

Multicomponent Polyanions. 52. Crystal Structure of Hexacaesium Monohydrogen Decamolybdo(VI)divanado(IV)phosphate(7-) Dihydrate

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The structure of the title compound, $\text{Cs}_6\text{HPMo}^{\text{VI}}_{10}\text{V}^{\text{IV}}_2\text{O}_{40}\cdot 2\text{H}_2\text{O}$ has been determined by a single-crystal X-ray diffraction method. The compound crystallises in two different space groups. Crystal **A**: monoclinic, $P2_1$, $a=10.988(3)$, $b=10.615(3)$, $c=17.472(2)$ Å, $\beta=91.55(1)^\circ$, $V=2037(7)$ Å³ and $Z=2$. Crystal **B**: monoclinic, Pn , $a=10.982(2)$, $b=10.614(3)$, $c=17.487(3)$ Å, $\beta=91.64(1)^\circ$, $V=2037(7)$ Å³ and $Z=2$. The R -values based on F were 0.0487 for **A** and 0.0485 for **B** for 4491 (**A**) and 4464 (**B**) reflections with $F_o > 4.0\sigma(F_o)$ and 353 parameters, and $S=1.048$ (**A**) and 1.026 (**B**). The polyanion has a so-called α -Keggin structure in each crystal. The two vanadium atoms are delocalised in the 12 addenda atom positions in the anion.

Heteropolyoxometallates have long been investigated both for their basic chemistry and practical use.¹ Nowadays, great attention is paid to them as heterogeneous and homogeneous catalysts.² For example, heteropoly compounds having so-called α -Keggin structure³ (Fig. 1a) with general formula $[\text{XM}_{12}\text{O}_{40}]^{n-}$ (X: heteroatom, e.g. P^{V} , As^{V} , Si^{IV} , Ge^{IV} ; M: addenda atom, e.g. Mo^{VI} , W^{VI} , V^{V} , Nb^{V}), are the most favoured as catalysts. However, the basic chemistry of their catalytic functions is still not very clear and is yet to be investigated.

Selling *et al.* have studied the aqueous speciation of the molybdovanadophosphate system, $\text{H}^+ - \text{MoO}_4^{2-} - \text{HVO}_4^{2-} - \text{HPO}_4^{2-}$, and focussed their studies on solutions where molybdovanadophosphates with α -Keggin structure, $[\text{PMo}_{12-x}\text{V}_x\text{O}_{40}]^{(3+x)-}$ ($x \leq 3$), are the predominant species.^{4,5} In addition, some β -Keggin species (Fig. 1b) were also found in the systems studied. For $x \geq 2$, positional Keggin isomers can be formed, and the five possible isomers of α - $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ (Fig. 2) were identified and characterised by ³¹P and ⁵¹V NMR.⁴ Moreover, since molybdovanadophosphates have been shown to be good homogeneous redox catalysts, the reduced molybdovanadophosphate system was studied by adding electrons ($e^-/\text{V}^{\text{V}} \leq 1$) to the abovementioned system.⁶ Reduced molybdovanadophosphate species

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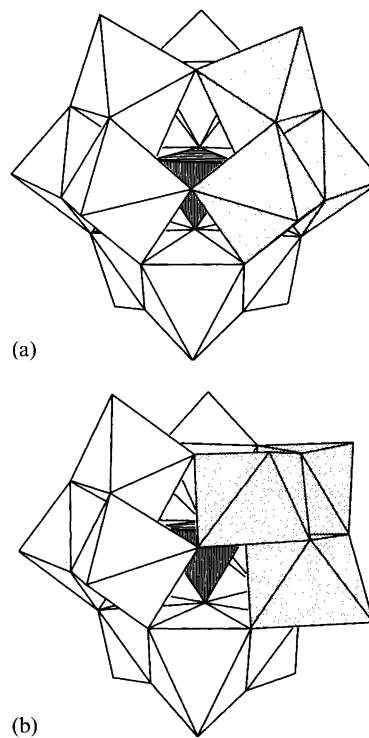


Fig. 1. Polyhedral models of the (a) α - and (b) β -isomers of the Keggin structure with a general formula $[\text{XM}_{12}\text{O}_{40}]^{n-}$.

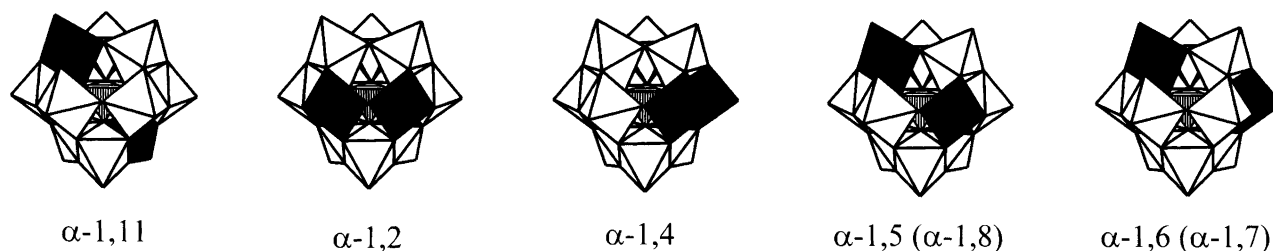


Fig. 2. The five positional isomers of the $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ polyanion. The grey octahedra represent the positions of VO_6 .

with the Keggin compositions $\text{PMo}^{\text{VI}}_{11}\text{V}^{\text{IV}}\text{O}_{40}$, $\text{PMo}^{\text{VI}}_{10}\text{V}^{\text{IV}}\text{V}^{\text{V}}\text{O}_{40}$ and $\text{PMo}^{\text{VI}}_{10}\text{V}^{\text{IV}}_2\text{O}_{40}$ were established. Since all these species are NMR silent, possible positional isomers of the reduced species could not be identified.

