A Novel Phosphomolybdate Structure: Crystal Structure of $[NH_4]_5[(MoO_3)_5(PO_4)(HPO_4)],3H_2O$

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The crystal structure of the title compound has been studied by *X*-ray diffraction methods from counter data. Crystals are orthorhombic, space group $P2_12_12_1$, with parameters a = 14·699(2), b = 9·725(1), c = 18·201(2) Å. The structure was solved by direct methods and refined by full-matrix least squares to R 0·029 for 4 808 observed reflections. The anion consists of a ring of five distorted MoO_6 octahedra. Of the five links in the ring, four involve shared edges, and the fifth a shared apex of MoO_6 octahedra. The crown thus formed is capped on one face by PO_4^{3-} and on the other by HPO_4^{2-}. The three phosphate oxygen atoms shared by the MoO_6 octahedra are of two types: one type (two on each phosphate) consists of oxygen atoms bridging two molybdenum atoms, and the other, the third phosphate oxygen, is shared by only one molybdenum atom. The phosphomolybdate anions are held together by a network of strong hydrogen bonds.

THE most characteristic tungsten and molybdenum heteropolyanions are species presenting a molybdenum or tungsten : heteroatom ratio of twelve (series twelve); these include $[SiW_{12}O_{40}]^{4-}$ and $[PMo_{12}O_{40}]^{5-}$ whose structure has been determined by Keggin.[1] When the central atom is phosphorus or arsenic, there are compounds which contain two heteroatoms, such as $[P_2W_{18}O_{62}]^{6-}$. These compounds are obtained under conditions different from those in the first group, but they have similar properties. Their structure, derived from Keggin's model, was determined by Dawson:[2] in these compounds, the phosphate anions are surrounded

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[1] J. F. Keggin, *Proc. Roy. Soc.*, 1934, **A1444**, 75.

[2] B. Dawson, *Acta Cryst.*, 1953, **6**, 113.

by WO_6 octahedra and each phosphate oxygen is bonded to at least one tungsten atom. The PO_4 tetrahedra are located at the centre of the cavity formed by the assemblage of WO_6 octahedra.

The moderate alkaline hydrolysis of the series twelve compounds yields new compounds presenting molybdenum or tungsten : heteroatom ratios of eleven, *e.g.* $[PW_{11}O_{39}]^{7-}$; under more stringent conditions, the compounds are completely hydrolysed into tungstate or molybdate, according to reaction (1). In the case

$$[PMo_{11}O_{39}]^{7-} + 17OH^- \longrightarrow [HPO_4]^{2-} + 11[MoO_4]^{2-} + 8H_2O \quad (1)$$

of the phosphomolybdates, however, an intermediate step exists in which a series of compounds containing molybdenum : heteroatom ratios of 5/2 are formed according to reaction (2). Under moderate conditions,

$$2[PMo_{11}O_{39}]^{7-} + 26OH^- \longrightarrow [P_2Mo_5O_{23}]^{6-} + 17[MoO_4]^{2-} + 13H_2O \quad (2)$$

these compounds can be hydrolysed to $[HP_2Mo_5O_{23}]^{5-}$ and, eventually, to $[HPO_4]^{2-}$ and $[MoO_4]^{2-}$.[3] In this case, it is not likely that the PO_4 tetrahedra occupy the centre of cavities formed by assemblages of MoO_6 octahedra, because of the small number of octahedra available. Since no crystalline structure of a member of this class of compounds was known, we have determined that of the compound $[NH_4]_5[(MoO_3)_5(PO_4)(HPO_4)],3H_2O$ by *X*-ray diffraction methods.

