Table 2. *Selected geometric parameters (Å, °)*

Cu—O12$^{\rm i}$	1.961 (6)	O12—C10	1.251 (10)
Cu—O21	1.962 (6)	O21—C20	1.268 (10)
Cu—O22$^{\rm i}$	1.966 (6)	O22—C20	1.263 (11)
Cu—O11	1.966 (6)	O1—C1	1.226 (12)
Cu—O1	2.156 (6)	C1—N2	1.301 (14)
Cu—Cu$^{\rm i}$	2.633 (2)	C1—N1	1.33 (2)
O11—C10	1.267 (10)		
O12$^{\rm i}$—Cu—O21	87.8 (3)	O11—Cu—O1	100.1 (2)
O12$^{\rm i}$—Cu—O22$^{\rm i}$	90.8 (3)	O12$^{\rm i}$—Cu—Cu$^{\rm i}$	81.4 (2)
O21—Cu—O22$^{\rm i}$	169.1 (3)	O21—Cu—Cu$^{\rm i}$	86.9 (2)
O12$^{\rm i}$—Cu—O11	167.9 (3)	O22$^{\rm i}$—Cu—Cu$^{\rm i}$	82.2 (2)
O21—Cu—O11	89.0 (3)	O11—Cu—Cu$^{\rm i}$	86.8 (2)
O22$^{\rm i}$—Cu—O11	90.1 (3)	O1—Cu—Cu$^{\rm i}$	172.6 (2)
O12$^{\rm i}$—Cu—O1	91.8 (2)	O12—C10—O11	124.9 (8)
O21—Cu—O1	95.6 (3)	O22—C20—O21	126.5 (8)
O22$^{\rm i}$—Cu—O1	95.2 (3)	C1—O1—Cu	121.7 (6)
Cu—O11—O12—Cu$^{\rm i}$	−3.0 (3)	Cu—O21—O22—Cu$^{\rm i}$	0.3 (3)

Symmetry code: (i) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$.

The space group $R\bar{3}$ was deduced from the systematic absences and on the basis of the previous study of the isostructural $Cu_2(benz)_4.4(CH_3OH)$ (Bkouche-Waksman, Bois, Popovitch & L'Haridon, 1980). Its choice was confirmed by the successful refinement. All H atoms were found in the difference electron density map, apart from those of the urea ligand, and were included in the refinement at calculated positions with isotropic displacement parameters $1.5U_{\rm eq}$ of the attached heavy atoms. The final difference synthesis contained a peak of $+1.25\,{\rm e\,Å^{-3}}$, but we could not interpret it as an additional methanol or water molecule. Additionally, the large thermal displacement parameters of the urea moiety suggest disorder or decomposition of the compound. The rather high value of the final R factor is ascribed to the inferior quality of the crystals. Two sets of diffraction data from two different crystals were collected in Leipzig and in Ljubljana. Results based on the better set are reported here. The sealed crystals exhibited slight decomposition during the data collection. Calculations were performed on a PC 486/16MB.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4-*PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971) and *PLUTON* (Spek, 1991). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1294). Services for accessing these data are described at the back of the journal.

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Bis(piperazinium) Pentakis(trioxomolybdo)bis(phenylphosphonate) Dihydrate

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Abstract

The title compound, bis(piperazine-1,4-diylium) bis(phenylphosphonato)-1κO,2:3κ^2O',4:5κ^2O'';1:2κ^2O,3:4κ^2O',5$\kappa O''$-penta-μ-oxo-1:2κ^2O;1:5κ^2O;2:3κ^2O;3:4κ^2O;4:5κ^2O-decaoxo-1κ^2O,2κ^2O,3κ^2O,4κ^2O,5κ^2O-pentamolybdenum(4−) dihydrate, $(C_4H_{12}N_2)_2[Mo_5O_{15}(C_6H_5O_3P)_2].2H_2O$, contains isolated five-unit rings of vertex- and edge-sharing distorted octahedral MoO_6 units, doubly capped by PC_6H_5 entities (as $[PO_3C_6H_5]^{2-}$ phenylphosphonate groups), to result in $[(MoO_3)_5\{(C_6H_5)PO_3\}_2]^{4-}$ {or $[Mo_5P_2O_{21}(C_6H_5)_2]^{4-}$} anions. Doubly protonated piperazinium cations and water molecules complete the structure.

