

determined disordered form of $[\text{DyCl}_3(\text{EO3})]_{18}$ -crown-6 (also determined at 123 K) the Dy—Cl(1) equatorial distance is shorter at 2.605 (2) Å than the Dy—Cl(2) axial separation of 2.626 (2) Å. Indeed, that is true of all of the previously structurally characterized complexes containing the $[\text{MCl}_3(\text{EO3})]$ unit, though some variation in the magnitude of the difference is observed for various hydrogen-bonding environments. In the title complex this situation is reversed. The axial distance [Dy—Cl(2) = 2.607 (2) Å] is shorter than the equatorial Dy—Cl(1) separation of 2.621 (2) Å. Since there are no hydrogen bonds to the Cl atoms it is probable that packing effects are responsible for these differences. An analysis of non-bonding contacts around each Cl position in both complexes does in fact reveal interesting differences. The non-bonding contacts between Cl(1) and Cl(2) and the other atoms in the metal coordination sphere are similar for both complexes; however, non-bonded contacts between these atoms and other symmetry-related formula units are different. In the disordered complex the closest non-bonded contacts of the latter type for equatorial Cl(1) are six Cl...C [crown ether C(8), C(9)] separations ranging from 3.616 (7) to 3.760 (7) Å. The closest equatorial Cl contacts of this type in the title complex are much longer and there are only four under 4 Å: two Cl(1)...C(9) (crown) contacts at 3.987 (5) Å and two Cl(1)...C(3) (glycol) contacts of 3.954 (6) Å. The equatorial Cl in the disordered complex, Cl(2), has only three such contacts under 4 Å, two to glycol carbon atoms: Cl(2)...C(2) = 3.86 (1), Cl(2)...C(3)' = 3.88 (2) Å and one to the crown ether: Cl(2)...C(5) = 3.957 (7) Å. The Cl(2) contacts in this category in the title complex under 4 Å range from 3.538 (6) to 3.977 (6) Å. There are five such contacts, all to atoms in the crown ether. For both complexes, the shortest Dy—Cl separation occurs for the Cl having five or six Cl...crown ether contacts under 4 Å regardless of its position in an axial or equatorial coordination site. The

longest observed Dy—Cl separation occurs when there are only a few (four or less) contacts under 4 Å and when these are quite long (>3.8 Å).

The Dy—O separations are slightly different in the two determinations of $[\text{DyCl}_3(\text{EO3})]_{18}$ -crown-6. The Dy—O alcoholic distance is just over 3σ shorter in the title complex [2.316 (4) versus 2.331 (4) Å] and the Dy—O etheric separation is just over 3σ longer than observed previously [2.455 (4) versus 2.442 (5) Å]. The glycol ligand itself in the title complex is normal with O—C—C—O torsion angles alternating $\pm g$ [C(1)—C(2) = -50.0 ; C(3)—C(3') = 59.1°] and the C—C—O—C angles *anti* [C(2)—O(2) = -175.7 ; C(3)—O(2) = 176.7°]. The average bonding parameters are C—O = 1.440 (9), C—C = 1.51 (2) Å, C—O—C = 112.6 (4) and C—C—O = 106.2 (4) $^\circ$.

The 18-crown-6 molecule displays its full D_{3d} symmetry and accepts one hydrogen bond on each side of the macrocycle. The average bonding parameters are C—O = 1.421 (9), C—C = 1.506 (8) Å, C—O—C = 111 (1) and C—C—O = 108.7 (6) $^\circ$.

