

# Multicomponent Polyanions. 48. The Crystal Structure of Trihydrogen Dodecamolybdophosphate-Benzene(1/3)

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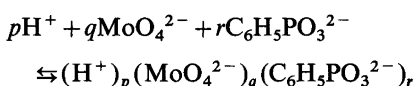
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A novel organic solvated heteropoly compound,  $\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 3(\text{C}_6\text{H}_6)$ , crystallised in the monoclinic form,  $P2_1/n$  (No. 14), with  $a=12.189(2)$ ,  $b=13.981(2)$ ,  $c=12.978(1)$  Å and  $\beta=98.59(1)^\circ$ . The refinement of 340 parameters with 3705 reflections [ $I > 3.0\sigma(I)$ ] gave a final  $R$ -value of 0.061 ( $R_w=0.067$ ). The polyanion, having a so-called  $\alpha$ -Keggin structure, is disordered around an inversion centre. One of three benzene molecules is sandwiched between polyanions, and the other two are accommodated in a cavity surrounded by polyanions. The links between polyanions and benzene rings are mainly due to hydrogen bonds. The phosphate and benzene in the compound were formed by hydrolysis of phenylphosphonate.

The present work forms a part of a research project aimed at elucidating the equilibrium conditions and determining the structures of species formed in some aqueous polyoxometallate systems containing Mo and/or V.<sup>1</sup> Owing to the complexity of the systems, a variety of different techniques has to be used. For example, in the molybdophosphate system we have used potentiometry<sup>2</sup> and spectroscopy (NMR,<sup>2</sup> IR,<sup>3</sup> Raman,<sup>4</sup> UV/VIS<sup>5</sup>). Furthermore, X-ray diffraction has been applied to concentrated solutions<sup>6</sup> and to crystals.<sup>7</sup> The result of the equilibrium analysis was very complicated. Among species identified, a series of complexes with Mo/P=9, proposed to have a tripodal  $\text{PO}_4$  group, could not be characterised structurally. Hence, a molybdophenylphosphonate system was studied in order to block one coordinative site of phosphate and to simplify the speciation.<sup>8</sup>

In the equilibrium analysis of the system, equilibria were written as



where the integers  $p$ ,  $q$  and  $r$  define the complexes formed. When referring to nuclearities, the complexes will be designated  $\text{Mo}_q(\text{PhP})_r$ . For species in proton series, the charge will also be given. From combined potentiometric and  $^{31}\text{P}$  NMR data the aqueous speciation could be solved.<sup>8</sup> As seen in the distribution diagram in Fig. 1, several molybdophenylphosphonate species were formed, but no  $\text{Mo}_9\text{PhP}$  species could be identified. Of the three different nuclearities established, only  $\text{Mo}_5(\text{PhP})_2$  has

been characterised structurally.<sup>9</sup> The structures of the other two nuclearities,  $\text{Mo}_6\text{PhP}$  and  $\text{Mo}_7\text{PhP}$ , could only be proposed, since experiments to obtain single crystals containing such species were not successful.

In order to establish the structures of these complexes in solution, a series of large-angle X-ray scattering (LAXS) measurements on concentrated solutions ( $\text{Mo} = 1.50 \text{ M}$ ) is in progress. To obtain high concentrations of Mo and PhP without precipitating, lithium was used instead of sodium as the counter cation. The distribution diagram in Fig. 1 has been constructed with equilibrium constants obtained from the previous study on solutions with low concentrations ( $\text{Mo} \leq 0.080 \text{ M}$ ) and in  $0.600 \text{ M NaCl}$  medium.<sup>8</sup> However,  $^{31}\text{P}$  NMR analysis on the concentrated solutions in  $\text{Li}^+$  medium, prepared for the LAXS measurements, is in very good agreement with the diagram.