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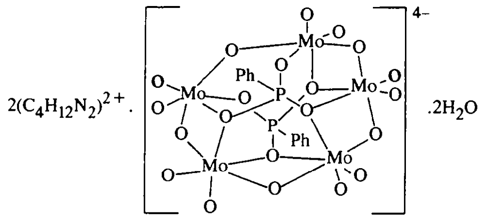
Comment

We have recently reported the hydrothermal syntheses and crystal structures of a family of layered alkali metal/ammonium molybdenum methylphosphonates (Harrison, Dussack & Jacobson, 1995), which is based on the hexagonal tungsten oxide motif of vertex-sharing octahedra (Gérand, Nowogrocki, Guenot & Figlarz, 1979). We report here the preparation and characterization of $(C_4H_{12}N_2)_2[(MoO_3)_5\{(C_6H_5)PO_3\}_2].2H_2O$, (I), a molecular species prepared under similar conditions from closely related starting materials. It is related to similar clusters prepared earlier (Kwak, Pope & Scully, 1975; Lyxell & Strandberg, 1988; Harrison, Dussack & Jacobson, 1997*a*).



(I)

All Mo centers show a two short–two intermediate–two long Mo—O bond-distance distribution within the distorted octahedral MoO_6 unit, which is typical of Mo^{VI} in these systems (Stalick & Quicksall, 1976; Lyxell & Strandberg, 1988). Each MoO_6 center has two short 'oxo' Mo═O bonds in a *cis* configuration, both of which are *trans* to a long Mo—O link, and the two remaining bonds are intermediate in length between these two extremes. All Mo═O links are terminal bonds, not joined to any other atoms in the cluster (three of them, O6, O11 and O12, are receptors for hydrogen bonding). The MoO_6 units are fused together into an isolated five-unit ring *via* one vertex-sharing and four edge-sharing links. Average Mo—O bond lengths and molybdenum bond-valence sum (BVS) values (Brese & O'Keeffe, 1991) are typical: $d_{\rm ave}$(Mo1—O) = 2.005 (3) Å, BVS(Mo1) = 6.00; $d_{\rm ave}$(Mo2—O) = 1.973 (2) Å, BVS(Mo2) = 6.08; $d_{\rm ave}$(Mo3—O) = 1.982 (2) Å, BVS(Mo3) = 6.03; $d_{\rm ave}$(Mo4—O) = 1.984 (2) Å, BVS(Mo4) = 6.05; $d_{\rm ave}$(Mo5—O) = 1.978 (2) Å, BVS(Mo5) = 6.03.

Both faces of the Mo/O five-unit ring in this phase are capped by PC_6H_5 entities, as $[(C_6H_5)PO_3]^{2-}$ phenylphosphonate groups, resulting in tetrahedral coordination for P. For both distinct phenylphosphonate groups, one P—O—Mo bond and two P—O—(Mo,Mo′) links are formed, the latter O atoms being parts of inter-octahedral edges. The 21 O atoms associated with the cluster fall into the following classes: O5, O6, O11, O12, O16, O17, O18, O19, O20 and O21 are terminal O atoms attached only to Mo; O1, O4, O8, O9 and O13 form bicoordinate Mo—O—Mo′ bridges; O3 and O14 form bicoordinate Mo—O—P bonds; O2, O7, O10 and O15 form tricoordinate (Mo,Mo′)—O—P centers (Fig. 1).