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References

- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72, 99, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 ROGERS, R. D. & ETZENHOUSER, R. D. (1988). *Acta Cryst.* **C44**, 1400–1402.
 ROGERS, R. D., VOSS, E. J. & ETZENHOUSER, R. D. (1988). *Inorg. Chem.* **27**, 533–542.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1988). **C44**, 1535–1538

The Structure of Tetraguanidinium Pentamolybdodiphenylphosphonate*

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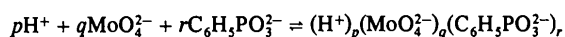
Abstract. $[\text{C}(\text{NH}_2)_3]_4[(\text{C}_6\text{H}_5\text{P})_2\text{Mo}_5\text{O}_{21}]$, $M_r = 1272.2$, tetragonal, $P4_1$, $a = 15.682$ (2), $c = 31.267$ (5) Å, V

$= 7690$ (2) Å³, $Z = 8$, $D_x = 2.20$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.735$ mm⁻¹, $F(000) = 4976$, $T = 298$ K, $R = 0.035$, based on 9345 unique observed reflexions. The structure contains $(\text{C}_6\text{H}_5\text{P})_2\text{Mo}_5\text{O}_{21}^{4-}$

* Multicomponent Polyanions. 42.

anions joined in a three-dimensional framework by hydrogen and ionic bonds from the $C(NH_2)_3^+$ cations. The anion consists of a central polymolybdate core to which two phenylphosphonate ligands are attached from the outside. In the core, five MoO_6 octahedra are coupled together forming a ring. The octahedra share edges but in one contact there is corner sharing. Mean Mo—Mo distances are 3.389 (7) Å when edge-sharing and 3.696 (3) Å when a corner is shared. The Mo—O distances are distributed in three different groups, depending on coordination, with mean values of 1.71 (1), 1.93 (2) and 2.31 (8) Å. In the tetrahedral coordination around phosphorus, the P—O distances are 1.51–1.55 Å and the P—C distances 1.78–1.80 Å. The guanidinium ions are approximately planar with a mean C—N distance of 1.33 (1) Å.

Introduction. The present crystal structure determination forms part of a research project in our department aimed at elucidating the equilibrium conditions in some aqueous three-component systems. The studies have been focused on systems containing Mo^{VI} and/or V^V where so-called heteropolyanions are formed. The equilibrium of one of the systems studied, the molybdophenylphosphonate system, may be written as



where the integers p , q and r define the complexes formed. In the equilibrium analyses, including potentiometric and ^{31}P NMR studies, complexes with $q:r$ ratios 5:2, 6:1 and 7:1 have been established (Yagasaki, Andersson & Pettersson, 1987).

To obtain structural information on the complexes formed, X-ray diffraction investigations of crystalline phases are carried out. This paper presents the result of the structure determination of a 5:2 complex, which has the composition (10,5,2). A report on the preparation of such a complex and its characterization by chemical analysis and spectroscopic measurements was given by Kwak, Pope & Scully (1975).

Experimental. In the crystal preparation 9.68 g $Na_2MoO_4 \cdot 2H_2O$ (0.04 mol) and 1.58 g $C_6H_5PO(OH)_2$ (0.01 mol) were dissolved in 100 ml of water and the solution adjusted to pH = 3.3 with 4.1 ml 12 M HCl. Then 0.38 g $C(NH_2)_3Cl$ (0.004 mol) was added to 10 ml of the solution, which was set to evaporate at room temperature. Within two or three weeks, colourless octahedral crystals, stable in air, were formed. The crystal used in this investigation was of approximate size $0.25 \times 0.20 \times 0.18$ mm. The content of C, H and N was determined by elemental analyses (Department of Chemistry, The University of Tokyo). Found (calc.) weight %: C 14.8 (15.1), H 2.9 (2.7), N 13.0 (13.2).

