O(3e)–W(3e)–O(23)	103.7(6)
O(11)–W(1)–O(11)	85.9(8)	O(23)–W(3e)–O(23)	87.2(8)
O(11)–W(1)–O(12)	90.3(6)	O(23)–W(3e)–O(23)	86.4(9)
O(11)–W(1)–O(1P)	73.6(6)	O(23)–W(3e)–O(32i)	76.3(9)
O(12)–W(1)–O(1P)	84.0(6)	O(3e)–W(3i)–O(23)	85.7(6)
O(1)–W(1)–O(1P)	166.4(8)	O(23)–W(3i)–O(23)	89.3(9)
O(2)–W(2)–O(22a)	103.1(7)	O(23)–W(3i)–O(23)	90.1(9)
O(2)–W(2)–O(22b)	99.8(7)	O(23)–W(3i)–O(31i)	86(3)
O(2)–W(2)–O(12)	100.6(7)	O(3e)–W(3i)–O(31i)	169(5)
O(2)–W(2)–O(23)	98.8(7)	W(1)–O(11)–W(1)	121.6(9)
O(12)–W(2)–O(2P)	82.2(6)	W(2)–O(22a)–W(2)	149(1)
O(12)–W(2)–O(22a)	87.9(7)	W(2)–O(22b)–W(2)	120.9(7)
O(12)–W(2)–O(22b)	87.3(7)	W(2)–O(2P)–P	127.1(8)
O(23)–W(2)–O(2P)	78.4(7)	W(1)–O(12)–W(2)	152.1(8)
O(2)–W(2)–O(2P)	173.4(7)		

Symmetry code: (I) *x*,1 + *x* − *y*,*z*; (II) *y*,*x*,$\frac{1}{2}$ + *z*; (III) *x*,2*x*,*z*; (IV) *y* − *x*,*x*,*z*; (V) 1 − *y*, 1 − *x*,*z*

octahedra and consists of a 'cap' of three edge-sharing octahedra [W(1)] and a 'belt' of six octahedra [W(2)]. The belt octahedra are linked by alternate corner- and edge-sharing, and also share corners with the cap. Each W(3) atom in the equatorial plane of the anion is linked *via* O(23) atoms with a pair of edge-linked WO_6 octahedra in the belt above, and with a pair in the belt below, *i.e.* is bonded to oxygen atoms at the vertices exposed by the generation of $PW_9O_{34}{}^{9-}$ from $PW_{12}O_{40}{}^{3-}$. The anion exhibits three-fold disorder about the principal axis. The *X*-ray analysis shows that each W(3) is split between adjacent exterior and interior *mm* sites, W(3e) (more distant from the principal axis) and W(3i) (nearer the axis). The refinement of alternative models and of the site-occupancy factors strongly indicates that these equatorial sites are occupied in the ratio W(3e):W(3i) = 1:2. Thus the true anion symmetry, as confirmed by the ^{183}W n.m.r. spectrum, is *mm* (C_{2v}). The disorder as revealed by *X*-rays is nevertheless confined to the equatorial plane. There are no indications of alternative sites for W(1) and W(2), and the W–O, P–O, and W ··· W distances in the $PW_9O_{34}{}^{9-}$ moieties (Table 2) agree well with the values found[13] for the similar units in α-$[P_2W_{18}O_{62}]^{6-}$ and $[KP_2W_{20}O_{72}]^{13-}$.

Three oxygen atoms O(3e) lie in the equatorial plane, at *mm* sites exterior to the W(3e) and W(3i) atoms. A reasonable assumption is that O(3e) is actually H_2O when bonded to W(3i) [W–O 2.16(2) Å] but is unprotonated when bonded to W(3e) [W–O 1.56(2) Å]. There are also three regions of more diffuse electron density between the three W(3) atoms and the triad axis. These appear to arise from the presence of additional oxygen atoms; but because of the three-fold disorder, the *X*-ray data do *not* clearly distinguish between *three* interior oxygens on or near *mm* sites, each bonded to one W(3), and *two* interior oxygens each bonded to W(3i) only. In either case the short interior O ··· O distances (*ca.* 2.4 Å) seem consistent only with the presence of hydrogen bonds. The ^{183}W spectra which will now be discussed are relevant to this problem.