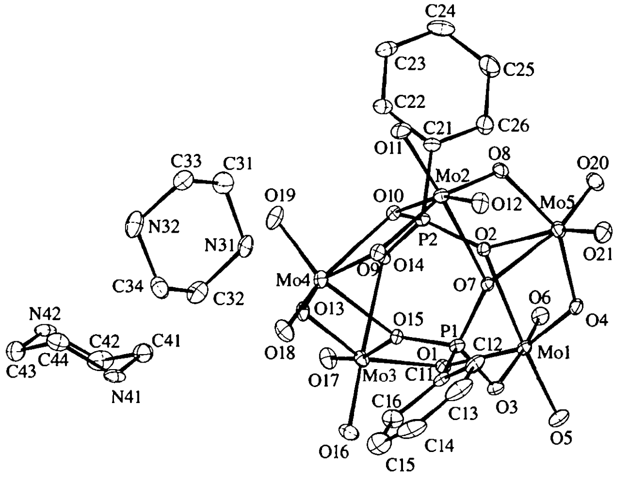


Fig. 1. *CAMERON* (Watkin, Prout & Pearce, 1996) view of the asymmetric unit of (I) and the atom-labelling scheme (20% probability displacement ellipsoids). H atoms and water O atoms have been omitted for clarity

The overall formulation of the cluster is $[(MoO_3)_5\{(C_6H_5)PO_3\}_2]^{4-}$, assuming the sole presence of Mo^{VI}, which is consistent with the crystal color and BVS calculations. Charge compensation for the anionic cluster is provided by a pair of doubly protonated $(C_4H_{12}N_2)^{2+}$ piperazinium cations. Both these species adopt typical chair geometries with normal N—C and C—C bond lengths and angles. Based on their calculated positions, all of the N—H protons are involved in hydrogen bonding, either to O atoms in the $[(MoO_3)_5\{(C_6H_5)PO_3\}_2]^{4-}$ cluster or to water molecules (extra-cluster O atoms). There are two water molecules of crystallization (O31 and O32).

The unit-cell packing for $(C_4H_{12}N_2)_2[(MoO_3)_5\{(C_6H_5)PO_3\}_2].2H_2O$ results in a layered arrangement of the anionic clusters aligned such that the plane formed by the five Mo cations lies approximately normal to [001]. This results in pseudo-channels aligned along [100] which are occupied by the piperazinium cations and water molecules.

The title compound may be briefly compared with the guanidinium-containing phase, $(CH_6N_3)_4[(MoO_3)_5\{(C_6H_5)PO_3\}_2]$ (Lyxell & Strandberg, 1988), which contains the same molybdenum oxide phenylphosphonate anion. The anionic cluster geometries in the two phases are very similar, with the same distortion modes for the MoO_6 groups observed in both cases. For the guanidinium phase, it was suggested that steric considerations led to a structure without stabilizing water molecules, whereas the piperazinium phase contains two water molecules of crystallization, in common with related phases (Harrison, Dussack & Jacobson, 1997*a*).

In both phases, a complex network of hydrogen bonds (based on calculated H-atom positions) links the cations and anions into a three-dimensional network.

Experimental

Single crystals of (I) were prepared hydrothermally from a mixture of 0.1795 g (2.084 mmol) piperazine, 0.6 g (4.168 mmol Mo) MoO_3 and 0.468 g (4.168 mmol P) 98% $C_6H_5PO_2H_2O$ in 8 ml deionized H_2O (initial piperazine:Mo:P ratio of 1:2:2). The reactants were sealed in a 23 ml teflon-lined Parr reaction vessel and heated to 408 K for 5 d. After slow cooling to ambient temperature over 24 h, the solid product was recovered by vacuum filtration and washing. Clear air-stable slightly translucent crystals of (I) (to 2 mm maximum linear dimension) and very dark-blue rhombs of a Keggin-ion like piperazinium molybdophosphate (Harrison, Dussack & Jacobson, 1997*b*) were recovered.