Syntex R3 four-circle diffractometer, graphite-monochromatized $MoK\alpha$; cell parameters by least-squares

refinement from 25 automatically centered reflexions ($25 < 2\theta < 28^\circ$); θ - 2θ scan, $3 \leq 2\theta \leq 60^\circ$, $0 \leq h \leq 22$, $0 \leq k \leq 22$, $0 \leq l \leq 44$; 12 271 reflexions measured, 11 481 unique, 9345 observed [$I \geq 3\sigma(I)$]; 2θ scan rate $2-6^\circ \text{ min}^{-1}$, 2θ scan width 1.3° plus the α_1 - α_2 dispersion, background measured on each side of the peak for a total time equal to the scan time; four standard reflexions (004, 228, 3,2,11, 3,3,21) measured every 50 reflexions, maximum variation $\pm 4.5\%$; empirical absorption correction, 16 reflexions evenly distributed in 2θ , each reflexion being rotated around its diffraction vector in steps of 10° , relative transmission factor 0.862–1.000; Lorentz and polarization corrections; Patterson synthesis and standard heavy-atom methods; anisotropic full-matrix least-squares refinements minimizing $w(|F_o| - |F_c|)^2$. Final $R = 0.035$, $wR = 0.037$, $S = 1.309$ for 1008 refined parameters, $1/w = \sigma^2(F_o) + (0.0154F_o)^2$ with $\sigma(F_o)$ from counting statistics. Owing to the large number of parameters the refinements had to be divided into three overlapping blocks and the standard deviations may therefore be somewhat underestimated.

No extinction correction was necessary. $(\Delta/\sigma)_{\max} = 0.01$ [β_{33} for N3(7)]. $(\Delta\rho)_{\max} = 0.64$, $(\Delta\rho)_{\min} = -0.60 \text{ e \AA}^{-3}$. Scattering factors used were for Mo^{3+} , P, O⁻, N and C; account was taken of the anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). Attempts to locate the H atoms were not made.

The computer programs used were supplied with the Syntex R3 crystallographic systems or described by Antti (1976). Computations were performed with the Data General Nova 3 computer at our department and the CDC Cyber 180/850 computer at the University Computer Centre.

Discussion. The structure consists of $(C_6H_5P)_2Mo_5O_{21}^{4-}$ anions joined in a three-dimensional framework by numerous hydrogen bonds to the $C(NH_2)_3^+$ cations. The phenyl groups give the anions a volume-consuming structure and as a result of this, the crystal growth is dominated by steric problems. These are solved by forming a three-dimensional network structure which does not require stabilizing water molecules. Final positional parameters, together with B_{eq} values, of the nonhydrogen atoms are given in Table 1.*

The $(C_6H_5P)_2Mo_5O_{21}^{4-}$ anion (Fig. 1) consists of a central polymolybdate ring to which two phenylphosphonate ligands are attached from the outside. The structure is analogous to that of the well known

* Lists of structure factors, anisotropic thermal parameters, P—Mo distances and O—Mo—O angles, and distances and angles in the cations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51009 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and B_{eq} values (Hamilton, 1959) with e.s.d.'s in parentheses

For the O atoms O(*i*), O(*ij*) and OP(*ij*), the index means that the atom is bonded to Mo atoms *i* (and *j*) and P indicates that it is also bonded to the P atom. For the N atoms N(*i*) the index means that the atom is bonded to C atoms *i*.