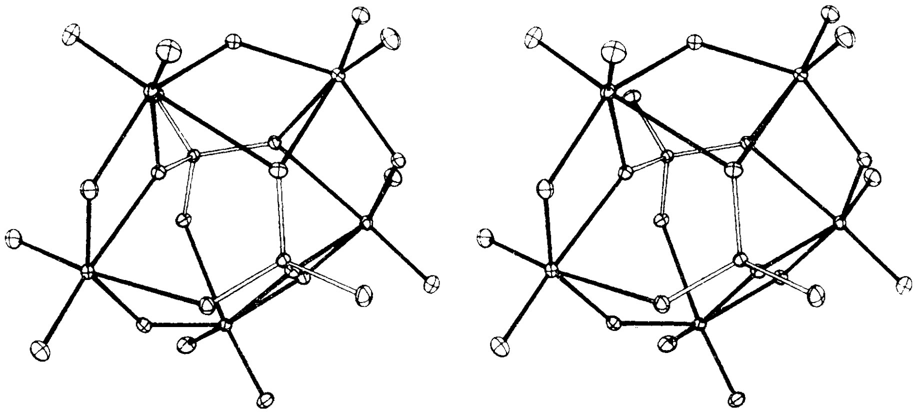

FIGURE 1 Stereoview of the anion $[(MoO_3)_5(PO_4)(HPO_4)]^{5-}$; MoO_6 octahedra are shown by filled bonds, PO_4 tetrahedra by open bonds

EXPERIMENTAL

Crystals of the title compound were prepared by the method of ref. 4. Preliminary cell data were obtained from precession photographs. Refined unit-cell dimensions and their estimated standard deviations were obtained by the method of Busing and Levy,[5] from diffractometer data, with Mo-K_α radiation.

Crystal Data.—$[NH_4]_5[(MoO_3)_5(PO_4)(HPO_4)],3H_2O$, $M = 1054{\cdot}9$, $a = 14{\cdot}699(2)$, $b = 9{\cdot}725(1)$, $c = 18{\cdot}201(2)$ Å, $D_m = 2{\cdot}65$ (by flotation), $Z = 4$, $D_c = 2{\cdot}69$, $U = 2601$ Å^3, $F(000) = 2040$. Space group $P2_12_12_1$ (D_2^4, No. 19) from systematic absences. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 25·33 cm^{-1}.

Data Collection.—A small cube of side 140 μm cut from the available crystals was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a four-circle Picker diffractometer controlled by a PDP 8I computer, by use of graphite-monochromated Mo-K_α radiation, with 2θ 11·84° ($\theta = 5{\cdot}57°$).

Intensity data were collected by the θ–2θ scan technique with a scan rate of 2° min^{-1}. The scan range was 1·4° and stationary background counts were recorded for 20 s at each end of the scan. Attenuators were used whenever the scan count exceeded 7000 counts sec^{-1}. The intensities of three standard reflections monitored throughout data collection at intervals of 80 measurements, were constant. A standard deviation was assigned to each measured intensity using the expression:

$$\sigma(I) = |C + (t_c/t_b)^2(B_1 + B_2) + (pI)^2|^{1/2}$$

where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are respectively scan and background times, and p is an empirical coefficient of the net count I. An initial p value of 0·05 was used. A total of 11 733 reflections were measured in the range $6{\cdot}0° < 2\theta < 90°$, of which 4808 had $\sigma(I)/I < 0{\cdot}35$ and were considered observed. Absorption corrections were computed by numerical integration using the program DATAP.[6] Since the absorption factors varied between 1·207 and 1·234, no absorption corrections were applied.

Structure Solution and Refinement.—The presence of five molybdenum atoms in the asymmetric unit precludes the use of Patterson methods, and the crystal structure was therefore solved by direct methods. Normalized structure factors were computed for all reflections having $\sigma(I)/I < 0{\cdot}45$, using the programs SAP1 and SAP2 [7] (Table 1). The origin- and enantiomorph-fixing reflections were

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[3] P. Souchay and J. Faucherre, *Bull. Soc. chim. France*, 1951, **18**, 355.

[4] P. Souchay, 'Ions Minéraux Condensés,' Masson, 1969, p. 96.

[5] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

[6] P. Coppens, 'Crystallographic Computing,' Munksgaard, Copenhagen, 1970, p. 255.

[7] F. A. Ahmed, ref. 6, p. 55.

determined by the program MULTAN.[8] The reflections used were:

			α	E	
2	9	0	0	3·40	origin
5	6	0	$\pi/2$	3·00	
0	2	11	0	2·42	
2	0	21	$\pi/2$	2·07	enantiomorph

With these reflections and 12 phases determined by the Σ_1 procedure, the values of 93 initial phases were reliably determined by the subroutine FASTAN.