^{183}W *N.M.R. Spectrum*.—The ^{183}W nucleus has spin $\frac{1}{2}$ and is 14.3% abundant. The spectrum of $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ shows seven main lines together with coupling satellites (Figure 2). The lines are labelled A to G in order of decreasing frequency (Table 3). Their respective intensities are in the ratio 2:4:4:4:4:1:2. In certain cases (sodium salts with more than $4Na^+$ per anion in D_2O-rich solvent) lines A and B overlap but can sometimes be separated after a lorentzian–gaussian treatment of the free-induction decay. The anion clearly does not have trigonal ($\bar{6}2m$) symmetry, which would require the spectrum to consist of three lines only, with relative intensities 6:12:3. Figure 3 shows how crystallographically indistinguishable atoms form sub-sets for true anion symmetry *mm*: two W(1a) and four each of W(1b), W(2a), W(2b), and W(2c). With the inclusion of two W(3i) and one W(3e), the 2:4:4:4:4:1:2 pattern is explained. The first five main lines, A—E, are close doublets as the result of coupling through oxygen to ^{31}P ($I = \frac{1}{2}$). They must be assigned to W atoms of the $PW_9O_{34}{}^{9-}$ moieties, while lines F and G are unsplit and are assigned on the basis of their relative intensities to W(3e) and W(3i) respectively, which do not share oxygens with PO_4 groups. A comparison with the ^{183}W n.m.r. spectrum of the $[As^{III}{}_2W_{21}O_{69}(OH_2)]^{6-}$ anion[5,14,15] is instructive. This anion contains two AsW_9O_{33} moieties linked *via* one six-co-ordinate and two five-co-ordinate equatorial W atoms. The five-co-ordinate W gives rise to an n.m.r. line at −43.8 p.p.m., implying weaker shielding compared with all other W nuclei in the anion including the third equatorial W (−212 p.p.m.). In the present spectrum, however, the lines for W(3e) and W(3i) at −152 and −226 p.p.m. show these atoms to be the most shielded of all and presumably six-co-ordinate, which requires the presence of *three* interior equatorial oxygens.

Further assignments may be made from an examination of the ^{183}W–O–^{183}W couplings. The evidence to date[9] is that the coupling in polyoxotungstates is distinctly stronger if the WO_6