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
Mo1	0.22249 (4)	0.40273 (4)	0.60893 (3)	2.33 (1)
Mo2	0.21305 (4)	0.32928 (4)	0.71085 (3)	2.20 (1)
Mo3	0.30648 (4)	0.13484 (4)	0.71447 (3)	2.02 (1)
Mo4	0.31899 (4)	0.06730 (4)	0.60145 (2)	1.92 (1)
Mo5	0.29609 (4)	0.24776 (4)	0.54322*	2.22 (1)
Mo6	0.28804 (4)	0.37874 (4)	0.10591 (3)	2.04 (1)
Mo7	0.29744 (4)	0.31765 (4)	0.20956 (3)	2.11 (1)
Mo8	0.20381 (4)	0.12311 (4)	0.21893 (3)	2.18 (1)
Mo9	0.19564 (4)	0.04200 (4)	0.10797 (3)	2.28 (1)
Mo10	0.21869 (4)	0.21468 (4)	0.04394 (3)	2.28 (1)
P1	0.15975 (11)	0.19677 (11)	0.62887 (6)	1.90 (4)
P2	0.38491 (11)	0.26897 (11)	0.64349 (6)	1.85 (4)
P3	0.12721 (11)	0.24785 (11)	0.14287 (6)	1.79 (4)
P4	0.35349 (11)	0.17588 (11)	0.13183 (6)	1.94 (4)
O(12)	0.1601 (3)	0.3789 (3)	0.6600 (2)	2.63 (13)
O(15)	0.3029 (3)	0.3609 (3)	0.5671 (2)	2.54 (12)
O(23)	0.2866 (3)	0.2478 (3)	0.7376 (2)	2.47 (12)
O(34)	0.3177 (3)	0.0698 (3)	0.6624 (1)	2.03 (11)
O(45)	0.2860 (3)	0.1260 (3)	0.5498 (2)	2.28 (12)
O(67)	0.3497 (3)	0.3619 (3)	0.1578 (2)	2.26 (12)
O(610)	0.2112 (3)	0.3322 (3)	0.0641 (2)	2.35 (12)
O(78)	0.2227 (3)	0.2403 (3)	0.2379 (2)	2.39 (12)
O(89)	0.1967 (3)	0.0518 (3)	0.1696 (2)	2.24 (12)
O(910)	0.2287 (3)	0.0947 (3)	0.0533 (2)	2.63 (13)
OP(12)	0.3198 (3)	0.3372 (3)	0.6556 (2)	2.17 (11)
OP(15)	0.1895 (3)	0.2624 (3)	0.5955 (2)	1.95 (11)
OP(23)	0.2011 (3)	0.2120 (3)	0.6727 (2)	2.02 (11)
OP(3)	0.4045 (3)	0.2114 (3)	0.6812 (2)	2.06 (11)
OP(4)	0.1813 (3)	0.1071 (3)	0.6146 (2)	2.21 (11)
OP(45)	0.3548 (3)	0.2138 (3)	0.6058 (2)	1.90 (10)
OP(67)	0.1919 (3)	0.3179 (3)	0.1534 (2)	2.12 (11)
OP(610)	0.3231 (3)	0.2381 (3)	0.0967 (2)	2.23 (12)
OP(78)	0.3136 (3)	0.1962 (3)	0.1755 (2)	2.33 (12)
OP(8)	0.1075 (3)	0.1938 (3)	0.1819 (2)	2.11 (11)
OP(9)	0.3317 (3)	0.0847 (3)	0.1203 (2)	2.37 (12)
OP(910)	0.1595 (3)	0.1881 (3)	0.1070 (2)	2.06 (11)
O1(1)	0.2741 (4)	0.4962 (3)	0.6210 (2)	3.25 (15)