With respect to structures of molybdovanadophosphates, only those in the fully oxidised state have been published so far and reported to have α -Keggin structure.⁷⁻¹⁰ As for the structures of reduced Keggin-type heteropoly compounds, several examples have been reported to have either α -type (Fig. 1a)¹¹⁻¹⁶ or β -type (Fig. 1b)¹⁷ isomers. In order to ascertain whether the reduced molybdovanadophosphate Keggin species have an α or β structure and whether some specific positional isomers are favoured, single-crystal structure analyses were performed on crystals obtained from aqueous solution subjected to the equilibrium analysis. Single crystals of caesium salts, suitable for X-ray intensity measurements, were obtained from decamolybdovanadophosphate solutions of Keggin ratio ($\text{Mo}/\text{V}/\text{P} = 10.2/1.8/1.0$ composition) with one electron added per V^{V} . Results of the structure determination of these crystals are reported.

Experimental

Chemicals. Commercially available caesium chloride, CsCl (E. Merck, *p.a.*), was used without further purification. Molybdate stock solutions were prepared by dissolving crystalline disodium molybdate, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (E. Merck, *p.a.*) which had been recrystallised once. Molybdenum was analysed by evaporating water from a known amount of stock solution, drying the residue at 110°C and then weighing as anhydrous Na_2MoO_4 . Sodium metavanadate, NaVO_3 , and sodium dihydrogenphosphate, NaH_2PO_4 , were purified before use, as described in the literature.¹⁸

Preparation of the molybdovanadophosphate solution. The fully oxidised molybdovanadophosphate solution was prepared as previously described.^{4,5} The reduced molybdovanadophosphate solution was prepared by adding a certain amount of electrons to this fully oxidised solution with the use of a potentiostat. After mixing, the solution was bubbled with argon and left at 25°C for up to 24 h in order to reach equilibrium. The electrons were added coulometrically under calm stirring and an Ar stream (25°C) using an automated potentiostat developed at

our department. The conditions of the samples were $\text{Mo}/\text{V}/\text{P} = 10.2/1.8/1.0$, $\text{pH} \sim 4.8$, and $1.0 \text{ e}^-/\text{V}^{\text{V}}$.

Preparation of the crystal. A 0.2 M CsCl/0.6 M NaCl solution was prepared by dissolving 0.3367 g of CsCl and 0.3507 g of NaCl into ion-exchanged and Ar-purged water to make a 10 ml solution. The resulting solution was also purged with argon. To 2 ml of the reduced molybdovanadophosphate solution, prepared as above, 1 ml of the caesium/sodium chloride solution was added in an Ar-purged glove box. The mixed solution was stored in a tightly closed screw vial filled with argon at ambient temperature. After one night, deep blue tabular crystals appeared. The crystals were isolated in the Ar-filled glove box, washed with deaerated water, and dried in the glove box under argon at room temperature for one day. The elemental analysis of Cs, Mo and V for $\text{Cs}_6\text{H}_5\text{O}_{42}\text{Mo}_{10}\text{PV}_2$ was determined by ICP: calcd. Cs 31.1%, Mo 37.4%, V 3.97%; obsd. Cs 27.3%, Mo 39.4%, V 4.18%.

Intensity measurements. Single crystals with dimensions $0.15 \times 0.15 \times 0.15 \text{ mm}^3$ (A) and $0.10 \times 0.10 \times 0.10 \text{ mm}^3$ (B) were mounted on a Rigaku AFC6R diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation (0.71073 Å) at 298 K. Conditions for data collections are summarised in Table 1. Intensities were monitored by three standard reflections listed in Table 1 at every 150 reflections, and no significant decay was observed. Psi-scans were carried out with the reflections listed in Table 1. Four different crystals were tested in data collections and structure determinations. Two of them resulted in almost equal *R*-values despite different space groups, and were used for further calculations.

Determination of the structure and refinement of parameters. An empirical absorption correction, based on the ψ -scans and the Lorenz polarisation correction, was applied for each crystal by *TEXSAN*.¹⁹ No decay correction was applied. All other calculations were carried out on a NEC HSP computer at the Computer Centre, Institute for Molecular Science, Okazaki, Japan. Results of the refinement for each crystal are summarised in Table 2. According to the systematic absences of reflections, there were five possible space groups; $P2_1$ (No. 4), Pn (No. 7), $P2_1/m$ (No. 11), $P2_1/n$ (No. 13) and $P2_1/n$ (No. 14). All these five space groups were tested for each crystal. $P2_1/m$

Table 1. Experimental conditions in intensity measurements of crystals **A** and **B**.

	A	B
Formula	Cs ₆ H ₅ Mo ₁₀ PO ₄₂ V ₂	Cs ₆ H ₅ Mo ₁₀ PO ₄₂ V ₂
FW	2566.70	2566.70
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁	<i>P</i> n
<i>a</i> /Å	10.988(3)	10.982(2)
<i>b</i> /Å	10.615(3)	10.614(3)
<i>c</i> /Å	17.472(2)	17.487(3)
β/°	91.55(1)	91.64(1)
<i>V</i> /Å ³	2037(7)	2037(7)
<i>Z</i>	2	2
<i>F</i> (000)	2304	2304
μ(Mo Kα)/mm ⁻¹	8.84	8.84
Crystal size/mm ³	0.15 × 0.15 × 0.15	0.10 × 0.10 × 0.10
Scan speed/° min ⁻¹	16	8
Range of measurements/°	4 < 2θ < 65	4 < 2θ < 70
<i>h</i>	0 ≤ <i>h</i> ≤ 16	0 ≤ <i>h</i> ≤ 17
<i>k</i>	0 ≤ <i>k</i> ≤ 16	0 ≤ <i>k</i> ≤ 17
<i>l</i>	-26 ≤ <i>l</i> ≤ 26	-28 ≤ <i>l</i> ≤ 28
Standard reflections and deviations of intensity (%)	0 0 6 (0.5) -2 -2 -4 (1.4) -1 3 -3 (1.8)	-3 -3 0 (1.1) 2 -2 -4 (2.6) 2 -1 -5 (2.1)
Reflections for ψ-scans	-2 2 2 -5 3 3 -5 3 4	4 -2 -1 5 -3 -3 3 -2 -1
No. of reflections for cell parameters (2θ range/°)	20 (14–18)	20 (15–20)

Table 2. Conditions and results of refinements for crystals **A** and **B**.