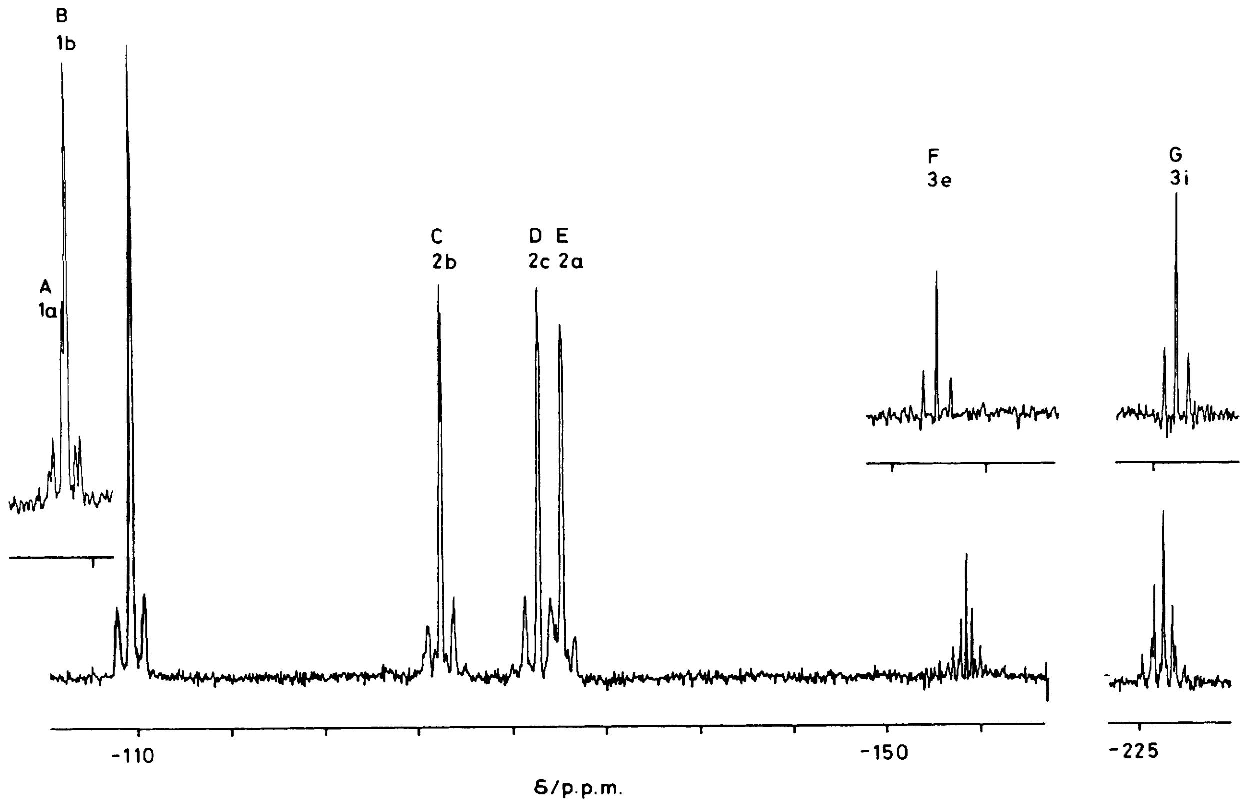

Figure 2. ^{183}W N.m.r. spectrum of $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$ (15.005 MHz, 303 K, 13 g salt in 4 g solvent; 15 000 scans; reference 2 mol dm^{-3} Na_2WO_4 in D_2O). Lower: Na_6 salt in D_2O–H_2O (1.4:1). Upper (lines A, B, F, G only; external lock): Na_4H_2 salt in D_2O

Table 3. ^{183}W N.m.r. chemical shifts and coupling constants for $Na_4H_2[P_2W_{21}O_{71}(OH_2)_3]$ in water

			Coupling constants ±0.3 Hz	
Line	Assignment	Chemical shift, δ ± 0.1 p.p.m.	^2J[W(i)–O–W(j)]	^2J[W(i)–O–P]
A	W(1a)	−108.3	W(1b) 9.6, W(2a) 21.5	0.7
B	W(1b)	−108.5	W(1a) 9.6; W(2b), W(2c) 22.0	0.9
C	W(2b)	−124.7	W(2a) 8.5, W(1b) 22.0, W(2c) 25.2, W(3i) 19.4	1.6
D	W(2c)	−129.7	W(1b) 21.5, W(2b) 25.2, W(3e) 21.9	1.4
E	W(2a)	−131.2	W(2b) 8.5, W(1a) 21.5, W(3i) 19.4	1.5
F	W(3e)	−152.3	W(2c) 21.9	No coupling
G	W(3i)	−225.9	W(2a), W(2b) 19.4	No coupling

octahedra in question share corners (^2J *ca.* 20 Hz) than if they share edges (^2J 8—9 Hz). Despite the overlappings of lines the following connectivities can be deduced:

Atom	Number in anion	Corner-linked to:	Edge-linked to:
W(1a)	2	Two W(2a)	Two W(1b)
W(1b)	4	One W(2b), one W(2c)	One W(1a)
W(2a)	4	One W(1a), one W(2c)	One W(2b)
W(2b)	4	One W(1b), one W(2c), one W(3i)	One W(2a)
W(2c)	4	One W(1b), one W(2b), one W(3e)	None
W(3i)	2	Two W(2a), two W(2b)	None
W(3e)	1	Four W(2c)	None