TABLE 1

Distribution of normalized structure factors computed using reflections with $\sigma(I)/I < 0{\cdot}45$

	Found	Calc. for non-centro.
$\langle\lvert E\rvert\rangle$	0·9587	0·886
$\langle\lvert E^2\rvert\rangle$	1·0706	1·000
$\langle\lvert E^2 - 1\rvert\rangle$	0·6176	0·736
% $E > 3$	0·06	0·01
% $E > 2$	1·35	1·80
% $E > 1$	42·30	36·80

The Σ_2 relationships were computed[7] by use of the program DP3 with the 500 reflections having the highest E values, and the initial set of 97 reflections was refined and extended by use of the program DP4.[7] An E map computed using the phases determined for 487 reflections revealed the positions of the five molybdenum atoms; this model gave R 0·33. A Fourier map computed with these positions revealed the position of all other non-hydrogen atoms. The positions of the nitrogen atoms were assigned on the basis of the known contact distance of 4 Å between neighbouring NH_4^+ cations; R was then 0·18.

In all structure-factor calculations, the scattering factors used were taken from ref. 9, modified according to ref. 10, and with corrections for the effects of anomalous dispersion for molybdenum and phosphorus atoms, taken from ref. 11. The initial model was then refined with isotropic temperature factors for all atoms.[12] The function minimized was: $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. After three cycles R was 0·06, and the weighted factor R' was 0·07 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}\}$. Anisotropic temperature factors were introduced for all atoms and refinement was continued. At this stage, the p value was changed to 0·03 to satisfy Cruickshank's[13] weighting criterion. After three cycles of refinement, all changes in parameters were $< 0{\cdot}1\ \sigma$ and refinement was terminated.

TABLE 2

Atomic co-ordinates and anisotropic temperature factors * ($\times 10^5$), with their standard deviations in parentheses

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	11503(2)	31371(5)	36724(1)	195(1)	380(3)	76(0)	−31(2)	21(1)	−9(1)
Mo(2)	11892(2)	63177(3)	43509(1)	168(1)	297(3)	106(1)	26(2)	17(1)	28(1)
Mo(3)	8863(2)	62259(3)	61879(1)	165(1)	312(3)	99(0)	−8(2)	13(1)	−26(1)
Mo(4)	9370(2)	29100(3)	67341(1)	174(1)	378(3)	74(0)	3(2)	5(1)	3(1)
Mo(5)	14069(2)	8853(3)	52893(1)	174(1)	252(3)	105(1)	5(2)	21(1)	0(1)
P(1)	−1583(7)	36850(14)	51368(5)	102(4)	375(10)	93(2)	−12(6)	1(2)	−9(4)
P(2)	23790(7)	39908(11)	53039(7)	113(4)	315(10)	99(2)	−3(5)	5(2)	7(4)