Crystal data

$(C_4H_{12}N_2)_2[Mo_5O_{15}(C_6H_5O_3P)_2].2H_2O$
$M_r = 1244.20$
Monoclinic
$P2_1/a$
$a = 13.133\,(4)$ Å
$b = 18.932\,(6)$ Å
$c = 14.646\,(9)$ Å
$\beta = 95.70\,(3)°$
$V = 3623\,(4)$ Å^3
$Z = 4$
$D_x = 2.27$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6.3–11.6°$
$\mu = 1.87$ mm^{-1}
$T = 298$ K
Faceted block
0.5 × 0.5 × 0.3 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.53$, $T_{max} = 0.57$
5006 measured reflections
4621 independent reflections

4307 reflections with $I > 0$
$R_{int} = 0.013$
$\theta_{max} = 22.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 20$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.022$
$wR = 0.035$
$S = 1.84$
4307 reflections
489 parameters
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.006$

$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 20.7 (13)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected bond lengths (Å)*

Mo1—O1	1.903 (4)	Mo4—O10	2.418 (3)
Mo1—O2	2.414 (3)	Mo4—O13	1.952 (3)
Mo1—O3	2.406 (3)	Mo4—O15	2.204 (3)
Mo1—O4	1.880 (4)	Mo4—O18	1.687 (4)
Mo1—O5	1.716 (4)	Mo4—O19	1.703 (4)
Mo1—O6	1.708 (4)	Mo5—O2	2.240 (3)
Mo2—O7	2.293 (3)	Mo5—O4	1.925 (4)
Mo2—O8	1.894 (4)	Mo5—O7	2.341 (3)
Mo2—O9	1.935 (4)	Mo5—O8	1.955 (4)
Mo2—O10	2.301 (3)	Mo5—O20	1.703 (4)
Mo2—O11	1.715 (4)	Mo5—O21	1.704 (4)
Mo2—O12	1.708 (4)	P1—O3	1.515 (4)
Mo3—O1	1.904 (4)	P1—O7	1.533 (4)
Mo3—O13	1.931 (4)	P1—O15	1.550 (4)
Mo3—O14	2.346 (3)	P1—C11	1.790 (6)
Mo3—O15	2.301 (3)	P2—O2	1.538 (4)
Mo3—O16	1.709 (4)	P2—O10	1.536 (4)
Mo3—O17	1.702 (4)	P2—O14	1.519 (4)
Mo4—O9	1.940 (3)	P2—C21	1.800 (5)

One of the piperazinium cations is disordered between two chair conformations. A constrained refinement such that pop(N41) = pop(N42) = 1 − pop(N51) = 1 − pop(N52) (where pop is population) was carried out and resulted in an approximate 3:1 ratio between the two configurations (N41/N42 in the majority). Atoms N51 and N52 were refined with isotropic displacement factors. The H atoms H43–H54 are geometrically placed relative to the major conformation only. H atoms on the water molecules (O31 and O32) were not located.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *RC*85 (Baird, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996). Molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996). Software used to prepare material for publication: *CRYSTALS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1124). Services for accessing these data are described at the back of the journal.

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trans-$[(Mo_6Cl_8)(C_7H_7)_4\{P(n\text{-}C_4H_9)_3\}_2]$ and *trans*-$[(Mo_6Cl_8)(C_8H_5)_4\{P(n\text{-}C_5H_{11})_3\}_2]$.$2C_7H_8$

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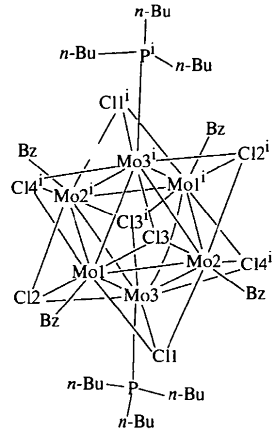
(*Received 16 October 1996; accepted 4 February 1997*)