O2(1)	0.1414 (4)	0.4349 (4)	0.5770 (2)	4.10 (17)
O1(2)	0.2564 (4)	0.4191 (3)	0.7325 (2)	3.20 (14)
O2(2)	0.1221 (3)	0.3134 (4)	0.7390 (2)	3.29 (15)
O1(3)	0.3871 (3)	0.0982 (4)	0.7459 (2)	2.96 (14)
O2(3)	0.2187 (3)	0.0835 (4)	0.7355 (2)	3.07 (14)
O1(4)	0.4260 (3)	0.0521 (3)	0.5918 (2)	2.79 (13)
O2(4)	0.2760 (3)	0.0296 (3)	0.5911 (2)	2.80 (13)
O1(5)	0.3891 (4)	0.2500 (4)	0.5152 (2)	3.53 (16)
O2(5)	0.2190 (4)	0.2609 (4)	0.5051 (2)	3.73 (16)
O1(6)	0.3702 (4)	0.4098 (4)	0.0735 (2)	3.20 (15)
O2(6)	0.2319 (3)	0.4717 (3)	0.1145 (2)	2.55 (12)
O1(7)	0.3891 (3)	0.3065 (4)	0.2385 (2)	3.14 (14)
O2(7)	0.2520 (3)	0.4088 (4)	0.2284 (2)	3.23 (15)
O1(8)	0.2905 (3)	0.0778 (4)	0.2433 (2)	3.07 (14)
O2(8)	0.1218 (4)	0.0908 (4)	0.2505 (2)	3.31 (15)
O1(9)	0.2388 (3)	0.0555 (3)	0.0997 (2)	3.14 (14)
O2(9)	0.0892 (3)	0.0260 (3)	0.0996 (2)	3.25 (14)
O1(10)	0.2963 (4)	0.2252 (4)	0.0060 (2)	3.89 (17)
O2(10)	0.1250 (4)	0.2175 (4)	0.0158 (2)	3.62 (16)
C9	0.0457 (4)	0.2050 (4)	0.6331 (2)	2.16 (16)
C10	0.0047 (6)	0.1727 (6)	0.6696 (3)	3.96 (24)
C11	0.0826 (7)	0.1748 (8)	0.6717 (4)	5.45 (34)
C12	0.1299 (5)	0.2063 (6)	0.6385 (4)	3.87 (24)
C13	0.0913 (5)	0.2362 (6)	0.6022 (4)	4.22 (26)
C14	0.0004 (5)	0.2372 (6)	0.6004 (3)	3.64 (22)
C15	0.4843 (4)	0.3163 (4)	0.6290 (2)	2.16 (15)
C16	0.5327 (6)	0.2801 (6)	0.5969 (3)	4.08 (25)
C17	0.6171 (6)	0.3068 (8)	0.5901 (3)	5.40 (33)
C18	0.6512 (6)	0.3701 (7)	0.6141 (4)	5.19 (31)
C19	0.6031 (6)	0.4076 (7)	0.6468 (4)	4.91 (29)
C20	0.5185 (6)	0.3797 (5)	0.6545 (3)	3.57 (22)
C21	0.0275 (4)	0.2925 (4)	0.1271 (2)	1.91 (15)
C22	0.0063 (5)	0.3603 (5)	0.1501 (3)	3.10 (20)
C23	0.0887 (5)	0.3871 (5)	0.1438 (3)	3.83 (23)
C24	0.1397 (5)	0.3466 (6)	0.1131 (3)	3.71 (23)
C25	0.1070 (5)	0.2787 (6)	0.0891 (3)	3.36 (21)
C26	0.0221 (5)	0.2514 (5)	0.0960 (3)	2.53 (17)
C27	0.4667 (4)	0.1839 (5)	0.1345 (2)	2.36 (16)
C28	0.5106 (5)	0.2150 (6)	0.0993 (3)	4.24 (26)