	A	B
Reflections measured	8019	9726
Reflections used [F _o ² > -3.0σ(F _o ²)]	7578	8873
No. of parameters	353	353
Extinction coefficient	0.00059(6)	0.00020(5)
Absorption range	0.6278–1.0000	0.7000–1.0000
Weighting scheme	<i>a</i> = 0.0348	<i>a</i> = 0.0349
Parameters ^a	<i>b</i> = 43.5960	<i>b</i> = 26.2234
<i>R</i> based on <i>F</i> ²	0.1146	0.1459
<i>R</i> for F _o > 4.0σ(F _o) (No. of reflections)	0.0487 (4491)	0.0485 (4464)
<i>R</i> _w based on <i>F</i> ²	0.1382	0.1362
<i>S</i>	1.048	1.026
Scale parameter of 'Enantiomeric twin' (BASF)	0.3(1)	0.00(8)
Maximum residue in the last Fourier map/e Å ⁻³	2.56	2.58

^aWeighting scheme: $w = 1/[\sigma^2(F_o)^2 + \{a((0.033(F_o)^2)_{\max} + 0.67(F_c)^2)\}^2 + b((0.033(F_o)^2)_{\max} + 0.67(F_c)^2)]$.

was rejected by Patterson vectors since no Harker plane arising from a mirror plane was observed. *P*2/*n* was aborted because heavy atoms could not be located successfully. The space group *P*2₁ gave the best result for **A**, and *P*n for **B**. For **A**, *P*n was rejected because the refinement failed, and for **B**, *P*2₁ was rejected according to Hamilton's test

(probability 0.001).²⁰ A centrosymmetric space group *P*2₁/*n* was also possible for both crystals. With *P*2₁/*n*, the polyanion must contain an inversion centre, although the polyanion ideally has *Td* symmetry, where no symmetry centre exists. A special reason which supports *P*2₁/*n* is thus necessary to justify the choice of this centrosymmetric space group. It is rather common to locate a symmetry centre on the centre of the polyanion, since the overall structure of the polyanion of this type can be regarded as a sphere. In such a case, however, remarkable improvements are observed in refinements. In this work, no unacceptable temperature factors, bond lengths or angles could be observed in *P*2₁ for **A**, *P*n for **B** or *P*2₁/*n* for either **A** or **B**. The refinement with *P*2₁/*n* gave no improvement in refinements of either crystal. The *R*, *R*_w and *S* were much worse, and the Hamilton test indicated that *P*2₁/*n* could be rejected at the 0.001 level. Thus, the asymmetric space groups were chosen. The 18 independent Mo/V and Cs atoms were located by the direct method calculated by *SHELXS86*,²¹ and all other atoms except H were found by the successive Fourier and difference Fourier syntheses. Refinements of parameters and Fourier/difference Fourier syntheses were carried out by *SHELXL93*.²² Of total 8019 (**A**) and 9726 (**B**) reflections measured, 7578 independent reflections for **A** and 8873 for **B** with $F_o^2 > -3.0\sigma(F_o^2)$ were used for the refinements. The scattering factors and anomalous dispersion factors, including real and imaginary parts, were taken from Ref. 23. An extinction correction was applied for each crystal, and the extinction coefficient was refined during the calculation. The vanadium atoms were treated as having the same fractional coordinates and thermal parameters as the corresponding molybdenum atoms. The occupation factors for molybdenum and vanadium atoms were refined for each calculation, to give the sum 1 for the occupation factors of Mo and V at the respective positions. Enantiomers were checked for each crystal by use of Flack's parameter.²⁴ An effect of enantiomeric twinning was included by *TWIN* and *BASF* instructions for both crystals, and the scale factor of the other 'enantiomer' was calculated as 0.3(1) for **A** and 0.00(8) for **B**. All Mo, V, P and Cs atoms were refined anisotropically and oxygens isotropically; attempts to refine oxygen atoms anisotropically were failed owing to negative equivalent thermal parameters for some O atoms. The full-matrix least-squares, based on *F*² with the threshold noted above, gave the *R*-value 0.1146 for **A** (353 parameters) and 0.1459 for **B** (353 parameters), the *R*_w-value 0.1382 for **A** and 0.1362 for **B** (weighting schemes are given in Table 2) and the goodness of fit 1.048 for **A** and 1.026 for **B**. The *R*-values based on *F* with $F_o > 4.0\sigma(F_o)$ from these refinements were 0.0487 for **A** (4491 reflections) and 0.0485 for **B** (4464 reflections), respectively. Rather high residues of electron density are located close to Cs atoms.

Structure description and discussion

ORTEP²⁵ views of the anion structures of **A** and **B** along with atomic notations are illustrated in Fig. 3. Positions