During the LAXS measurements on a solution with ca. pH 0.9 and  $\text{Mo}/\text{PhP}=5$  (vertical dashed line in Fig. 1), precipitation of a yellow–green crystalline phase occurred. According to the previous equilibrium study,<sup>8</sup> this solution should contain predominantly  $\text{Mo}_6\text{PhP}$ . Hence, a reasonable assumption was that the crystalline phase also contained a complex with a  $\text{Mo}_6\text{PhP}$  composition. A structure determination of this crystalline phase would thus provide essential information for analysis and interpretation of the LAXS data as well as equilibrium analysis data.

However, a  $^{31}\text{P}$ -NMR analysis on the remaining solution indicated that the crystals formed should contain a complex with  $\text{Mo}/\text{PhP}$  ratio exceeding that of 7. It thus seemed that a new species, not detected in the equilibrium

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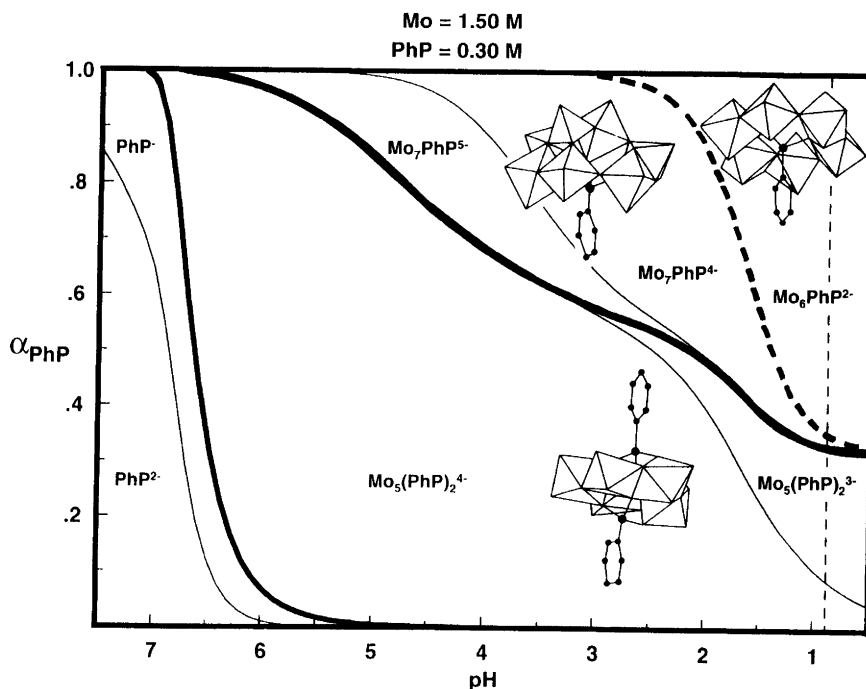


Fig. 1. A distribution diagram of PhP-containing species vs. pH at Mo/PhP=5 with anion structures inserted. The structure of  $\text{Mo}_5(\text{PhP})_2$  has been reported earlier.<sup>9</sup> For the  $\text{Mo}_6\text{PhP}$  and  $\text{Mo}_7\text{PhP}$  species, the structures proposed in Ref. 8 are shown. The thick lines separate complexes with different nuclearity. The species in rapid exchange on the NMR timescale are separated by the dashed line. The thin lines demarcate proton series of the complexes.

analysis of the system, had been formed, making a single-crystal X-ray diffraction investigation of the phase worthwhile.

### Experimental

Crystals of the title compound were obtained in an aqueous molybdophenylphosphonate solution with  $[\text{Mo}]_{\text{tot}} = 1.50 \text{ M}$  and Mo/PhP=5, prepared for a LAXS measurement.  $\text{Li}_2\text{MoO}_4$  (prepared from a  $\text{MoO}_3$  and  $\text{Li}_2\text{CO}_3$  mixture, fused at 1070 K, E. Merck, *p.a.*),  $\text{MoO}_3$  (E. Merck, *p.a.*) and  $\text{C}_6\text{H}_5\text{PO}(\text{OH})_2$  (Aldrich, *p.a.*), were dissolved in water. The pH value of the solution was adjusted to ca. 0.9 using HCl (E. Merck, *p.a.*). Faintly yellow-green crystals appeared after about 10 days of irradiation with Ag  $K\alpha$  ( $\lambda = 0.56080 \text{ \AA}$ ). An atomic absorption analysis revealed that the crystals contained no lithium, indicating that the crystallised compound was in the acid form.