* Arbitrarily fixed.

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
C29	0.6020 (6)	0.2171 (7)	0.1013 (4)	5.27 (32)
C30	0.6430 (5)	0.1873 (6)	0.1355 (4)	4.27 (26)
C31	0.6001 (6)	0.1551 (7)	0.1702 (4)	4.88 (29)
C32	0.5104 (5)	0.1528 (6)	0.1690 (3)	3.83 (24)
C1	0.0761 (5)	0.4064 (5)	0.6879 (3)	3.00 (20)
C2	0.0690 (5)	0.4939 (5)	0.5322 (3)	3.01 (20)
C3	0.6019 (5)	0.0436 (5)	0.5256 (2)	2.93 (19)
C4	0.6125 (5)	0.1123 (5)	0.6845 (3)	2.60 (18)
C5	0.5976 (5)	0.3773 (5)	0.1958 (3)	3.21 (20)
C6	0.5832 (5)	0.4551 (6)	0.0367 (3)	3.58 (22)
C7	0.0740 (6)	0.0182 (5)	0.0275 (2)	3.25 (21)
C8	0.1094 (5)	0.0871 (5)	0.1719 (3)	2.78 (18)
N1(1)	0.0222 (5)	0.4259 (5)	0.6572 (3)	4.07 (21)
N2(1)	0.0497 (5)	0.3655 (5)	0.7227 (3)	3.77 (20)
N3(1)	0.1582 (4)	0.4310 (5)	0.6847 (2)	3.78 (20)
N1(2)	0.0061 (5)	0.4522 (5)	0.5139 (3)	4.24 (22)
N2(2)	0.1444 (5)	0.4531 (5)	0.5369 (3)	4.41 (22)
N3(2)	0.0583 (5)	0.5712 (5)	0.5483 (3)	4.82 (24)
N1(3)	0.6802 (4)	0.0528 (5)	0.5104 (2)	3.61 (19)
N2(3)	0.5764 (5)	0.0292 (5)	0.5450 (3)	4.21 (21)
N3(3)	0.5451 (5)	0.1051 (5)	0.5216 (3)	4.61 (23)
N1(4)	0.5721 (5)	0.0667 (5)	0.6550 (3)	4.04 (21)
N2(4)	0.6928 (4)	0.0930 (4)	0.6941 (3)	3.59 (19)
N3(4)	0.5746 (4)	0.1746 (4)	0.7053 (2)	3.31 (18)
N1(5)	0.5408 (5)	0.4051 (5)	0.1667 (3)	4.58 (23)
N2(5)	0.5710 (5)	0.3307 (5)	0.2282 (2)	4.13 (21)
N3(5)	0.6796 (5)	0.3943 (5)	0.1924 (3)	4.27 (22)
N1(6)	0.6636 (5)	0.4465 (6)	0.0248 (3)	5.47 (27)
N2(6)	0.5240 (5)	0.3979 (5)	0.0248 (3)	4.87 (24)
N3(6)	0.5571 (5)	0.5227 (6)	0.0595 (4)	6.09 (30)
N1(7)	0.0029 (5)	0.0497 (5)	0.0089 (3)	4.21 (21)
N2(7)	0.0740 (5)	0.0620 (5)	0.0414 (3)	4.86 (24)
N3(7)	0.1418 (5)	0.0676 (5)	0.0307 (3)	4.66 (23)
N1(8)	0.0714 (5)	0.0413 (5)	0.1414 (2)	4.13 (21)
N2(8)	0.1905 (4)	0.0734 (5)	0.1808 (2)	3.24 (18)
N3(8)	0.0674 (4)	0.1489 (5)	0.1932 (2)	3.58 (19)

Mo₅P₂O₂₃ group (Pope, 1983) but with the two unshared phosphate oxygen atoms substituted by phenyl groups. The five MoO₆ octahedra are coupled by edge sharing but in one contact only a corner is shared. In each octahedron two O atoms are unshared.

Selected distances within the anion are given in Table 2. Two groups of Mo—Mo distances can be distinguished. When the MoO₆ octahedra share edges the Mo—Mo distances vary between 3.383 (1) and 3.400 (1) Å, while when corner sharing they increase to 3.694 (1) and 3.698 (1) Å, respectively. A comparison between the different anions, Mo₅P₂O₂₃⁶⁻, HMo₅P₂O₂₃⁵⁻, H₂Mo₅P₂O₂₃⁴⁻ and (C₆H₅P)₂Mo₅O₂₁⁴⁻, shows that the Mo—Mo distances in the two last mentioned are almost equivalent. It can also be seen that the first attached H atom causes an increase in Mo—Mo distances when corner sharing while the second H atom also gives rise to increasing distances when edge sharing (Hedman, 1973; Strandberg, 1973; Fischer, Ricard & Toledano, 1974; Hedman, 1977; Hedman & Strandberg, 1979). Cross distances, Mo—Mo, within the anion vary between 5.476 and 5.662 Å. The MoO₆ octahedra are far from regular, which can be seen from Table 2. As expected the Mo—O distances increase with the number of atoms coordinating the O atom. Each octahedron comprises two unshared O atoms, two O atoms shared between two Mo and two O atoms shared between P as well as one or two Mo. Consequently, there are three groups of Mo—O distances and the distances within each group are: 1.69–1.72, 1.91–1.97, 2.20–2.48 Å.