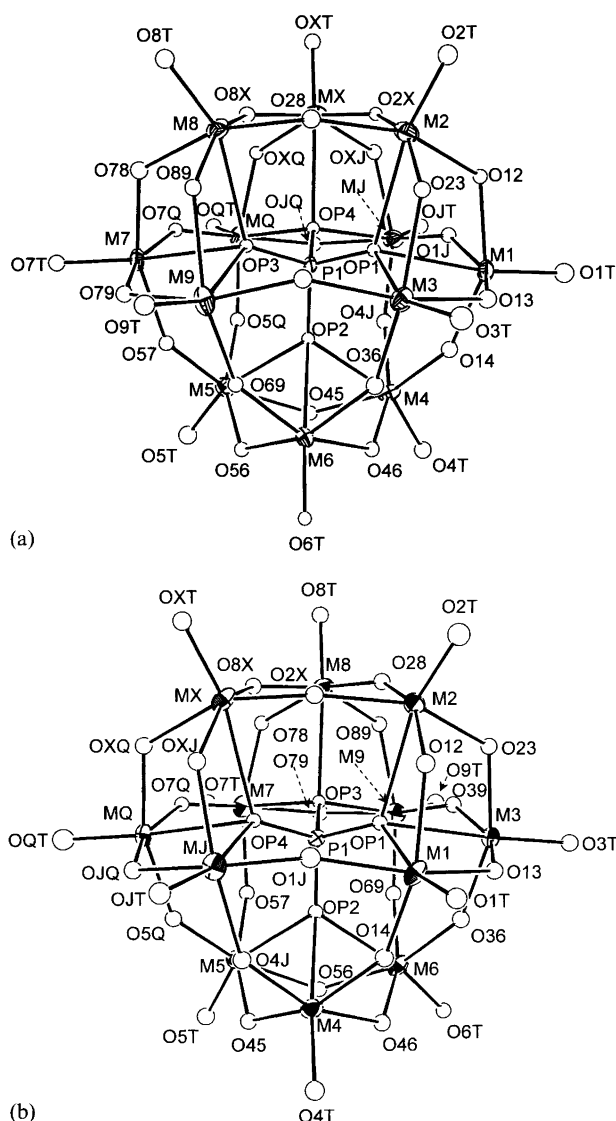
Table 3. Atomic coordinates, equivalent (Mo, V, P and Cs) and isotropic (O) thermal parameters, and site occupation factors (s.o.f.) of Mo and V for crystal A with e.s.d. values in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}/U_{iso}^a	s.o.f.
Mo1	0.2618(2)	0.0825(2)	0.4257(1)	0.0208(7)	0.85(2)
Mo2	-0.0135(2)	0.1136(2)	0.3261(1)	0.0245(8)	0.85(2)
Mo3	0.1181(2)	0.3737(2)	0.4136(1)	0.0216(7)	0.80(2)
Mo4	0.5356(2)	0.2194(2)	0.3505(1)	0.0212(7)	0.85(2)
Mo5	0.5201(2)	0.3907(2)	0.1788(1)	0.0213(7)	0.87(2)
Mo6	0.3961(2)	0.5120(2)	0.3446(1)	0.0233(7)	0.91(2)
Mo7	0.2350(2)	0.4196(2)	0.0756(1)	0.0220(7)	0.79(2)
Mo8	-0.0277(2)	0.2926(2)	0.1484(1)	0.0217(7)	0.85(2)
Mo9	0.1123(2)	0.5509(2)	0.2373(1)	0.0219(7)	0.91(2)
MoX	0.1193(2)	-0.0124(2)	0.1550(1)	0.0229(7)	0.84(2)
MoJ	0.3916(2)	-0.0500(2)	0.2557(1)	0.0223(7)	0.76(2)
MoQ	0.3851(2)	0.1185(2)	0.0872(1)	0.0222(8)	0.65(2)
V1	0.2618(2)	0.0826(2)	0.4257(1)	0.0208(7)	0.15(2)
V2	-0.0135(2)	0.1136(2)	0.3261(1)	0.0245(8)	0.15(2)
V3	0.1181(2)	0.3737(2)	0.4136(1)	0.0216(2)	0.20(2)
V4	0.5356(2)	0.2194(2)	0.3505(1)	0.0212(7)	0.15(2)
V5	0.5201(2)	0.3907(2)	0.1788(1)	0.0213(8)	0.13(2)
V6	0.3961(2)	0.5120(2)	0.3446(1)	0.0233(7)	0.09(2)
V7	0.2350(2)	0.4196(2)	0.0756(1)	0.0220(7)	0.21(2)
V8	-0.0277(2)	0.2926(2)	0.1484(1)	0.0217(7)	0.15(2)
V9	0.1123(2)	0.5509(2)	0.2373(1)	0.0219(7)	0.09(2)
VX	0.1193(2)	-0.0124(2)	0.1550(1)	0.0229(7)	0.16(2)
VJ	0.3916(2)	-0.0500(2)	0.2557(1)	0.0223(7)	0.24(2)
VQ	0.3851(2)	0.1185(2)	0.0872(1)	0.0222(8)	0.35(2)
P1	0.2531(6)	0.2500(7)	0.2505(4)	0.0125(6)	
O1T	0.282(1)	-0.005(2)	0.5015(9)	0.034(4)	
O2T	-0.144(2)	0.044(2)	0.345(1)	0.039(4)	
O3T	0.056(2)	0.446(2)	0.488(1)	0.039(5)	
O4T	0.659(2)	0.188(2)	0.4039(10)	0.038(4)	
O5T	0.640(2)	0.457(2)	0.1418(10)	0.031(4)	
O6T	0.437(1)	0.642(1)	0.3949(8)	0.024(3)	
O7T	0.245(1)	0.498(2)	-0.0069(9)	0.036(4)	
O8T	-0.160(1)	0.288(2)	0.0998(8)	0.026(3)	
O9T	0.038(2)	0.688(2)	0.245(1)	0.041(5)	
OXT	0.037(2)	-0.120(2)	0.1084(10)	0.036(4)	
OJT	0.466(2)	-0.181(2)	0.265(2)	0.037(4)	
OQT	0.450(1)	0.077(2)	0.007(1)	0.038(4)	
O12	0.094(1)	0.035(2)	0.3973(8)	0.029(3)	
O23	-0.019(1)	0.255(2)	0.3935(8)	0.030(3)	
O13	0.188(1)	0.232(2)	0.4704(8)	0.031(3)	
O45	0.607(1)	0.299(1)	0.2643(8)	0.029(3)	
O56	0.500(1)	0.521(1)	0.2589(8)	0.029(3)	
O46	0.503(1)	0.390(1)	0.3873(8)	0.026(3)	
O78	0.070(1)	0.371(1)	0.0672(8)	0.030(3)	
O89	-0.031(1)	0.462(2)	0.1888(9)	0.032(3)	
O79	0.171(1)	0.565(1)	0.1360(8)	0.029(3)	
OXJ	0.249(1)	-0.112(2)	0.2028(8)	0.032(3)	
OJQ	0.449(1)	-0.006(2)	0.1535(9)	0.034(3)	
OXQ	0.241(1)	0.019(1)	0.0748(7)	0.020(2)	
O14	0.407(1)	0.169(2)	0.4154(9)	0.033(3)	
O1J	0.311(1)	-0.024(2)	0.3448(9)	0.031(3)	
O28	-0.060(1)	0.222(1)	0.2426(8)	0.028(3)	
O2X	0.050(1)	0.010(1)	0.2474(8)	0.030(3)	
O36	0.274(1)	0.439(1)	0.4066(8)	0.025(3)	
O39	0.067(1)	0.464(1)	0.3297(8)	0.031(3)	
O4J	0.507(1)	0.075(1)	0.2934(8)	0.028(3)	
O57	0.386(1)	0.459(1)	0.1263(8)	0.027(3)	
O5Q	0.498(1)	0.239(1)	0.1301(8)	0.029(3)	
O69	0.266(1)	0.568(2)	0.2813(8)	0.030(3)	
O7Q	0.288(1)	0.261(1)	0.0573(8)	0.026(3)	
O8X	0.044(1)	0.138(1)	0.1195(8)	0.029(3)	
OP1	0.185(1)	0.219(1)	0.3230(7)	0.022(2)	
OP2	0.374(1)	0.316(1)	0.2722(7)	0.022(3)	
OP3	0.175(1)	0.342(1)	0.1988(7)	0.022(2)	
OP4	0.279(1)	0.131(1)	0.2056(7)	0.023(3)	