The intensity data were collected with a SYNTEX R3 automated four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. The background was measured on each side of every reflection for a time equal to the peak measurement. The cell parameters were determined by 25 reflections with  $21.5 < 2\theta < 28.2^\circ$ . A psi-scan was carried out at 10 reflections selected from intensity measurement in the range of  $10.9 < 2\theta < 38.7^\circ$  with a step scan of  $10^\circ$ . Experimental details are listed in Table 1. Calculations were carried out using of the Xtal3.2 program package.<sup>10</sup>

Of total 7305 reflections, 3705 with  $I > 3.0\sigma(I)$  were used for calculation. The Mo atoms were located from Patterson vectors, and all other non-H atoms were found by successive Fourier synthesis. Scattering factors used ( $\text{Mo}^0$ ,  $\text{P}^0$ ,  $\text{O}^0$ ,  $\text{C}^0$ ) and anomalous dispersion factors including imaginary parts were taken from Ref. 11. A Lorenz polarisation correction and an empirical absorption correction based on the psi-scan were applied. Extinction correction gave no significant improvement and was not included in the final calculation. All atoms found were refined anisotropically. The full-matrix least-squares refinement of 340 parameters gave a final  $R$ -value of 0.061 ( $R_w = 0.067$ ). Details of the calculations are also listed in Table 1.

### Discussion

An ORTEP<sup>12</sup> view of the structure with atomic notations is shown in Fig. 2. The polyanion has an  $\alpha$ -Keggin structure with the formula  $\text{Mo}_{12}\text{PO}_{40}^{3-}$ .<sup>13-15</sup> As the phosphate in the centre of the anion shows disordering as described below, one of the orientations has been chosen in Fig. 2. The atomic coordinates and equivalent thermal parameters are listed in Table 2. No abnormal temperature factors or standard deviations were found.

The packing diagram of the compound is shown in Fig. 3. The polyanion lies on a crystallographic inversion centre. There are two crystallographically independent benzene molecules; one of the three benzene molecules is positioned with its centre on an inversion centre

Table 1. Crystal and experimental data for  $\text{H}_3\text{Mo}_{12}\text{PO}_{40} \cdot 3(\text{C}_6\text{H}_6)$ .

Formula	$\text{C}_{18}\text{H}_{21}\text{O}_{40}\text{Mo}_{12}\text{P}$
$M_r$	2059.6
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
$a/\text{\AA}$	12.189(2)
$b/\text{\AA}$	13.981(2)
$c/\text{\AA}$	12.978(1)
$\beta/^\circ$	98.59(1)
$V/\text{\AA}^3$	2186.7(4)
$Z$	2
$D_c/\text{Mg m}^{-3}$	3.123
$\mu(\text{Mo } K\alpha)$	3.40
$F(000)$	1928.87
Crystal size/mm	$0.2 \times 0.15 \times 0.1$
Temperature/K	293
No. of reflns. for cell determination ( $2\theta$ range/ $^\circ$ )	25 ( $21.5 < 2\theta < 28.2$ )
Scan mode	$\theta$ - $2\theta$
$2\theta$ range/ $^\circ$	$4.3 < 2\theta < 60.1$
$hkl$ range	$0 \leq h \leq 17$ $0 \leq k \leq 19$ $-18 \leq l \leq 18$
$2\theta$ scan speed/ $^\circ \text{ min}^{-1}$	2-6.5
Total no. of reflns. measured	7305
Test reflns. (deviation %)	-1 0 1 (1.4) -1 1 -3 (1.4) -1 1 5 (1.9)
No. of observed independent reflns. [ $I > 3.0\sigma(I)$ ]	3705
No. parameters refined	340
Weights calcd. according to	$w = 1/(\sigma^2 + 47.9 - 0.024F - 64.6 \sin \theta)$
$R$ ( $R_w$ )	0.061 (0.067)
$S$	1.111
Max. resid. electron density/ $e \text{\AA}^{-3}$	2.17