Clearly, the strong couplings predominate. Coupling constants are listed in Table 3. The line assignments are assisted by a moderately well resolved two-dimensional COSY contour plot (Figure 4). Line G (−226 p.p.m.) is connected to C (−125 p.p.m.) and E (−131 p.p.m.), and line F (−152 p.p.m.) to D (−130 p.p.m.). Since F and G correspond to equatorial atoms W(3e) and W(3i), C, D, and E correspond to belt W(2) atoms. After a suitable line-broadening treatment no weak-coupling lines appear at the foot of line D which therefore corresponds to W(2c) whose connections with all other W [except the second W(2c)] are *via* corner sharing. The assignments of line C to W(2b) and of line E to W(2a) follow from the relative intensities of the strong-coupling lines, while the main line intensities identify A with W(1a) and B with W(1b).

Further information is obtainable from the dependence of the

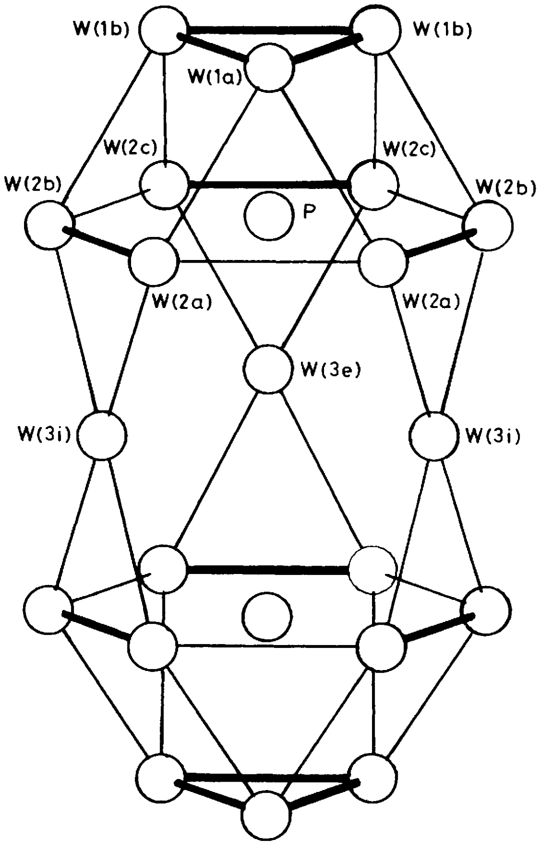

Figure 3. Tungsten framework labelled for *mm* (C_{2v}) symmetry. Thick lines imply that the WO_6 octahedra share edges, and thin lines that they share corners

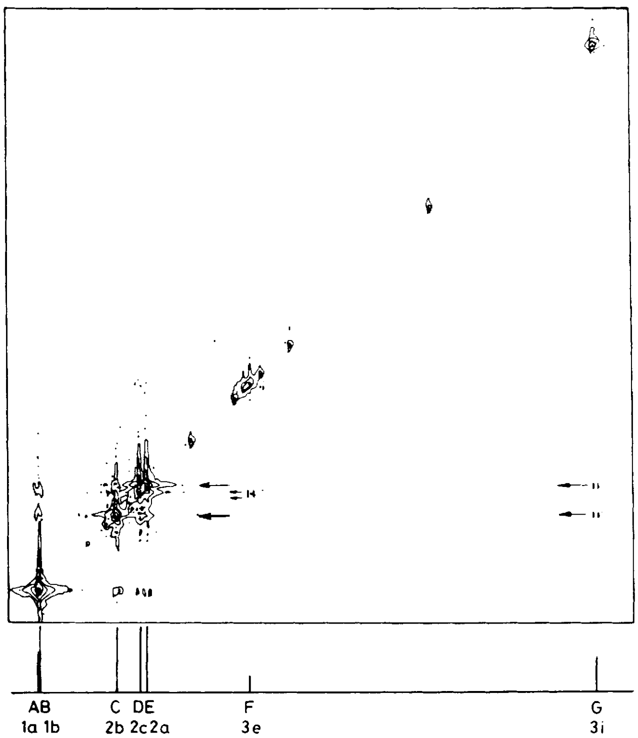

Figure 4. Two-dimensional COSY ^{183}W n.m.r. spectrum of $Na_4H_2[P_2W_{21}O_{71}(OH_2)_3]$ in D_2O–H_2O (*ca.* 4:1) at 303 K. The single and the paired arrows respectively imply couplings involving W(3i) and W(3e)