Table 3. (Continued.)

Atom	x/a	y/b	z/c	U_{eq}/U_{iso}^a	s.o.f.
Cs1	0.5809(2)	-0.1240(2)	0.4429(1)	0.0452(5)	
Cs2	0.2129(2)	-0.0212(2)	0.6738(1)	0.0439(5)	
Cs3	0.2766(2)	0.5309(3)	-0.1774(1)	0.0439(5)	
Cs4	-0.1476(2)	0.2377(2)	0.5559(1)	0.0539(6)	
Cs5	0.6461(2)	0.2613(2)	-0.0473(1)	0.0538(6)	
Cs6	0.0920(2)	0.1354(2)	-0.0576(1)	0.0491(6)	
OW1	0.144(3)	0.268(4)	0.637(2)	0.11(1)	
OW2	0.340(4)	0.226(5)	-0.162(2)	0.14(1)	

$$^a U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$


 Fig. 3. ORTEP views of the polyanions in crystals **A** (a) and **B** (b) along with the atomic notations.

of addenda atoms, where molybdenum and vanadium atoms are distributed, are marked as M. The polyanion from both **A** and **B** has a so-called α -Keggin structure of which a polyhedral model is shown in Fig. 1. The addenda atoms are octahedrally coordinated, and the

heteroatom, P, is tetrahedrally coordinated. Three MO_6 octahedra form a trimer of M_3O_{13} by sharing edges. The four oxygen atoms shared by three metal atoms, OP1, OP2, OP3 and OP4, are also shared by P. Each M_3O_{13} moiety is linked to the other three by sharing two corners for respective M_3O_{13} . The polyanions are, as a whole, ordered in both crystals. However, molybdenum and vanadium atoms are disordered in the twelve addenda atom sites in each polyanion.

The atomic coordinates, equivalent or isotropic thermal parameters and occupation factors of Mo and V atoms for both crystals are listed in Tables 3 and 4. The origin of the unit cell was chosen so that the phosphorus atom on each crystal has approximately similar atomic coordinates, around (0.25, 0.25, 0.25), for easy comparison, and all corresponding atoms have quite similar positions as seen in the table. No abnormal thermal parameter was found in either of the crystals. The Mo and V atoms were refined to have the same positional and thermal parameters at respective positions. The site occupation factors of Mo and V were also refined. The result, which is listed in Tables 3 and 4, indicates that the Mo and V atoms are not evenly distributed. The factors of two Mo atoms were refined remarkably lower than the averaged values (0.83); MoJ [0.76(2)] and MoQ [0.65(2)] for **A**, and Mo3 [0.68(2)] and MoQ [0.77(2)] for **B**. On the contrary, the factors of Mo6 [0.91(2)] and Mo9 [0.91(2)] in **A** and Mo8 [0.89(2)] and MoX [0.91(2)] in **B** were refined considerably higher than 0.83. This indicates that (i) there is a slightly dominating isomer of the $PMo_{10}V_2O_{40}$ heteropolyanion present in each case, or (ii) there are some positions favoured by a vanadium or a molybdenum atom in both crystal structures. In the case of (i), the isomer can be α -1,4 for **A** and α -1,11 for **B**. In both crystals, the sum of the site occupation factors of molybdenum, 9.93 for **A** and 10.01 for **B**, and vanadium, 2.07 for **A** and 1.99 for **B**, agrees very well with the stoichiometry of the molybdovanadophosphate, $PMo^{VI}_{10}V^{IV}_2O_{40}$.

Interatomic distances in the polyanion of **A** and **B** are listed in Table 5. The M-O(-M) distances of the bridging oxygen between two M_3O_{13} moieties (Ob') range from 1.81(2) to 1.94(2) Å, averaging 1.88 Å for **A**, and from 1.80(2) to 1.96(2) Å, averaging 1.88 Å for **B**. These distances are shorter than those in the M_3O_{13} moieties,