Abstract

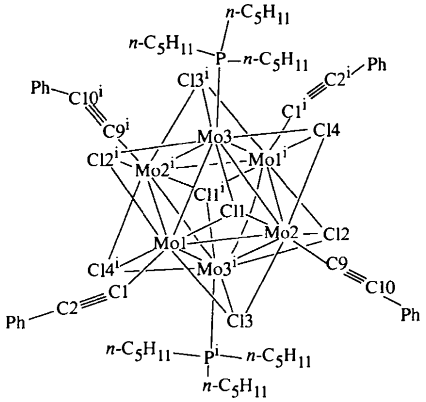
The title compounds, tetrabenzyl-2κC,3κC,4κC,5κC-octa-μ_3-chloro-bis(tributylphosphine)-1κP,6κP-*octahedro*-hexamolybdenum(12*Mo—Mo*), (1), and tetrakis(phenylethynyl)-2κC,3κC,4κC,5κC-octa-μ_3-chloro-bis(tripentylphosphine)-1κP,6κP-*octahedro*-hexamolybdenum(12*Mo—Mo*)–toluene (1/2), (2), containing octahedral Mo clusters with four σ-C ligands, were prepared by the reaction of *trans*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$ with tribenzylaluminium and tris(phenylethynyl)aluminium, respectively, and their structures determined. The octahedral Mo_6 cores of both compounds are on inversion centres and are almost regular. Average interatomic distances in the clusters for (1) are Mo—Mo_{edge} 2.618, Mo$\cdots$$Mo_{opposite}$ 3.703, Mo—Cl 2.477 and Mo—C 2.26 Å, and for (2) are Mo—Mo_{edge} 2.626, Mo$\cdots$$Mo_{opposite}$ 3.714 and Mo—C 2.13 Å.

Comment

Classic examples of molybdenum cluster complexes with the $[Mo_6Cl_8]^{4+}$ core are $[Mo_6Cl_{14}]^{2-}$ and $[Mo_6Cl_8(H_2O)_6]^{4+}$. The $[Mo_6Cl_8]^{4+}$ core can accept various kinds of ligands and recent examples are $(CF_3SO_3)^-$ (Johnston, Gaswick, Lonergan, Stern & Shriver, 1992) and $[Mn(CO)_2Cp]^-$ (Johnston, Stern & Shriver, 1992). We have reported the preparation and structural analysis of the molybdenum cluster complexes *trans*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$ (R = n-C_3H_7, n-C_4H_9, n-C_5H_{11}) and an alkyl derivative all-*trans*-$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]$ (Saito, Nishida, Yamagata, Yamagata & Yamaguchi, 1986). In this communication, we report the synthesis and structural characterization of a benzyl complex, *trans*-$[(Mo_6Cl_8)(C_7H_7)_4\{P(n\text{-}C_4H_9)_3\}_2]$, (1), and an alkynyl complex, *trans*-$[(Mo_6Cl_8)(C_8H_5)_4\{P(n\text{-}C_5H_{11})_3\}_2]$.$2C_7H_8$, (2).



(1)



(2)

In both (1) and (2), the cluster units are at the crystallographic inversion centres and the shape of the Mo_6 core is an almost perfect octahedron. The regular shape is consistent with the number of metal cluster electrons (24 e) of these cluster complexes. The molecular structures of (1) and (2) are shown in Figs. 1 and 2, respectively. Selected geometric parameters are listed in Tables 1 and 2.

Three non-bonding Mo$\cdots$Mo distances between the opposite Mo atoms in the Mo_6 core are 3.699 (3), 3.704 (3) and 3.705 (3) Å for (1), and 3.709 (2), 3.715 (2) and 3.718 (2) Å for (2). The averages of these distances are comparable in (1) and (2) (3.703 and 3.714 Å, respectively). The average Mo—Cl distances in (1) and (2) are also very similar to one another (2.477 and 2.474 Å, respectively). The Mo—C distances of (1), 2.239 (14) and 2.271 (15) Å, are similar