structure of lines F and G, respectively due to W(3e) and W(3i), on the solvent (D_2O/H_2O) composition. As shown in Figure 5, in pure water both atoms give rise to a triplet consisting of a main line and two equally spaced satellites whose relative intensities are *ca.* 0.30:1:0.30 [calculated, 0.333:1:0.333 for coupling to four W, if ^{183}W 14.28% abundant; note that the W(3i)–W(2a) and W(3i)–W(2b) ^2J coupling constants are identical]. In D_2O–H_2O, however, both the F and G resonances become a triplet of triplets whose relative intensities depend on the D_2O/H_2O ratio (Figure 5). We regard this as due to slow hydrogen-deuterium exchange on protonated ligands of W(3) atoms. This is the β effect described elsewhere, for example for some carbohydrates where the ^{13}C resonance for a hydroxylated atom is shifted upfield on deuteriation and appears as a doublet under conditions of slow exchange.[16] Where the magnetic nucleus is adjacent to a ligand with *n* exchangeable protons, slow exchange results in a multiplet of ($n + 1$) lines; an example is the 13-peak ^{59}Co resonance for $[Co(en)_3]^{3+}$ (en = ethylenediamine) in H_2O–D_2O.[17] In the present case, the evidence indicates that two, and only two, H atoms in the equatorial plane undergo slow exchange. The H_2O ligand exterior to W(3i) is expected to undergo rapid exchange; therefore the two slowly exchanging protons are in the interior of the anion. The most satisfactory picture is one in which W(3e) carries one interior H_2O ligand, hydrogen-bonded to the interior oxo oxygen atom on each W(3i), as shown in Figure 6. The $[As^{III}{}_2W_{21}O_{69}]^{6-}$ anion, in contrast, contains just one oxo atom and no H_2O in interior sites in the equatorial plane,[5] and no β effect can be detected[15] in its ^{183}W n.m.r. spectrum. In the present case, the replacement of H_2O by D_2O weakens the internal hydrogen bonds but does not affect the ^2J W(2)–O–W(3) couplings; the W(3e) resonance moves upfield by 0.587 p.p.m., while the W(3i) resonance moves downfield by 0.980 p.p.m. We have not been able to observe the ^1H resonance of the slowly exchanging atoms directly. The β effect is independent of pH in solutions of $Na_xH_{6-x}[P_2W_{21}O_{71}(OH_2)_3]$ (x = 0—6), and the spectra do not change over a period of months although white deposits slowly form on the walls of the container. Solutions of the acid when treated with more than 6 equivalents of NaOH show complex spectra lacking the characteristic lines A—G and showing that degradation of the anion has occurred.