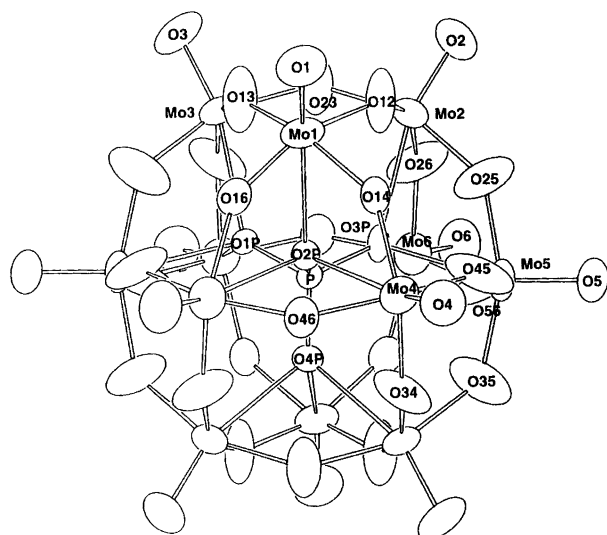


Fig. 2. An ORTEP view of the polyanion along with atomic notations.

(Type A), and the other two are located in general positions (Type B). Thus the crystal shows a pseudo-body-centred structure. As a polyanion with the  $\alpha$ -Keggin structure is very close to a sphere, a difference in the orientation of the anion often plays a small role for the packing in the crystal.

The  $\alpha$ -Keggin structure ideally has  $Td$  symmetry, where

no inversion centre exists. Owing to the space group of  $P2_1/n$  and  $Z=2$ , the polyanion in the present compound has an inversion centre on its P atom. Thus, the Keggin structure heteropolyanion shows a disorder around this inversion centre. The phosphate group  $\text{PO}_4$ , which also has  $Td$  symmetry, shows an anti-trigonal prism-like structure due to the disordering, as shown in Fig. 4. The occupation factors of the four independent oxygen atoms in the phosphate group were set to 0.5 during the refinement. The  $\text{PO}_4$  group shows a good tetrahedron, as seen in Fig. 4. The other oxygen and molybdenum atoms in the polyanion were located at their mean positions generated by the inversion centre. Their positions for each orientation were not taken into account because no separated electron density could be observed around these Mo and O atoms in Fourier and difference Fourier maps. This treatment caused rather large temperature factors of these atoms, as can be seen in Table 2 and Fig. 2.

The benzene A is strictly planar and is sandwiched by two polyanions along the  $b$  axis. An  $\alpha$ -Keggin-type heteropolyanion can be regarded as a sphere with a diameter of about  $11 \text{\AA}$ , the van der Waals radius of oxygen taken into account. The length of the  $b$  axis is  $13.981 \text{\AA}$ , and the interspace between two polyanions is ca.  $3 \text{\AA}$ . Considering the size of the interspace and the thickness of benzene ring (ca.  $3.4 \text{\AA}$ ), the benzene A is strongly held at its position. This is supported by the

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters with e.s.d.s in parentheses.