Table 4. Atomic coordinates, equivalent (Mo, V, P and Cs) and isotropic (O) thermal parameters, and occupation factors (s.o.f.) of Mo and V for crystal **B** with e.s.d. values in parentheses.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}/U_{iso}^a	s.o.f.
Mo1	0.2574(2)	0.0827(2)	0.4262(1)	0.0207(7)	0.82(2)
Mo2	-0.0168(2)	0.1133(2)	0.3270(1)	0.0219(7)	0.86(2)
Mo3	0.1132(2)	0.3709(3)	0.4138(1)	0.0228(8)	0.68(2)
Mo4	0.5338(2)	0.2190(2)	0.3507(1)	0.0209(7)	0.84(2)
Mo5	0.5173(2)	0.3908(2)	0.1809(1)	0.0237(7)	0.85(2)
Mo6	0.3925(2)	0.5112(2)	0.3451(1)	0.0239(7)	0.87(2)
Mo7	0.2311(2)	0.4190(2)	0.0760(1)	0.0227(7)	0.83(2)
Mo8	-0.0305(2)	0.2915(2)	0.1481(1)	0.0230(7)	0.89(2)
Mo9	0.1094(2)	0.5482(2)	0.2379(1)	0.0227(7)	0.85(2)
MoX	0.1159(2)	-0.0133(2)	0.1553(1)	0.0247(7)	0.91(2)
MoJ	0.3887(2)	-0.0519(2)	0.2570(1)	0.0229(7)	0.84(2)
MoQ	0.3815(2)	0.1173(2)	0.0881(1)	0.0212(7)	0.77(2)
V1	0.2574(2)	0.0827(2)	0.4262(1)	0.0207(7)	0.18(2)
V2	-0.0168(2)	0.1133(2)	0.3270(1)	0.0219(7)	0.14(2)
V3	0.1132(2)	0.3709(3)	0.4138(1)	0.0228(8)	0.32(2)
V4	0.5338(2)	0.2190(2)	0.3507(1)	0.0209(7)	0.16(2)
V5	0.5173(2)	0.3908(2)	0.1809(1)	0.0237(7)	0.15(2)
V6	0.3925(2)	0.5112(2)	0.3451(1)	0.0239(7)	0.13(2)
V7	0.2311(2)	0.4190(2)	0.0760(1)	0.0227(7)	0.17(2)
V8	-0.0305(2)	0.2915(2)	0.1481(1)	0.0230(7)	0.11(2)
V9	0.1094(2)	0.5482(2)	0.2379(1)	0.0227(7)	0.15(2)
VX	0.1159(2)	-0.0133(2)	0.1553(1)	0.0247(7)	0.09(2)
VJ	0.3887(2)	-0.0519(2)	0.2570(1)	0.0229(7)	0.16(2)
VQ	0.3815(2)	0.1173(2)	0.0881(1)	0.0212(7)	0.23(2)
P1	0.2500(6)	0.2492(7)	0.2500(4)	0.0128(5)	
O1T	0.279(1)	-0.009(2)	0.5020(9)	0.032(4)	
O2T	-0.137(2)	0.042(2)	0.360(1)	0.043(5)	
O3T	0.058(1)	0.443(5)	0.4871(9)	0.030(3)	
O4T	0.653(1)	0.185(1)	0.4070(9)	0.032(3)	
O5T	0.647(2)	0.459(2)	0.155(1)	0.036(4)	
O6T	0.433(1)	0.633(1)	0.3967(8)	0.028(3)	
O7T	0.244(1)	0.497(2)	-0.0059(9)	0.032(3)	
O8T	-0.165(1)	0.284(1)	0.1002(9)	0.031(3)	
O9T	0.037(2)	0.687(2)	0.244(1)	0.042(5)	
OXT	0.035(1)	-0.129(1)	0.1101(8)	0.031(3)	
OJT	0.466(2)	-0.182(2)	0.265(1)	0.034(4)	
OQT	0.453(2)	0.079(2)	0.007(1)	0.046(5)	
O12	0.092(1)	0.027(1)	0.3969(8)	0.028(3)	
O23	0.020(1)	0.250(1)	0.3926(7)	0.026(3)	
O13	0.187(1)	0.224(1)	0.4700(7)	0.026(3)	
O45	0.607(1)	0.388(1)	0.2647(8)	0.027(3)	
O56	0.500(1)	0.519(1)	0.2617(7)	0.027(3)	
O46	0.505(1)	0.388(1)	0.3905(8)	0.028(3)	
O78	0.065(1)	0.362(1)	0.0659(7)	0.027(3)	
O89	-0.034(1)	0.454(1)	0.1885(8)	0.028(3)	
O79	0.166(1)	0.560(1)	0.1347(8)	0.032(3)	
OXJ	0.246(1)	0.114(1)	0.2034(7)	0.026(3)	
OJQ	0.450(1)	-0.011(1)	0.1519(8)	0.029(7)	
OXQ	0.240(1)	0.014(1)	0.0761(8)	0.028(3)	
O14	0.401(1)	0.168(1)	0.4149(7)	0.028(3)	
O1J	0.311(1)	-0.032(1)	0.3458(8)	0.032(3)	
O28	-0.062(1)	0.219(1)	0.2429(8)	0.028(3)	
O2X	0.050(1)	0.007(1)	0.2483(8)	0.027(3)	
O39	0.065(1)	0.461(1)	0.3292(8)	0.029(3)	
O4J	0.507(1)	0.071(1)	0.2947(8)	0.028(3)	
O57	0.387(1)	0.456(1)	0.1273(8)	0.027(3)	
O5Q	0.497(1)	0.233(1)	0.1320(8)	0.029(3)	
O69	0.262(1)	0.566(1)	0.2812(8)	0.030(3)	
O7Q	0.290(1)	0.259(1)	0.0567(7)	0.024(2)	
O8X	0.046(1)	0.136(1)	0.1209(7)	0.028(3)	
OP1	0.184(1)	0.217(1)	0.3235(7)	0.022(2)	
OP2	0.372(1)	0.315(1)	0.2712(7)	0.022(2)	
OP3	0.174(1)	0.337(1)	0.2007(6)	0.019(2)	
OP4	0.276(1)	0.129(1)	0.2072(6)	0.020(2)	

Table 4. (Continued.)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{eq}}/U_{\text{iso}}^a$	s.o.f.
Cs1	−0.2776(2)	0.0329(2)	0.1761(1)	0.0427(5)	
Cs2	0.4073(2)	0.3666(2)	0.5582(2)	0.0455(5)	
Cs3	0.0800(2)	0.1259(2)	−0.0558(1)	0.0492(5)	
Cs4	0.2858(2)	0.5170(2)	−0.1747(1)	0.0426(6)	
Cs5	−0.1418(2)	0.2450(2)	0.5530(1)	0.0523(6)	
Cs6	0.6495(2)	0.2674(2)	−0.0524(2)	0.0573(6)	
OW1	−0.141(3)	0.759(3)	0.375(2)	0.11(1)	
OW2	0.661(3)	0.722(3)	0.165(2)	0.110(10)	

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Table 5. Interatomic distances (in Å) in the polyanions in crystals **A** and **B**.^a