O(1)	4924(29)	24646(44)	29808(21)	325(20)	703(47)	104(10)	−80(26)	−15(12)	−39(18)
O(2)	16296(29)	31613(48)	74780(21)	305(20)	705(45)	115(9)	7(26)	−50(11)	−11(18)
O(3)	8009(26)	50240(41)	35980(20)	249(17)	504(35)	97(8)	5(21)	−15(10)	21(15)
O(4)	17383(22)	43151(35)	43686(19)	156(14)	312(30)	97(8)	−10(17)	7(9)	1(14)
O(5)	12883(26)	15413(34)	42940(19)	205(16)	351(32)	105(9)	−18(18)	10(10)	−37(14)
O(6)	−1757(22)	31918(39)	43495(19)	152(13)	542(35)	89(8)	−5(19)	0(9)	−3(16)
O(7)	22114(28)	31712(44)	32845(22)	260(18)	702(43)	147(11)	−35(24)	71(12)	−62(20)
O(8)	3507(28)	74900(42)	41753(23)	263(19)	498(39)	208(13)	121(23)	−1(12)	20(18)
O(9)	15214(26)	67729(37)	53288(20)	232(16)	317(29)	118(9)	−45(19)	17(10)	−11(15)
O(10)	1477(23)	51852(34)	51905(20)	153(15)	310(31)	123(9)	−4(18)	−10(9)	1(15)
O(11)	21398(28)	69489(45)	39285(21)	247(17)	633(43)	156(11)	−43(24)	52(11)	82(19)
O(12)	−7(28)	73454(42)	62169(22)	266(19)	516(41)	169(12)	119(23)	25(12)	−38(18)
O(13)	16197(28)	68472(44)	68405(21)	242(18)	690(41)	147(11)	−87(24)	−7(11)	−64(18)
O(14)	18771(23)	43304(35)	60288(19)	156(14)	351(32)	93(8)	19(18)	10(9)	−24(13)
O(15)	3520(23)	46787(37)	66830(20)	152(14)	413(33)	126(9)	29(18)	28(10)	−25(15)
O(16)	4693(23)	27453(35)	55866(19)	160(14)	344(30)	106(9)	19(18)	−5(9)	−22(14)
O(17)	15699(25)	13471(37)	63302(20)	242(16)	328(30)	110(9)	52(19)	−2(10)	8(15)
O(18)	113(28)	20536(43)	70781(22)	258(18)	598(42)	151(11)	−50(24)	67(11)	38(19)
O(19)	22367(29)	−3032(41)	51896(27)	266(21)	401(36)	247(14)	41(22)	32(14)	0(20)
O(20)	4381(28)	−695(41)	53428(23)	242(19)	484(37)	168(12)	−85(22)	52(12)	5(18)
O(21)	25563(25)	24418(35)	52685(22)	140(15)	357(30)	152(10)	20(18)	21(10)	2(16)
O(22)	−11291(25)	35804(45)	54906(21)	122(14)	915(47)	130(10)	−62(23)	28(10)	−64(18)
O(23)	32338(25)	48127(39)	52085(23)	142(15)	466(36)	191(11)	−65(20)	16(11)	2(18)
N(1)	36569(39)	5973(56)	26176(33)	244(24)	689(52)	338(21)	−74(31)	−72(19)	43(27)
N(2)	−3886(33)	830(52)	38050(28)	223(20)	611(48)	211(15)	−12(26)	28(14)	43(23)
N(3)	−15016(37)	39256(71)	33252(31)	250(22)	1442(82)	234(16)	84(38)	−2(16)	198(33)
N(4)	−14147(34)	73255(56)	49305(30)	186(20)	677(54)	268(18)	−16(29)	45(16)	19(25)
N(5)	38225(43)	48967(71)	36786(34)	383(30)	1173(78)	226(16)	109(43)	43(19)	112(32)
W(1)	15515(38)	20034(54)	16983(27)	426(27)	1451(60)	208(13)	−89(40)	0(16)	−137(25)
W(2)	20469(38)	−4284(47)	32611(26)	557(28)	659(46)	156(13)	22(31)	97(17)	37(21)
W(3)	35060(38)	38335(71)	72985(28)	432(27)	1842(94)	205(14)	−291(48)	56(16)	−223(32)