Atom	x/a	y/b	z/c	$U_{eq}^a/\text{\AA}^2$
Mo1	-0.0347(1)	0.20119(8)	0.15817(9)	0.0486(6)
Mo2	0.1805(1)	0.19987(8)	0.0020(1)	0.0516(6)
Mo3	-0.1010(1)	0.21976(7)	-0.1182(1)	0.0463(5)
Mo4	0.0748(1)	-0.01547(9)	0.27532(8)	0.0480(5)
Mo5	0.28255(9)	-0.0231(1)	0.1093(1)	0.0516(6)
Mo6	0.2095(1)	0.0018(1)	-0.1636(1)	0.0507(6)
P	0.00000	0.00000	0.00000	0.027(1)
O1	-0.048(1)	0.2955(9)	0.2331(9)	0.072(7)
O2	0.264(1)	0.2913(9)	-0.001(1)	0.073(7)
O3	-0.145(1)	0.3232(9)	-0.168(1)	0.070(7)
O4	0.113(1)	-0.0223(9)	0.4025(8)	0.068(6)
O5	0.4175(8)	-0.0312(9)	0.161(1)	0.067(6)
O6	0.3058(9)	0.001(1)	-0.2437(9)	0.073(7)
O12	0.1064(9)	0.230(1)	0.1127(9)	0.082(8)
O13	-0.1018(9)	0.244(1)	0.0285(9)	0.083(8)
O14	0.0523(9)	0.1177(9)	0.258(1)	0.086(8)
O16	-0.158(1)	0.1290(9)	0.176(1)	0.087(8)
O23	0.0531(9)	0.243(1)	-0.0909(8)	0.075(8)
O25	0.272(1)	0.1123(9)	0.086(1)	0.084(8)
O26	0.216(2)	0.1256(9)	-0.117(1)	0.088(8)
O34	0.079(1)	-0.1460(9)	0.235(1)	0.083(8)
O35	0.236(1)	-0.151(1)	0.114(1)	0.092(9)
O45	0.218(1)	-0.002(1)	0.233(1)	0.10(1)
O46	-0.082(1)	-0.034(1)	0.259(1)	0.096(9)
O56	0.290(1)	-0.0373(9)	-0.0339(9)	0.089(8)
O1P	-0.081(1)	-0.047(1)	-0.088(1)	0.029(6)
O2P	-0.030(1)	0.036(1)	0.102(1)	0.030(6)
O3P	0.117(1)	0.033(1)	-0.009(1)	0.038(7)
O4P	-0.010(1)	-0.108(1)	-0.009(1)	0.032(7)
C1	0.020(1)	0.513(1)	-0.100(1)	0.055(7)
C2	0.103(1)	0.483(1)	-0.024(2)	0.07(1)
C3	-0.082(1)	0.531(1)	-0.075(1)	0.062(8)
C11	0.121(2)	0.251(2)	0.664(2)	0.10(2)
C12	0.161(2)	0.192(2)	0.599(3)	0.12(2)
C13	0.118(5)	0.198(3)	0.494(4)	0.20(5)
C14	0.052(4)	0.254(5)	0.468(2)	0.22(5)
C15	0.002(2)	0.317(3)	0.522(4)	0.15(3)
C16	0.038(3)	0.316(2)	0.626(3)	0.11(2)

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

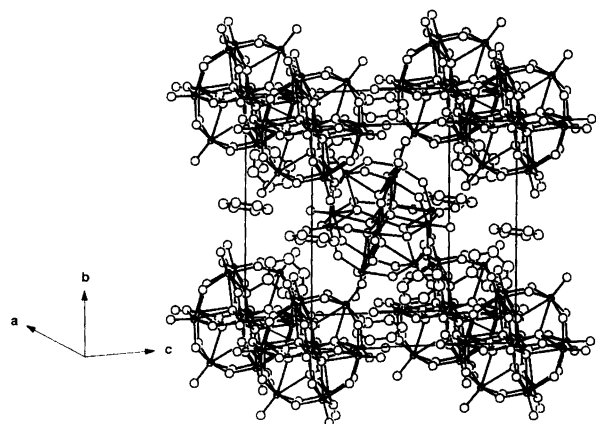


Fig. 3. A packing diagram of  $H_3Mo_{12}PO_{40} \cdot 3(C_6H_6)$ .

rather small temperature factors of the carbon atoms in benzene A. On the other hand, the benzene B is accommodated in a big cavity, which has an inversion centre