	A	B		A	B
M1–O1T	1.63(2)	1.66(2)	M7–O79	2.01(2)	1.95(1)
M1–O12	1.96(1)	1.97(1)	M7–O57	1.91(1)	1.96(1)
M1–O13	1.95(2)	1.86(1)	M7–O7Q	1.81(2)	1.85(1)
M1–O14	1.85(2)	1.84(1)	M7–OP3	2.42(1)	2.44(1)
M1–O1J	1.90(2)	1.96(2)	M8–O8T	1.67(1)	1.68(2)
M1–OP1	2.44(1)	2.42(1)	M8–O78	1.99(2)	1.96(1)
M2–O2T	1.66(2)	1.64(2)	M8–O89	1.93(2)	1.86(1)
M2–O12	1.89(2)	1.92(1)	M8–O28	1.85(1)	1.86(1)
M2–O23	1.91(2)	1.85(1)	M8–O8X	1.89(2)	1.92(1)
M2–O28	1.92(1)	1.90(1)	M8–OP3	2.43(1)	2.46(1)
M2–O2X	1.91(2)	1.94(1)	M9–O9T	1.68(2)	1.68(2)
M2–OP1	2.45(1)	2.47(1)	M9–O79	1.91(2)	1.93(1)
M3–O3T	1.67(2)	1.62(2)	M9–O89	2.01(2)	2.04(1)
M3–O13	1.95(2)	2.00(1)	M9–O39	1.93(2)	1.92(1)
M3–O23	1.99(2)	1.97(1)	M9–O69	1.85(1)	1.84(1)
M3–O36	1.85(1)	1.86(1)	M9–OP3	2.42(1)	2.44(1)
M3–O39	1.83(2)	1.83(1)	MX–OXT	1.66(2)	1.70(2)
M3–OP1	2.41(1)	2.41(1)	MX–OXJ	1.95(2)	1.96(1)
M4–O4T	1.65(2)	1.66(2)	MX–OXQ	1.99(1)	1.99(1)
M4–O45	1.91(2)	1.90(1)	MX–O2X	1.82(2)	1.81(1)
M4–O46	1.96(2)	1.95(1)	MX–O8X	1.90(2)	1.86(1)
M4–O14	1.92(2)	1.94(1)	MX–OP4	2.46(1)	2.48(1)
M4–O4J	1.85(2)	1.87(1)	MJ–OJT	1.62(2)	1.63(2)
M4–OP2	2.44(1)	2.45(1)	MJ–OXJ	1.92(2)	1.92(1)
M5–O5T	1.64(2)	1.68(2)	MJ–OJQ	1.97(2)	2.02(1)
M5–O45	2.00(1)	2.03(1)	MJ–O1J	1.83(2)	1.80(2)
M5–O56	1.99(2)	1.97(1)	MJ–O4J	1.94(2)	1.95(1)
M5–O57	1.86(1)	1.82(1)	MJ–OP4	2.43(1)	2.43(1)
M5–O5Q	1.84(2)	1.89(1)	MQ–OQT	1.64(2)	1.69(2)
M5–OP2	2.45(1)	2.42(1)	MQ–OXQ	1.91(1)	1.91(1)
M6–O6T	1.69(2)	1.63(2)	MQ–OJQ	1.88(2)	1.90(1)
M6–O46	1.89(1)	1.95(1)	MQ–O5Q	1.92(2)	1.91(1)
M6–O56	1.91(1)	1.91(1)	MQ–O7Q	1.92(1)	1.88(1)
M6–O36	1.92(1)	1.94(1)	MQ–OP4	2.41(1)	2.41(1)
M6–O69	1.88(1)	1.88(1)	P1–OP1	1.53(1)	1.53(1)
M6–OP2	2.44(1)	2.46(1)	P1–OP2	1.55(1)	1.55(1)
M7–O7T	1.67(2)	1.66(2)	P1–OP3	1.57(1)	1.51(1)
M7–O78	1.88(1)	1.92(1)	P1–OP4	1.52(2)	1.51(2)

^aM represents the addenda atom, Mo or V, at the corresponding position.

Ob, [1.88(2)–2.01(2), average 1.94 Å for **A** and 1.85(1)–2.04(1), average 1.94 Å for **B**] in both crystals, indicating stronger interactions between Ob and Cs or water than Ob'. These features are quite normal for the compounds of this type. The phosphate group in each compound showed a regular tetrahedral geometry. The O–P–O angles ranged from 108.4(8) to 110.6(8) for **A** and from 108.3(7) to 110.5(7) for **B**.

As can be seen in the packing diagrams shown in Fig. 4, these two crystals have quite similar overall structures. The essential difference is the orientation of the polyanion, which is generated by a two-fold screw axis 2_1 (**A**) and n -glide plane (**B**). Taking $P2_1/n$ as a space group for each, **A** and **B** become isostructural. Since the overall structure of the α -Keggin type heteropolyanion can be regarded as a sphere, the differ-