* In the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

[8] G. Germain, P. Main, and M. H. Woolfson, *Acta Cryst.*, 1970, **B26**, 274.

[9] F. M. Moore, *Acta Cryst.*, 1963, **16**, 1169.

[10] V. Vand, P. F. Eiland, and R. Pepinsky, *Acta Cryst.*, 1957, **10**, 303.

[11] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[12] C. T. Prewitt, 'SFLS Fortran IV Crystallographic least-squares program, Oak Ridge, Tennesse, Report ORNL TM 305, 1966.

[13] D. W. J. Cruickshank, 'Computing Methods in Crystallography,' Pergamon, Oxford, 1965, p. 114.

The final value of R was 0·029 and R' 0·030. The standard deviation of a unit weight observation was 1·06. The final Fourier map revealed no peaks $>0{\cdot}4$ eÅ^{-3}.

All computations were made with a Univac 1108 computer. Other programs used include ORTEP by C. K. Johnson [14] and local programs (by J. F.) for Fourier and least-squares planes.

Atomic co-ordinates and individual anisotropic thermal parameters are listed in Table 2. Observed and calculated structure factors are available in Supplementary Publication No. SUP 20941 (9 pp.).*

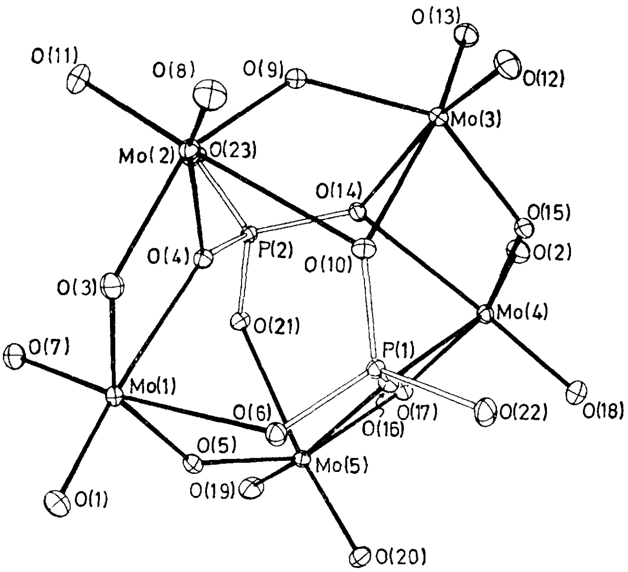

FIGURE 2 Numbering scheme in the anion

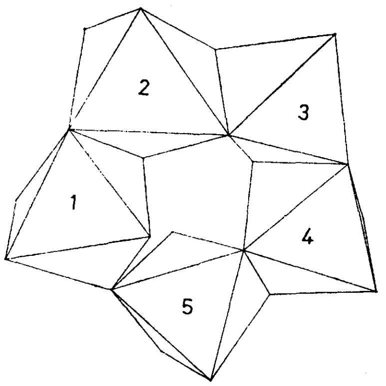

FIGURE 3 Assemblage of MoO_6 octahedra in the $(MoO_3)_5$ crown

DISCUSSION

Description of the Structure.—The crystal structure of $[NH_4]_5[(MoO_3)_5(HPO_4)(PO_4)],3H_2O$ is ionic; it is composed of an assemblage of complex $[(MoO_3)_5(HPO_4)(PO_4)]^{5-}$ anions, $[NH_4]^+$ cations, and molecules of water of crystallisation. Figure 1 is a stereoview of the anion. Figure 2 shows the numbering scheme adopted.

The molybdenum atoms are surrounded by six oxygen atoms and the five distorted MoO_6 octahedra are associated through the sharing of four edges and one

TABLE 3

Molecular dimensions in the $(MoO_3)_5$ crown, with standard deviation in parentheses

(*a*) Distances (Å)

Mo(1) · · · Mo(2)	3·331(6)	Mo(3)–O(12)	1·700(4)
Mo(2) · · · Mo(3)	3·374(5)	Mo(3)–O(13)	1·714(4)
Mo(3) · · · Mo(4)	3·375(5)	Mo(3)–O(9)	1·897(3)
Mo(4) · · · Mo(5)	3·357(5)	Mo(3)–O(15)	1·922(3)
Mo(5) · · · Mo(1)	3·688(6)	Mo(3)–O(10)	2·345(3)
Mo(1)–O(7)	1·712(4)	Mo(3)–O(14)	2·367(3)
Mo(1)–O(1)	1·717(4)	Mo(4)–O(2)	1·712(4)
Mo(1)–O(3)	1·910(4)	Mo(4)–O(18)	1·714(4)
Mo(1)–O(5)	1·931(3)	Mo(4)–O(15)	1·925(3)
Mo(1)–O(4)	2·270(3)	Mo(4)–O(17)	1·928(3)
Mo(1)–O(6)	2·307(3)	Mo(4)–O(16)	2·205(3)
Mo(2)–O(8)	1·709(4)	Mo(4)–O(14)	2·338(3)
Mo(2)–O(11)	1·709(4)	Mo(5)–O(19)	1·690(4)
Mo(2)–O(9)	1·898(3)	Mo(5)–O(20)	1·703(4)
Mo(2)–O(3)	1·946(3)	Mo(5)–O(5)	1·928(3)
Mo(2)–O(4)	2·172(3)	Mo(5)–O(17)	1·962(3)
Mo(2)–O(10)	2·427(3)	Mo(5)–O(21)	2·269(3)
		Mo(5)–O(16)	2·338(3)

(*b*) Angles (°)