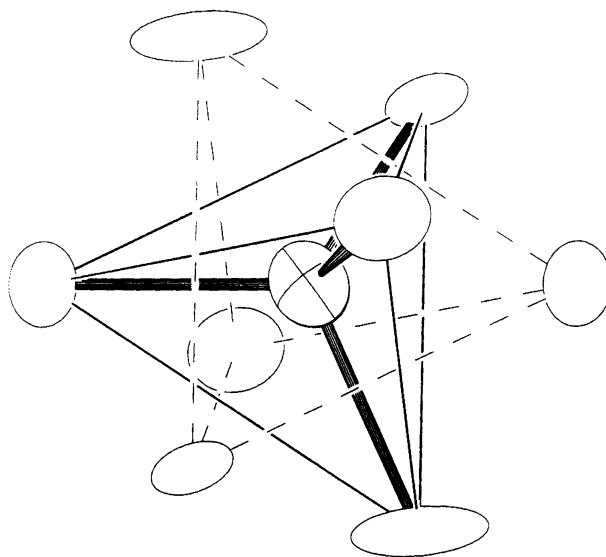


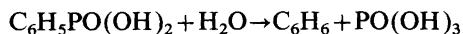
Fig. 4. Disorder of  $PO_4$  tetrahedron.

in the middle, and is surrounded by polyanions. The distance between two benzene molecules in this cavity is ca. 7.5 Å, making them more movable in the structure.

Selected interatomic distances and bond angles are listed in Table 3. The P–O distances [1.52(1)–1.55(1) Å] and O–P–O angles for each phosphate group [107.2(8)–111.7(9)°] are quite normal. Bond distances of Mo–O(terminal) [1.64(1)–1.69(1) Å], Mo–O(–P) [2.42(2)–2.52(1) Å] and Mo–O(–Mo) [1.83(1)–1.97(1) Å] are acceptable, but vary over wide ranges due to the disordering.

The bond angles around Mo and O atoms are beyond discussion because of the disordering. The C–C distances [1.35(2)–1.38(2) Å] and C–C–C angles [119(2)–121(2)°] in the benzene A are quite normal. Those of the benzene B [1.13(8)–1.39(4) Å and 115(3)–131(4)°] show a distortion of the benzene ring caused by a large mobility of the molecule in the cavity. Close contacts shorter than 3.35 Å between the polyanion and benzene molecule are listed in Table 4 and shown in Figs. 5a and 5b. These short O–C distances indicate a strong interaction between them.

The present compound contains phosphate and benzene although phenylphosphonate was used as starting material. This unexpected result must be caused by a hydrolysis of phenylphosphonate to benzene and phosphate as shown in the following scheme:



The present compound has three benzene molecules and one phosphate group, although benzene/P=1 in phenylphosphonate. After crystallisation, very little phosphate was detected in solution by  $^{31}P$ -NMR. These facts indicate that almost all of the benzene molecules formed by the hydrolysis entered the crystals. This implies a very low solubility of the present compound in water, although no further quantitative analysis of phosphate

Table 3. Selected interatomic distances (in Å) and bond angles (in °).

P-O1P	1.55(1)	P-O3P	1.52(1)
P-O2P	1.52(2)	P-O4P	1.52(1)
Mo1-O1	1.66(1)	Mo4-O4	1.65(1)
Mo2-O2	1.64(1)	Mo5-O5	1.69(1)
Mo3-O3	1.64(1)	Mo6-O6	1.68(1)
Mo1-O2P	2.42(2)	Mo4-O1P	2.48(2)
Mo1-O4P	2.46(2)	Mo4-O2P	2.52(1)
Mo2-O3P	2.46(2)	Mo5-O1P	2.45(1)
Mo2-O4P	2.45(2)	Mo5-O3P	2.47(1)
Mo3-O1P	2.45(1)	Mo6-O2P	2.49(2)
Mo3-O4P	2.51(1)	Mo6-O3P	2.48(2)
Mo1-O12	1.94(1)	Mo4-O14	1.89(1)
Mo1-O13	1.86(1)	Mo4-O34	1.90(1)
Mo1-O14	1.94(1)	Mo4-O45	1.91(2)
Mo1-O16	1.85(1)	Mo4-O46	1.91(1)
Mo2-O12	1.85(1)	Mo5-O25	1.92(1)
Mo2-O23	1.91(1)	Mo5-O35	1.88(1)
Mo2-O25	1.89(1)	Mo5-O45	1.92(2)
Mo2-O26	1.97(1)	Mo5-O56	1.88(1)
Mo3-O13	1.94(1)	Mo6-O16	1.93(1)
Mo3-O23	1.89(1)	Mo6-O26	1.83(1)
Mo3-O34	1.88(2)	Mo6-O46	1.89(1)
Mo3-O35	1.92(2)	Mo6-O56	1.90(1)
C1-C2	1.38(2)	C2-C3	1.36(3)
C1-C3	1.35(2)		
C11-C12	1.33(5)	C13-C14	1.13(8)
C11-C16	1.39(4)	C14-C15	1.33(7)
C12-C13	1.38(7)	C15-C16	1.36(6)
O1P-P-O2P	107.2(8)	O2P-P-O3P	108.8(9)
O1P-P-O3P	108.4(8)	O2P-P-O4P	111.7(9)
O1P-P-O4P	109.5(8)	O3P-P-O4P	111.1(9)
C1-C2-C3	120(2)	C2-C1-C3	119(2)
C1-C3-C2	121(2)		
C11-C12-C13	118(3)	C12-C13-C14	119(5)
C11-C16-C15	118(3)	C13-C14-C15	131(4)
C12-C11-C16	120(3)	C14-C15-C16	115(3)