Comparison with 21-*Tungstodiarsenate*(III).—The salts $K_4H_2[P^V{}_2W_{21}O_{71}(OH_2)_3]\cdot 28H_2O$ and $Rb_4H_2[As^{III}{}_2W_{21}O_{69}(OH_2)]\cdot 34H_2O$[5] crystallize in the same space group with similar cell dimensions and anion packing. In each case, the unique locatable cation (three per anion) lies in the equatorial plane 60° from the exterior W(3)–O bonds and serves to link the anions. The anions show three-fold disorder in both salts, but whereas the P_2W_{21} anion contains PO_4 tetrahedra oriented apex outwards along the anion axis, the As_2W_{21} anion contains trigonal-pyramidal AsO_3 groups with a lone pair on each As directed towards the equatorial region. Thus the As_2W_{21} anion may be regarded as derived from two α-B (not α-A) $As^{III}W_9O_{33}{}^{9-}$ units, each formed from α-$[As^VW_{12}O_{40}]^{3-}$ by the removal of three *edge*-linked WO_6 octahedra including one oxygen of the central AsO_4 group. These units are linked *via* three equatorial W atoms. A result of this is that the O(23) atoms bonded to the equatorial W(3) in As_2W_{21} are only 2.89 Å from the anion axis, and the midpoint between a pair bonded to the same W(3) is only 2.58 Å from the axis, whereas the corresponding distances in P_2W_{21} are 3.56 and 3.30(2) Å. In turn, the W(3) atoms in As_2W_{21} lie at only 3.028 and 2.474(5) Å from the axis, compared with 3.760 and 3.159(4) Å in P_2W_{21}.