Mo(1) · · · Mo(2) · · · Mo(3)	109·91(0·01)
Mo(2) · · · Mo(3) · · · Mo(4)	108·32(0·01)
Mo(3) · · · Mo(4) · · · Mo(5)	109·52(0·01)
Mo(4) · · · Mo(5) · · · Mo(1)	104·82(0·01)
Mo(5) · · · Mo(1) · · · Mo(2)	104·70(0·01)
O(1)–Mo(1)–O(3)	99·36(0·18)
O(3)–Mo(1)–O(4)	70·87(0·14)
O(4)–Mo(1)–O(5)	84·93(0·13)
O(5)–Mo(1)–O(1)	100·52(0·17)
O(6)–Mo(1)–O(1)	85·66(0·16)
O(6)–Mo(1)–O(3)	77·79(0·14)
O(6)–Mo(1)–O(4)	84·93(0·12)
O(6)–Mo(1)–O(5)	78·12(0·13)
O(7)–Mo(1)–O(1)	102·61(0·20)
O(7)–Mo(1)–O(3)	101·37(0·18)
O(7)–Mo(1)–O(4)	87·87(0·16)
O(7)–Mo(1)–O(5)	99·30(0·17)
O(3)–Mo(2)–O(4)	72·48(0·14)
O(4)–Mo(2)–O(9)	83·54(0·14)
O(9)–Mo(2)–O(8)	101·84(0·18)
O(8)–Mo(2)–O(3)	95·06(0·18)
O(10)–Mo(2)–O(3)	87·99(0·14)
O(10)–Mo(2)–O(4)	71·08(0·12)
O(10)–Mo(2)–O(9)	71·19(0·14)
O(10)–Mo(2)–O(8)	88·02(0·16)
O(11)–Mo(2)–O(3)	98·04(0·18)
O(11)–Mo(2)–O(4)	97·28(0·16)
O(11)–Mo(2)–O(9)	97·34(0·18)
O(11)–Mo(2)–O(8)	105·42(0·20)
O(9)–Mo(3)–O(10)	73·19(0·14)
O(10)–Mo(3)–O(15)	80·55(0·13)
O(15)–Mo(3)–O(13)	102·01(0·17)
O(13)–Mo(3)–O(9)	99·38(0·17)
O(12)–Mo(3)–O(9)	102·92(0·18)
O(12)–Mo(3)–O(10)	86·87(0·16)
O(12)–Mo(3)–O(15)	99·99(0·17)
O(12)–Mo(3)–O(13)	103·60(0·19)
O(14)–Mo(3)–O(9)	79·33(0·14)
O(14)–Mo(3)–O(10)	81·61(0·12)
O(14)–Mo(3)–O(15)	72·48(0·13)
O(14)–Mo(3)–O(13)	88·42(0·16)
O(14)–Mo(4)–O(15)	73·11(0·13)
O(15)–Mo(4)–O(18)	95·59(0·17)
O(18)–Mo(4)–O(17)	98·01(0·17)
O(17)–Mo(4)–O(14)	88·35(0·13)
O(16)–Mo(4)–O(14)	72·96(0·12)
O(16)–Mo(4)–O(15)	83·10(0·14)
O(16)–Mo(4)–O(18)	93·63(0·16)
O(16)–Mo(4)–O(17)	74·45(0·14)
O(2)–Mo(4)–O(14)	89·91(0·17)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, Index issue, 1973. (Items less than 10 pp. are sent as full size copies.)

[14] C. K. Johnson, ORTEP Oak Ridge National Laboratory, Tennessee, Report ORNL 3794, 1963, revised 1972.

TABLE 3 (*Continued*)

O(2)–Mo(4)–O(15)	100·16(0·18)
O(2)–Mo(4)–O(18)	104·63(0·20)
O(2)–Mo(4)–O(17)	97·30(0·18)
O(5)–Mo(5)–O(16)	84·73(0·14)
O(16)–Mo(5)–O(17)	70·81(0·13)
O(17)–Mo(5)–O(19)	99·90(0·15)
O(19)–Mo(5)–O(5)	101·00(0·17)
O(20)–Mo(5)–O(5)	99·12(0·15)
O(20)–Mo(5)–O(16)	85·17(0·13)
O(20)–Mo(5)–O(17)	99·89(0·17)
O(20)–Mo(5)–O(19)	103·68(0·18)
O(21)–Mo(5)–O(5)	80·27(0·13)
O(21)–Mo(5)–O(16)	85·79(0·14)
O(21)–Mo(5)–O(17)	76·84(0·14)
O(21)–Mo(5)–O(19)	85·26(0·13)

TABLE 4

Equation of least-squares plane through the molybdenum atoms, and deviations (Å) of these atoms from the plane

Plane: Mo(1)—(5)

$$-0{\cdot}9935x - 0{\cdot}0787y - 0{\cdot}0822z + 2{\cdot}1790 = 0$$

Mo(1) 0·2481, Mo(2) −0·1539, Mo(3) 0·0207, Mo(4) 0·1199, Mo(5) −0·1964; σ all 4

apex to form a crown of composition Mo_5O_{21}; Figure 3 shows this crown and demonstrates the assemblage of the edges of the Mo(1) and Mo(2), Mo(2) and Mo(3), Mo(3) and Mo(4), and Mo(4) and Mo(5) octahedra. The ring so formed is closed at Mo(1),Mo(5), which share an apex. Bond lengths and angles in the anion are listed in Table 3. The five molybdenum atoms are not coplanar, as shown by their distances from their least-squares plane (Table 4).