Table 4. Intermolecular distances (in Å) between polyanion and benzene molecule within 3.35 Å.

Type A			
C1-O1 <sup>i</sup>	3.22(2)	C2-O2 <sup>iv</sup>	3.30(2)
C1-O5 <sup>ii</sup>	3.17(2)	C3-O3 <sup>iv</sup>	3.20(2)
C1-O6 <sup>iii</sup>	3.15(2)	C3-O45 <sup>ii</sup>	3.25(2)
Type B			
C11-O16 <sup>v</sup>	3.16(3)	C14-O1	3.16(3)
C11-O34 <sup>vi</sup>	3.28(3)	C14-O14	3.33(5)
C11-O46 <sup>vi</sup>	3.25(3)	C14-O35 <sup>iii</sup>	3.21(6)
C12-O13 <sup>v</sup>	3.27(4)	C15-O2 <sup>ii</sup>	3.25(3)
C12-O46 <sup>vi</sup>	3.13(4)	C15-O25 <sup>ii</sup>	3.21(4)
C13-O4	3.30(5)	C15-O56 <sup>iii</sup>	3.24(4)
C13-O14	3.25(6)	C16-O56 <sup>iii</sup>	3.29(4)
C13-O35 <sup>iii</sup>	3.21(6)		

Symmetry operations:

<sup>i</sup>  $-x, 1-y, 1-z$ ; <sup>ii</sup>  $-1/2+x, 1/2-y, 1/2+z$ ; <sup>iii</sup>  $1/2-x, 1/2+y, 1/2-z$ ; <sup>iv</sup>  $x, y, 1+z$ ; <sup>v</sup>  $1/2+x, 1/2-y, 1/2+z$ ; <sup>vi</sup>  $-x, -y, 1-z$ .

and benzene has been performed. Attempts to obtain this compound by mixing phosphate, molybdate and benzene have so far not been successful.

The compound is interesting from a catalytic point of view. Many  $\alpha$ -Keggin-type heteropoly compounds are known to be good acid catalysts in both hetero- and homogeneous reactions.<sup>16</sup> In heterogeneous catalysis, acids and acidic salts of heteropoly compounds show a so-called 'pseudo-liquid phase', and even acid points in the bulk of the catalyst take part in the reaction following absorption of polar organic substances.<sup>16</sup> Structures of heteropolyacids solvated with polar organic molecules, such as DMSO<sup>17</sup> and pyridine,<sup>18</sup> have been determined, supporting this phenomenon. On the other hand, non-polar organic molecules such as benzene cannot be absorbed into the solid catalyst, and the reaction there-