The coordination round P is tetrahedral with bond distances P—O 1.51–1.55 and P—C 1.78–1.80 Å. In the C_6H_5 group the C_6 ring is almost planar with C—C distances 1.33–1.44 Å.

The C and N atoms in each guanidinium ion, $C(NH_2)_3^+$, are almost planar with C triangularly coordinated by N. The mean C—N distance is 1.33 Å while the mean value for the angle N—C—N is 120.0° . These are in accordance with earlier results (Haas, Harris & Mills, 1965). The connecting links between $(C_6H_5P)_2Mo_5O_{21}^{4-}$ anions are hydrogen bonds effected by the guanidinium ions. Although the H atoms were not located, a proposal for the hydrogen-bond system can be given by taking N—O distances and O—N—O angles into consideration. The system is complicated and each guanidinium has at least one N atom that connects the anions by bridges $O \cdots H-N-H \cdots O$. The N—O distances in these connections fall into the range 2.73–3.20 Å. Besides these pure $O \cdots H-N-H \cdots O$ bonds there are of course also numerous connections of the type $O \cdots H-N-C-N-H \cdots O$. As could be expected it is mainly the unshared oxygen atoms that act as hydrogen-bond acceptors in the bridges. Moreover, many hydrogen bonds may be bifurcated.

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Table 2. Selected distances (Å) within the $(C_6H_5P)_2Mo_5O_{21}^{4-}$ anions

Mo1—Mo2	3.392 (1)	Mo6—Mo7	3.383 (1)
Mo1—Mo5	3.385 (1)	Mo6—Mo10	3.400 (1)
Mo2—Mo3	3.385 (1)	Mo7—Mo8	3.398 (1)
Mo3—Mo4	3.694 (1)	Mo8—Mo9	3.698 (1)
Mo4—Mo5	3.384 (1)	Mo9—Mo10	3.387 (1)
Mo1—O1(1)	1.716 (5)	Mo6—O1(6)	1.710 (6)
Mo1—O2(1)	1.693 (6)	Mo6—O2(6)	1.723 (5)
Mo1—O(12)	1.909 (5)	Mo6—O(67)	1.908 (5)
Mo1—O(15)	1.931 (5)	Mo6—O(610)	1.921 (5)
Mo1—OP(12)	2.347 (5)	Mo6—OP(67)	2.321 (5)
Mo1—OP(15)	2.300 (5)	Mo6—OP(610)	2.292 (5)
Mo2—O1(2)	1.704 (6)	Mo7—O1(7)	1.709 (5)
Mo2—O2(2)	1.694 (6)	Mo7—O2(7)	1.702 (6)
Mo2—O(12)	1.956 (5)	Mo7—O(67)	1.942 (5)
Mo2—O(23)	1.914 (5)	Mo7—O(78)	1.905 (2)
Mo2—OP(12)	2.409 (5)	Mo7—OP(67)	2.414 (5)
Mo2—OP(23)	2.201 (5)	Mo7—OP(78)	2.197 (5)
Mo3—O1(3)	1.702 (5)	Mo8—O1(8)	1.713 (6)
Mo3—O2(3)	1.724 (6)	Mo8—O2(8)	1.699 (6)
Mo3—O(23)	1.939 (5)	Mo8—O(78)	1.953 (5)
Mo3—O(34)	1.929 (5)	Mo8—O(89)	1.908 (5)
Mo3—OP(23)	2.429 (5)	Mo8—OP(78)	2.475 (5)
Mo3—OP(3)	2.210 (5)	Mo8—OP(8)	2.203 (5)
Mo4—O1(4)	1.721 (5)	Mo9—O1(9)	1.692 (5)
Mo4—O2(4)	1.694 (5)	Mo9—O2(9)	1.707 (5)
Mo4—O(34)	1.907 (5)	Mo9—O(89)	1.934 (5)
Mo4—O(45)	1.931 (5)	Mo9—O(910)	1.967 (5)
Mo4—OP(4)	2.286 (5)	Mo9—OP(9)	2.269 (5)
Mo4—OP(45)	2.368 (4)	Mo9—OP(910)	2.360 (4)
Mo5—O1(5)	1.702 (6)	Mo10—O1(10)	1.707 (6)
Mo5—O2(5)	1.711 (6)	Mo10—O2(10)	1.713 (6)
Mo5—O(15)	1.928 (5)	Mo10—O(610)	1.952 (5)
Mo5—O(45)	1.928 (5)	Mo10—O(910)	1.911 (5)
Mo5—OP(15)	2.350 (5)	Mo10—OP(610)	2.353 (5)
Mo5—OP(45)	2.226 (5)	Mo10—OP(910)	2.217 (5)

