

Table 2. Bond distances (Å) and angles (°) with their *e.s.d.*'s

(a) Coordination polyhedron

Cu—O(1)	1.983 (4)	Cu—O(4)	1.986 (4)
Cu—O(2)	1.971 (4)	Cu—N(1)	2.145 (5)
Cu—O(3)	1.976 (5)	Cu—Cu	2.663 (1)
O(1)—Cu—O(3)	90.4 (2)	O(4)'—Cu—O(1)	87.6 (2)
O(3)—Cu—O(2)'	89.5 (2)	N(1)—Cu—Cu'	176.4 (3)
O(2)'—Cu—O(4)'	89.7 (2)		

(b) Acetate groups

C(10)—O(1)	1.242 (8)	C(30)—O(3)	1.275 (8)
C(10)—O(2)	1.256 (7)	C(30)—O(4)	1.257 (8)
C(10)—C(20)	1.532 (9)	C(30)—C(40)	1.495 (10)
C(20)—C(10)—O(1)	116.9 (5)	O(3)—C(30)—C(40)	117.4 (6)
C(20)—C(10)—O(2)	116.4 (6)	C(40)—C(30)—O(4)	118.8 (6)
O(2)—C(10)—O(1)	126.7 (6)	O(4)—C(30)—O(3)	123.8 (6)

(c) Benzimidazole molecule

N(1)—C(1)	1.316 (7)	C(4)—C(5)	1.381 (13)
C(1)—N(2)	1.343 (9)	C(5)—C(6)	1.383 (10)
N(2)—C(2)	1.392 (9)	C(6)—C(7)	1.378 (9)
C(2)—C(3)	1.388 (9)	C(7)—N(1)	1.389 (8)
C(3)—C(4)	1.373 (11)	C(2)—C(7)	1.401 (8)
C(1)—N(1)—C(7)	105.7 (5)	C(5)—C(6)—C(7)	116.6 (7)
N(1)—C(1)—N(2)	113.1 (6)	N(2)—C(2)—C(7)	105.4 (6)
C(1)—N(2)—C(2)	107.0 (5)	N(1)—C(7)—C(2)	108.8 (5)
C(2)—C(3)—C(4)	116.3 (6)	C(3)—C(2)—N(2)	132.6 (6)
C(3)—C(4)—C(5)	121.8 (7)	C(6)—C(7)—N(1)	130.3 (6)
C(4)—C(5)—C(6)	122.3 (7)		

(d) Shortened interatomic contact

N(2)—O(4)	2.859 (7)
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inclined at 84.7 (5)° to the plane of the four coordinated O atoms. Bond distances and angles of the imidazole ring (Table 2) are close to the values of

noncoordinated and coordinated rings, tabulated by Freeman (1967). As is shown in Table 2, there are intermolecular hydrogen-bond contacts, N(2)—O(4), of 2.859 (7) Å.

The magnetic properties of the compound are being investigated by J. Mroziński in Wrocław.

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Structure of Bis(tetraphenylarsonium) Hexamolybdate(VI)

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Abstract. [As(C₆H₅)₄]₂[Mo₆O₁₉], 2C₂₄H₂₀As⁺. Mo₆O₁₉²⁻, *M_r* = 1646.4, monoclinic, *P*2₁/*c*, *a* = 16.939 (2), *b* = 30.641 (2), *c* = 21.423 (2) Å, β = 108.73 (1)°, *U* = 10530 Å³, *Z* = 8, *D_x* = 2.077 Mg m⁻³; Mo *K*α

radiation, λ = 0.71069 Å, μ = 2.66 mm⁻¹, *T* = 291 K; *R* = 0.082 for 7656 observed reflexions. In the hexamolybdate anion, six MoO₆ distorted octahedra are fused together so that they all share a common vertex. O atoms are of three types: central, terminal and bridging, bonded to six, one and two Mo atoms,