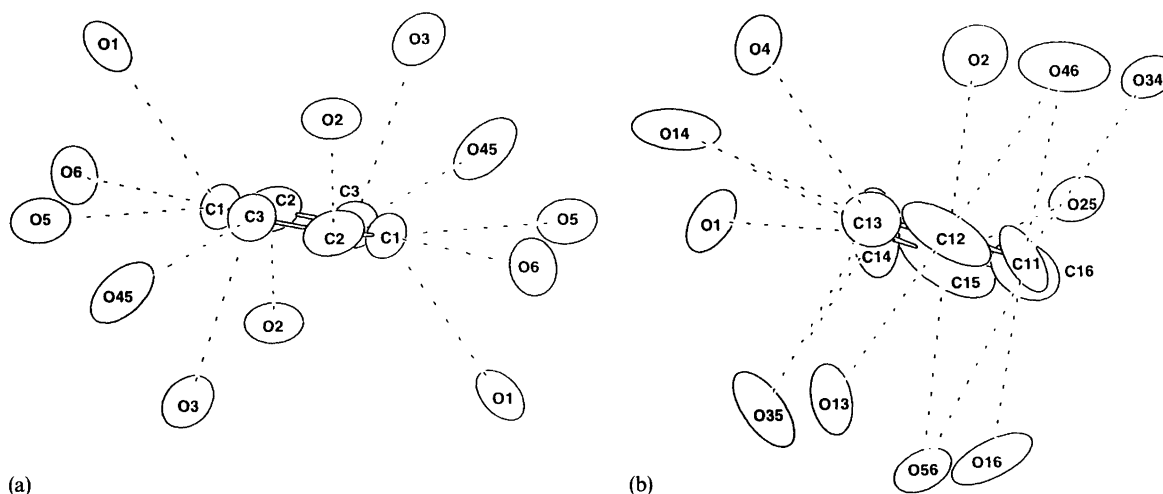


Fig. 5. Close contacts between the polyanions and the benzene molecules. (a) Benzene type A and (b) benzene type B.

fore occurs only on the surface. To the best of our knowledge, interactions between a heteropolyanion and a non-polar organic molecule have not been reported. Thus, the present work provides the first example visualising the interaction between a heteropolyanion and a non-polar molecule.

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### References

- Pettersson, L. *Mol. Eng.* 3 (1993) 29.
- Pettersson, L., Andersson, I. and Öhman, L.-O. *Inorg. Chem.* 25 (1986) 4726.
- Lyhamn, L. *Chem. Scr.* 12 (1977) 153.
- Lyhamn, L. and Pettersson, L. *Chem. Scr.* 12 (1977) 142.
- Lyhamn, L. and Pettersson, L. *Chem. Scr.* 16 (1980) 52.
- Johansson, G., Pettersson, L. and Ingri, N. *Acta Chem. Scand., Ser. A* 28 (1974) 1119.
- Lyxell, D.-G., Strandberg, R., Boström, D. and Pettersson, L. *Acta Chem. Scand.* 45 (1991) 681.
- Yagasaki, A., Andersson, I. and Pettersson, L. *Inorg. Chem.* 26 (1987) 3926.
- Lyxell, D.-G. and Strandberg, R. *Acta Crystallogr., Sect. C* 44 (1988) 1535.
- Hall, S. R., Flack, H. D. and Stewart, J. M. Eds. *Xtal3.2 Reference Manual*. Universities of Western Australia, Geneva and Maryland 1992.
- International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
- Johnson, C. K. *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN 1970.
- Keggin, J. F. *Nature (London)* 131 (1933) 908.
- D'Amour, H. and Allmann, R. *Z. Kristallogr.* 143 (1976) 1.
- Clark, C. J. and Hall, D. *Acta Crystallogr., Sect. B* 32 (1976) 1545.
- Misono, M. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Pope, M. and Müller, A., Eds., Kluwer Academic Publishers, Dordrecht 1994, p. 255.
- Oniani, E. S., Sergienko, V. S., Chuvaev, V. F. and Mistryukov, A. E. *Russ. J. Inorg. Chem.* 36 (1991) 1157 [*Zh. Neorg. Khim.* 36 (1991) 2048].
- Hashimoto, M. and Misono, M. *Acta Crystallogr., Sect. C* 50 (1994) 231.

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