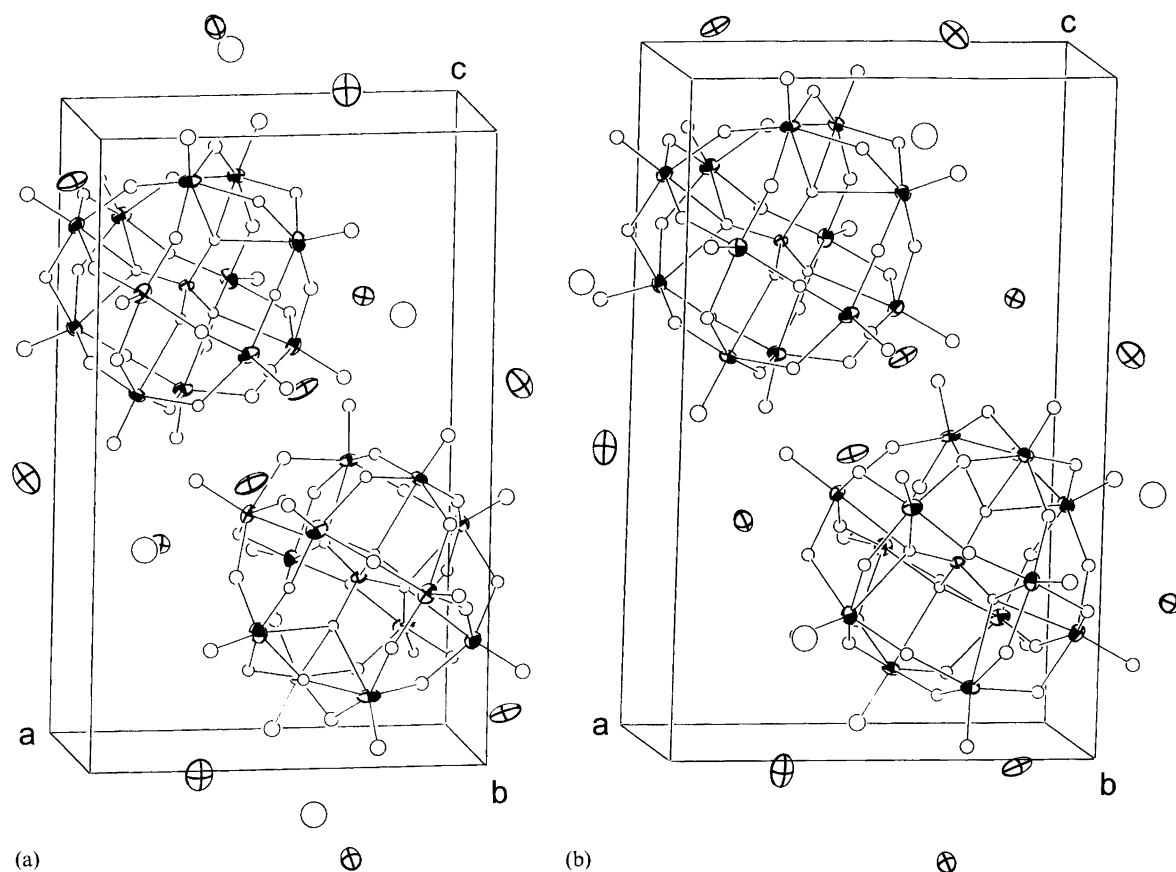


Fig. 4. Packing diagrams of crystals **A** (a) and **B** (b). The crossed ellipsoids and open circles outside the polyanions show the caesium cations and the oxygen atoms of the water molecules, respectively.

ence of orientation does not play a very important role in the packing. This often causes disordering in the orientation of the α -Keggin type heteropolyanion in a crystal. In this work, the disordered structure, i.e. the centrosymmetric structure, was rejected for the reasons mentioned in the experimental section. Close contacts within 3.4 Å in both crystals are listed in Table 6. The whole crystal structure is supported by hydrogen bonding and interactions among the polyanion, water molecules and caesium ions. The water molecules do not have any

interactions with each other. The caesium ions take a variety of coordination numbers. The numbers of oxygen atoms within 3.4 Å from Cs are: 5 (Cs4), 6 (Cs1), 7 (Cs2, Cs5) and 8 (Cs3, Cs6) for **A** and 5 (Cs6), 6 (Cs3), 7 (Cs1, Cs4 and Cs5) and 8 (Cs2) for **B**.

The bond valence^{26,27} was calculated for each M–O bond with the approximate assumption that both Mo^{VI} and V^{IV} contribute to the valence in the same proportion, with the corresponding site occupation factors. The contributions of water molecules and caesium ions were also taken into account. The sum of the valence at each metal position should be 5.666 [= (6 × 0.833) + (4 × 0.167)]. The averaged values calculated were 5.427 for **A** and 5.419 for **B**. That these values are somewhat lower than the above value, is perhaps a result of the approximation. No significant relationship between the valence, and the site occupation factor could be found. The values of the valences for most of the Ob' atoms were calculated to be greater than 2, which indicates that the Mo–Ob' distances obtained are short. Some of the terminal oxygen atoms were also calculated to have valences remarkably larger than 2, e.g. O1T (2.277) and OJT (2.266) in **A** and O8T (2.190) and OJT (2.209) in **B**. As the V^{IV} atoms are almost randomly distributed, the most basic position, which might be located close to V^{IV}, is expected to be delocalised also. Owing to the

Table 6. Close contacts (in Å) (<3.40 Å) from water molecules in crystals **A** and **B**.

A		B	
OW1–O13	2.83(4)	OW1–O2T ^v	3.02(4)
OW1–O2T ⁱ	2.96(5)	OW1–OOQT ^{vi}	3.04(4)
OW1–O9T ⁱⁱ	3.16(4)	OW1–OO9T	3.15(4)
OW1–O3T	3.20(4)	OW1–Cs4 ^{vi}	3.16(3)
OW1–Cs2	3.26(4)	OW1–OO7Q ^{vi}	3.29(3)
OW2–O5T ⁱⁱⁱ	2.89(5)	OW2–O5T	2.80(4)
OW2–OJT ^{iv}	3.00(4)	OW1–OJT ^v	2.97(4)
OW2–O56 ⁱⁱⁱ	3.30(5)	OW2–O56	3.28(4)
OW2–Cs3	3.32(5)	OW2–Cs1 ^{vii}	3.37(3)

Symmetry operations: ⁱ $-x, 1/2+y, 1-z$. ⁱⁱ $-x, -1/2+y, 1-z$. ⁱⁱⁱ $1-x, -1/2+y, -z$. ^{iv} $1-x, 1/2+y, -z$. ^v $x, 1+y, z$. ^{vi} $-1/2+x, 1-y, 1/2+z$. ^{vii} $1+x, 1+y, z$.

positional disordering of the addenda atoms and the less accurate bond valences calculated, it was not possible to determine the site of protonation on the polyanion. However, assuming that protonation will occur at the Ob position which has the higher basicity, i.e. the lower sum of bond valences, the following oxygen atoms can be candidates for a protonated position: O79 (1.769) and O56 (1.813) for **A** and O12 (1.821) for **B**. O13 in **A** may also be a candidate, considering its close contact to the water molecule. Some of the terminal oxygen atoms such as O9T (1.820) in **A** and O9T (1.799) in **B** have low values also. However, these values are not sufficiently decisive in determining the protonated position.

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