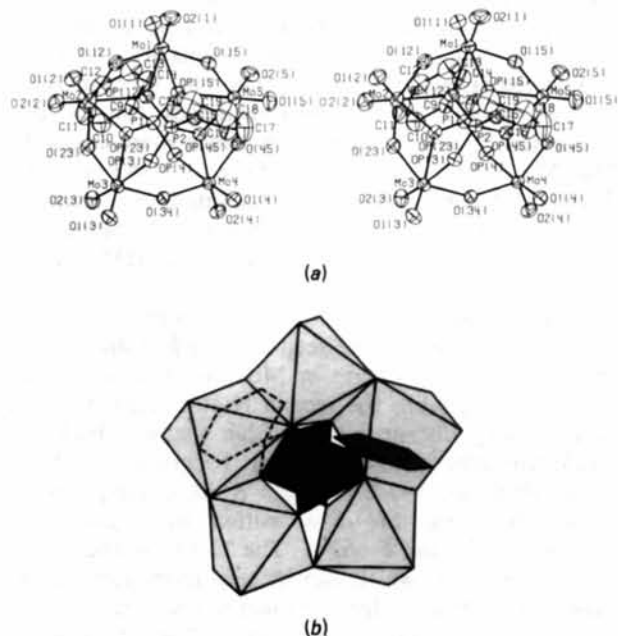


Fig. 1. (a) A stereoscopic view of the $(C_6H_5P)_2Mo_5O_{21}^{4-}$ anion. The thermal ellipsoids are scaled to include 50% probability (ORTEP II, Johnson, 1976). (b) The same anion drawn as linked polyhedra and with the phenyl groups as hexagons.

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References

- ANTTI, B.-M. (1976). *Acta Chem. Scand. Ser. A*, **30**, 24–30.
- FISCHER, J., RICARD, L. & TOLEDANO, P. (1974). *J. Chem. Soc. Dalton Trans.* pp. 941–946.
- HAAS, D. J., HARRIS, D. R. & MILLS, H. H. (1965). *Acta Cryst.* **19**, 676–679.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HEDMAN, B. (1973). *Acta Chem. Scand.* **27**, 3335–3354.
- HEDMAN, B. (1977). *Acta Cryst.* **B33**, 3083–3090.
- HEDMAN, B. & STRANDBERG, R. (1979). *Acta Cryst.* **B35**, 278–284.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–98, 149–150. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JOHNSON, C. K. (1976). ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KWAK, W., POPE, M. T. & SCULLY, T. F. (1975). *J. Am. Chem. Soc.* **97**, 5735–5738.
- POPE, M. T. (1983). *Heteropoly and Isopoly Oxometalates*, pp. 28–29. Berlin: Springer.
- STRANDBERG, R. (1973). *Acta Chem. Scand.* **27**, 1004–1018.
- YAGASAKI, A., ANDERSSON, I. & PETERSSON, L. (1987). *Inorg. Chem.* **26**, 3926–3933.