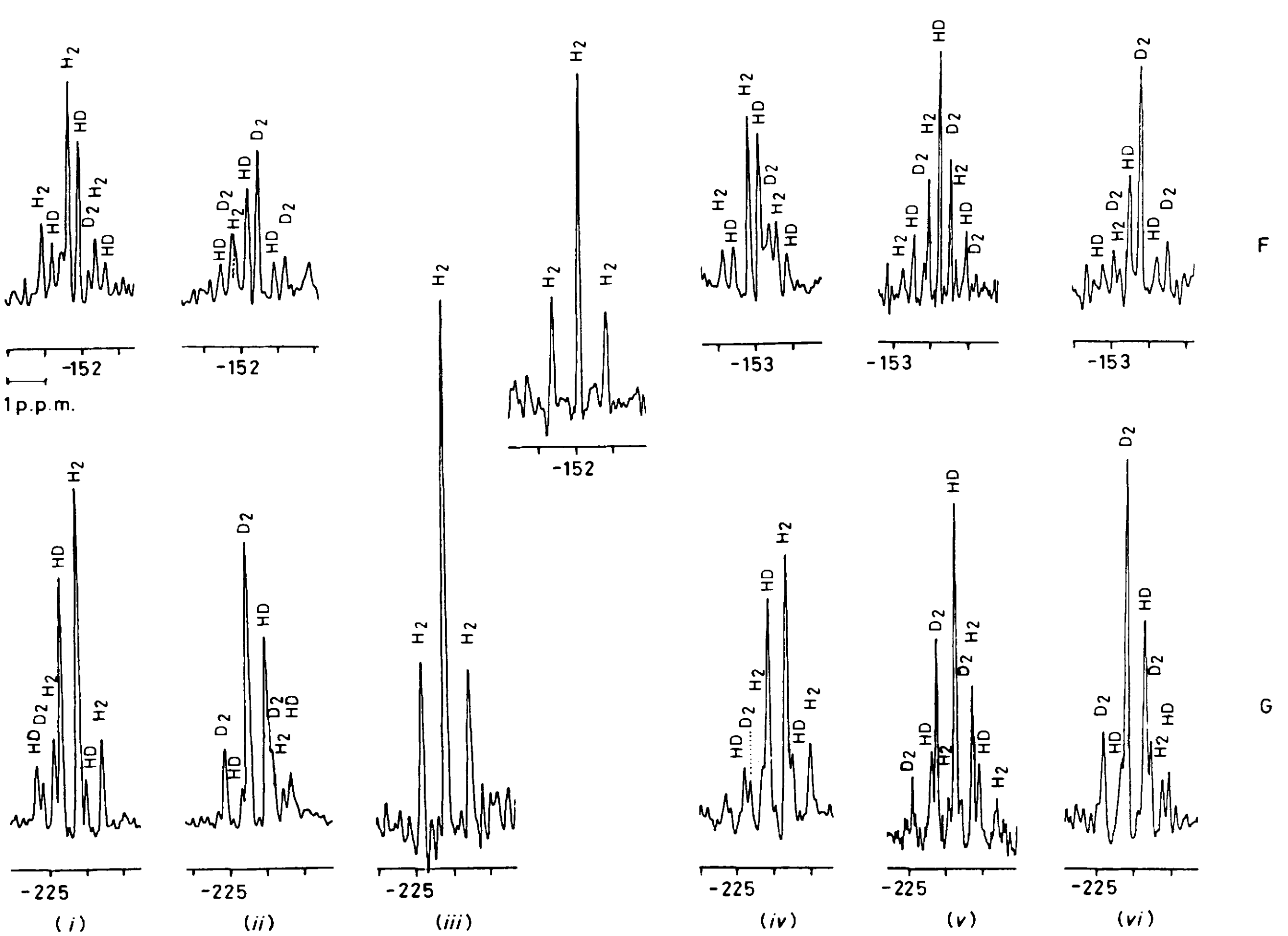

Figure 5. The ^{183}W n.m.r. signals due to W(3e) (line F) and W(3i) (line G) for $Na_xH_{6-x}[P_2W_{21}O_{71}(OH_2)_3]$ in D_2O-H_2O, showing the β effect. Values of *x* and the D_2O-H_2O ratio for (*i*) to (*vi*) are: 0, 0.4; 0, 4.0; 4, 0 (natural water); 4, 0.4; 6, 1.4; and 4, 4.5

Consequently As_2W_{21} cannot accommodate more than one interior equatorial oxygen atom, and two W(3) are in exterior sites with square-pyramidal co-ordination, while just one is in an interior site with an interior oxo atom and an exterior H_2O as unshared ligands. This contrasts with the situation inferred for $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$.

Experimental

21-*Tungstodiphosphate Anion.*—The sparingly soluble potassium salt was obtained from $K_3[PW_{12}O_{40}]$ *via* $K_7[PW_{11}O_{39}]$ by published methods,[1,18] and was recrystallized from 1 mol dm^{-3} HCl. The number of K^+ per anion (4—6) was sensitive to the acidity of the solutions; the most satisfactory single crystals contained 4—4.5 K^+ per anion. The crystalline free acid was obtained by passage of a saturated solution of the salt through a sulphonic-acid type cation exchanger and evaporation of the effluent. Solutions of the sodium salt were obtained by the addition of known amounts of $NaHCO_3$ to the aqueous acid.

^{183}W *N.M.R. Spectroscopy.*—Spectra were recorded by use of a Bruker WP-360 spectrometer equipped with a wide-bore probe head. Normally, sample tubes of 15 mm outside diameter were used, with D_2O as internal lock. Coaxial tubes (15 and 5 mm) were used in experiments with an external lock.

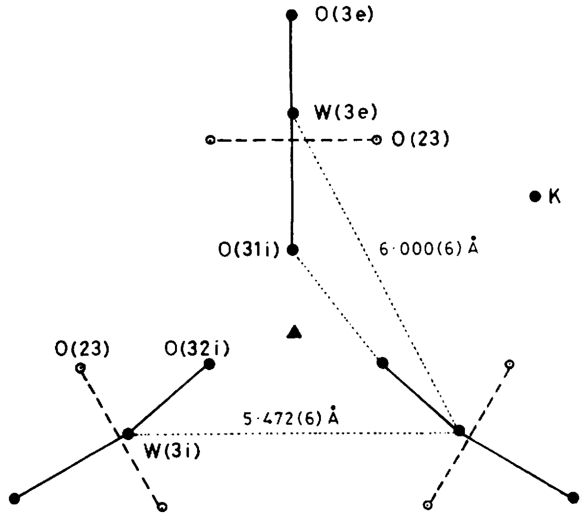

Figure 6. Atomic arrangement in the vicinity of the equatorial plane of $[P_2W_{21}O_{71}(OH_2)_3]^{6-}$

Solutions were equilibrated for 5—12 h and were passed through membrane filters before the spectra were recorded. The two-dimensional COSY ^{183}W measurements were made by use of a Bruker WP-400 instrument as described previously[10] (sodium salt in D_2O, 10-mm sample tubes).