However, the distances Mo(1) ··· Mo(5) and Mo(2) ··· Mo(4) are related by a pseudo-two-fold axis passing through the middle of Mo(1) ··· Mo(5) and by Mo(3). The existence of the two-fold axis is confirmed by the symmetry of the Mo(1) ··· Mo(2) ··· Mo(3) and Mo(3) ··· Mo(4) ··· Mo(5), and Mo(4) ··· Mo(5) ··· Mo(1), and Mo(5) ··· Mo(1) ··· Mo(2) angles on the one hand and the symmetry of the Mo(1) ··· Mo(2) and Mo(4) ··· Mo(5), and Mo(2) ··· Mo(3) and Mo(3) ··· Mo(4) distances on the other. This pseudo-symmetry is preserved for all the atoms of the complex anion, within a deviation of *ca.* 0·6 Å.

The MoO_6 octahedra are all deformed, as shown by the Mo–O bond lengths and the O–Mo–O angles (Table 4). The Mo–O bonds form three pairs. One contains the short Mo–O bonds of 1·690—1·717 Å, belonging to terminal oxygen atoms, and probably double Mo=O bonds. A second pair (1·897 and 1·962 Å) consists of the oxygen atoms shared by two molybdenum and the third (2·172 and 2·427 Å) is composed of the oxygen atoms shared by two molybdenum and one phosphorus atoms. The two phosphate anions cap the faces of the crown. Distances and angles in the PO_4 tetrahedra are listed in Table 5.

The trend observed for Mo–O is parallelled in the P–O bond lengths. Thus, for the oxygen atoms shared by the phosphorus and molybdenum atoms, the longest bond lengths (1·530—1·566 Å) correspond to those oxygen atoms shared by a phosphorus and two molybdenum atoms namely O(4), O(10), O(14), and O(16). The oxygen atoms O(6) and O(21), shared by one phosphorus and one molybdenum atom, have shorter distances (1·511 and 1·530 Å). The two oxygen atoms bonded only to phosphorus, [O(22) and O(23)], have distances of 1·569 and 1·499 Å, the latter being the shortest P–O bond length in the present structure, and therefore attributed to a double P=O bond. The other is the longest, and is ascribed to an OH radical, whence the formulation of the anion as $[(MoO_3)_5(PO_4)(HPO_4)]^{5-}$.

TABLE 5

Bond lengths (Å) and angles (°) in the phosphate anions, with standard deviation in parentheses

(*a*) Distances

P(1)–O(6)	1·511(3)	P(2)–O(23)	1·449(3)
P(1)–O(10)	1·530(3)	P(2)–O(21)	1·530(3)
P(1)–O(16)	1·535(3)	P(2)–O(14)	1·547(3)
P(1)–O(22)	1·569(3)	P(2)–O(4)	1·566(3)
P(1)–Mo(1)	3·330(1)	P(2)–Mo(1)	3·573(1)
P(1)–Mo(2)	3·539(1)	P(2)–Mo(2)	3·345(1)
P(1)–Mo(3)	3·482(1)	P(2)–Mo(3)	3·483(1)
P(1)–Mo(4)	3·408(1)	P(2)–Mo(4)	3·518(1)
P(1)–Mo(5)	3·576(1)	P(2)–Mo(5)	3·341(1)

(*b*) Angles

O(6)–P(1)–O(10)	111·60(0·20)
O(6)–P(1)–O(16)	109·08(0·20)
O(6)–P(1)–O(22)	110·68(0·21)
O(10)–P(1)–O(16)	110·90(0·19)
O(10)–P(1)–O(22)	107·65(0·20)
O(16)–P(1)–O(22)	106·81(0·20)
O(23)–P(2)–O(21)	112·16(0·22)
O(23)–P(2)–O(14)	112·61(0·21)
O(23)–P(2)–O(4)	107·88(0·21)
O(21)–P(2)–O(14)	109·09(0·20)
O(21)–P(2)–O(4)	105·56(0·20)
O(14)–P(2)–O(4)	109·25(0·19)