X-*Ray Structure Determination.*—Crystals of the potassium salt are well formed, usually bi-capped, hexagonal prisms. The crystals selected for data collection were cleaved on the basal plane to give roughly equidimensional fragments, *ca.* 0.1 mm on edge, and were protected after mounting with a film of paraffin oil.

Crystal data. $K_4H_2[P_2W_{21}O_{71}(OH_2)_3]\cdot 28H_2O$, M = 5 775.1, hexagonal, space group $P6_3/mmc$, a = 16.295(2), c = 19.771(5) Å, U = 4 546.4 Å^3, Z = 2, D_c = 4.219 g cm^{-3}, Mo radiation (λ = 0.710 69 Å), μ = 274 cm^{-1}, $F(000)$ = 5 080.

Data collection and reduction. Two data sets were collected on Enraf-Nonius CAD-4F diffractometers, in both cases by the ω-2θ scan method, $2\theta_{max.}$ 50°, and with Lorentz polarization corrections applied. Data set 1 (C.M.T. and G.F.T.): 1 540 unique data, absorption corrections by use of ψ scans (20 planes) in conjunction with the programs FACIES[19] (refinement of cell dimensions) and ABSORB.[20] Data set 2 (T. J. R. W.): 1 535 unique data, absorption correction by DIFABS[21] following isotropic refinement.

Structure solution and refinement. The structural analysis was carried out on both data sets at our respective laboratories, with very similar results. The W atoms were located by direct methods (MULTAN,[22] SHELX 76[23]) and the structure was expanded by alternating difference syntheses and cycles of full-matrix least-squares refinement.[23,24] It quickly became apparent that the anion attained effective three-fold symmetry as the result of disorder, from the anomalously large U_{iso} of W(3) and from the presence of residual peaks close to and on either side of W(3) at *mm* sites in the equatorial plane which could not be explained by thermal motion. Anisotropic refinement of two plausible models, with W(3e) and W(3i) present in 2:1 or alternatively in 1:2 ratio, converged at similar R values but the first model led to a negative U_{33} coefficient for W(3i). The site-occupancy factors were also refined (data set 2), giving 0.96(9) for W(3e) and 2.04(18) for W(3i). The second model was therefore adopted. Only one unique K$^+$ could be located; its thermal motion was large and considerably anisotropic, but attempts to model this by fractional occupancy of several adjacent sites were unsuccessful. Likewise, only three independent lattice H_2O molecules could be located (21 per anion). In the final stages the choice of three interior equatorial oxygens O(3i), rather than two O(3i) distributed over three equivalent sites, had to be made on the basis of the n.m.r. results as the same R was attained in either case with virtually identical parameters other than U[O(3i)]. For data set 2, refinement (on F) with three O(3i) converged at R 0.043 [unit weights, 1 172$|F| \geqslant 3\sigma(F)$, 66 parameters]. With both data sets, difference syntheses indicated that O(3i) had considerable density on either side of the vertical mirror plane through it and in the last cycles with data set 1, O(3i) was treated as two independent atoms, O(31i) [H_2O bonded to W(3e)] and O(32i) [unprotonated O bonded to W(3i)], on one-third-occupied *mm* and *m* sites respectively (Figure 6). The co-ordinates and derived dimensions listed in Tables 1 and 2 are those obtained with data set 1, with which convergence was reached at R 0.037, R' 0.047 (1 042 data, 76 parameters); the results obtained with data set 2 are not significantly different.

Acknowledgements

T. J. R. W. thanks the S.E.R.C. for use of the Diffractometer Service, and Drs. A. J. Welch and R. O. Gould for, respectively, collecting intensity data and running DIFABS. C. M. T. and G. F. T. thank the Centre de Pharmacologie C.N.R.S., Montpellier for use of the Bruker WP-360 spectrometer and M. Ch. Brevard for the COSY spectrum.

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Received 21*st November* 1985; *Paper* 5/2048