TABLE 6

Intramolecular contact distances, with standard deviation in parentheses

N(1) ··· O(15$^{\mathrm{II}}$)	2·811(8)	N(5) ··· O(23)	2·917(7)
N(1) ··· W(2)	2·823(8)	N(5) ··· O(18$^{\mathrm{II}}$)	2·924(8)
N(1) ··· O(13$^{\mathrm{VI}}$)	2·888(7)	N(5) ··· O(2$^{\mathrm{VI}}$)	2·964(8)
		N(5) ··· O(20$^{\mathrm{II}}$)	2·973(7)
N(2) ··· O(23$^{\mathrm{VII}}$)	2·708(6)	N(5) ··· O(7)	2·990(7)
N(2) ··· W(3$^{\mathrm{VII}}$)	2·790(7)		
N(2) ··· O(8$^{\mathrm{III}}$)	2·828(6)	W(1) ··· O(1)	2·842(6)
N(2) ··· O(5)	2·980(6)	W(1) ··· O(13$^{\mathrm{IV}}$)	2·923(7)
		W(1) ··· N(4$^{\mathrm{IV}}$)	2·988(8)
N(3) ··· O(6)	2·790(6)	W(1) ··· N(3$^{\mathrm{IV}}$)	2·995(8)
N(3) ··· W(3$^{\mathrm{VII}}$)	2·914(8)		
N(3) ··· O(7$^{\mathrm{VII}}$)	2·915(8)	W(2) ··· N(1)	2·823(7)
N(3) ··· W(1$^{\mathrm{V}}$)	2·995(7)	W(2) ··· O(11$^{\mathrm{III}}$)	2·828(7)
		W(2) ··· O(5)	2·907(6)
N(4) ··· O(19$^{\mathrm{VII}}$)	2·801(8)		
N(4) ··· O(23$^{\mathrm{VIII}}$)	2·842(8)	W(3) ··· N(2$^{\mathrm{II}}$)	2·760(6)
N(4) ··· O(8)	2·941(6)	W(3) ··· O(3$^{\mathrm{V}}$)	2·805(7)
N(4) ··· W(1$^{\mathrm{I}}$)	2·988(8)	W(3) ··· O(2)	2·854(7)
		W(3) ··· N(3$^{\mathrm{II}}$)	2·914(8)

Roman numeral superscripts refer to the following transformations of the co-ordinates:

I $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$
II $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$
III $x, -1 + y, z$
IV $\bar{x}, -\frac{1}{2} + y, \frac{1}{2} - z$
V $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$
VI $\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$
VII $-\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
VIII $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$

The anions are directly held together by only one contact <2·73 Å: O(21) ··· O(22) 2·575 Å. This contact is attributed to the presence of a strong hydrogen bond between the hydrogen phosphate and an oxygen atom of the $(MoO_3)_5$ ring. Table **6** lists contacts <3 Å between ammonium cations and water molecules. The analysis of these contacts shows that the structure is in fact a network of $[(MoO_3)_5(PO_4)(HPO_4)]^{5-}$ anions joined by hydrogen bonds.

The structure of the Mo_5O_{21} assemblage can be compared to that of the six molybdenum rings found[2] in $K_6[(WO_3)_{18}(PO_4)_2]$,$14H_2O$, in $[NH_4]_6[(MoO_3)_6TeO_6]$,$7H_2O$,[15] and in $NH_4[(WO_3)_6H_6O_6]$,$16H_2O$.[16] These structures have confirmed the model first suggested by Anderson[17] formed by a crown of six MO_6 octahedra. The cavity thus formed contains an octahedral deficiency, with three oxygen atoms located on each face of the cycle. It is thus possible to put a heteroatom within the cavity. In the present case, however, the volume of the cavity is no longer sufficient to contain a heteroatom. Because of the decrease of the diameter of the ring relative to that with six octahedra, the three oxygen atoms can no longer be bonded to an atom located within the cavity. Thus the two phosphate anions cap the two faces of the $(MoO_3)_5$ ring, and the novel structure therefore results.

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