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Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$		<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
Mo(1)	4330 (1)	5269 (1)	1558 (1)	46 (1)*	C(145)	5230	2337	6608	75 (8)
Mo(2)	5937 (1)	4767 (1)	2569 (1)	45 (1)*	C(146)	5441	2045	6188	71 (8)
Mo(3)	6028 (1)	5818 (1)	2326 (1)	52 (1)*	C(141)	6240	2052	6134	49 (6)
Mo(4)	4332 (1)	5954 (1)	2726 (1)	41 (1)*	C(212)	2956 (10)	6128 (4)	5712 (6)	53 (6)
Mo(5)	4256 (1)	4906 (1)	2978 (1)	45 (1)*	C(213)	3659	6353	6099	78 (8)
Mo(6)	5946 (1)	5459 (1)	3738 (1)	43 (1)*	C(214)	3629	6587	6648	77 (8)
Mo(1')	804 (1)	2841 (1)	8625 (1)	45 (1)*	C(215)	2895	6597	6812	73 (8)
Mo(2')	-703 (1)	2251 (1)	7660 (1)	51 (1)*	C(216)	2192	6372	6425	55 (7)
Mo(3')	-940 (1)	3305 (1)	7761 (1)	51 (1)*	C(211)	2223	6137	5875	37 (5)
Mo(4')	766 (1)	3464 (1)	7378 (1)	44 (1)*	C(222)	1621 (7)	5154 (5)	6339 (7)	50 (6)
Mo(5')	989 (1)	2410 (1)	7276 (1)	43 (1)*	C(223)	1461	4872	6795	75 (8)
Mo(6')	-758 (1)	2880 (1)	6416 (1)	45 (1)*	C(224)	677	4869	6878	64 (7)
As(1)	6551 (2)	1637 (1)	5596 (1)	48 (1)*	C(225)	53	5149	6504	73 (8)
As(2)	1265 (1)	5827 (1)	5379 (1)	47 (1)*	C(226)	214	5431	6048	54 (6)
As(3)	1508 (2)	752 (1)	5560 (1)	48 (1)*	C(221)	998	5433	5965	55 (6)
As(4)	3758 (1)	3206 (1)	4635 (1)	47 (1)*	C(232)	303 (9)	6623 (5)	5189 (7)	70 (8)
O(1)	3723 (12)	5196 (8)	760 (8)	108 (11)*	C(233)	-425	6865	4920	88 (9)
O(2)	6537 (12)	4349 (6)	2520 (9)	89 (10)*	C(234)	-1128	6669	4480	65 (7)
O(3)	6664 (11)	6166 (6)	2082 (9)	90 (10)*	C(235)	-1102	6231	4308	74 (8)
O(4)	3712 (10)	6389 (5)	2778 (7)	69 (8)*	C(236)	-374	5990	4576	65 (7)
O(5)	3618 (12)	4576 (6)	3212 (10)	99 (11)*	C(231)	329	6186	5016	53 (6)
O(6)	6536 (11)	5542 (7)	4524 (9)	96 (10)*	C(242)	1429 (9)	5780 (4)	4091 (7)	52 (6)
O(7)	5128 (8)	5350 (5)	2636 (6)	44 (6)*	C(243)	1713	5603	3601	62 (7)
O(12)	5154 (11)	4807 (5)	1697 (8)	71 (8)*	C(244)	2100	5195	3694	58 (7)
O(13)	5182 (11)	5644 (6)	1506 (7)	73 (8)*	C(245)	2204	4964	4276	76 (8)
O(14)	3818 (10)	5762 (5)	1812 (7)	64 (7)*	C(246)	1920	5141	4766	51 (6)
O(15)	3764 (9)	4897 (5)	2021 (8)	59 (7)*	C(241)	1533	5549	4673	54 (6)
O(23)	6518 (10)	5248 (6)	2334 (8)	76 (9)*	C(312)	1809 (7)	29 (5)	6443 (8)	67 (7)
O(25)	5075 (11)	4510 (5)	2847 (9)	70 (8)*	C(313)	1615	-307	6810	70 (8)
O(26)	6446 (10)	4948 (6)	3486 (8)	70 (8)*	C(314)	800	-356	6818	71 (8)
O(34)	5172 (11)	6212 (5)	2424 (8)	75 (9)*	C(315)	179	-70	6460	68 (8)
O(36)	6521 (9)	5802 (5)	3253 (7)	58 (7)*	C(316)	373	266	6094	67 (7)
O(45)	3756 (10)	5469 (5)	2961 (8)	64 (8)*	C(311)	1188	315	6086	48 (6)
O(46)	5155 (9)	5921 (5)	3583 (7)	56 (7)*	C(322)	646 (8)	1577 (5)	5460 (7)	67 (7)
O(56)	5067 (11)	5074 (6)	3794 (8)	74 (8)*	C(323)	-52	1847	5242	69 (8)
O(1')	1365 (13)	2813 (7)	9427 (8)	103 (10)*	C(324)	-790	1688	4796	62 (7)
O(2')	-1259 (13)	1808 (7)	7735 (10)	106 (11)*	C(325)	-830	1260	4568	67 (7)
O(3')	-1644 (12)	3619 (7)	7920 (10)	109 (11)*	C(326)	-132	990	4786	59 (7)
O(4')	1266 (11)	3907 (5)	7288 (9)	74 (9)*	C(321)	607	1149	5232	45 (6)
O(5')	1687 (14)	2097 (6)	7079 (11)	111 (13)*	C(332)	1746 (9)	771 (3)	4320 (7)	57 (7)
O(6')	-1333 (11)	2898 (7)	5597 (9)	98 (10)*	C(333)	1988	611	3800	51 (6)
O(7')	12 (9)	2863 (5)	7522 (7)	49 (7)*	C(334)	2212	173	3791	53 (6)
O(12')	89 (11)	2355 (6)	8538 (9)	87 (8)*	C(335)	2194	-104	4303	51 (6)
O(13')	-120 (12)	3192 (6)	8615 (7)	76 (9)*	C(336)	1952	56	4823	51 (6)
O(14')	1245 (10)	3345 (5)	8314 (7)	64 (7)*	C(331)	1728	494	4832	51 (6)
O(15')	1415 (9)	2479 (5)	8220 (8)	65 (8)*	C(342)	3247 (10)	949 (5)	5964 (6)	66 (7)
O(23')	-1347 (10)	2731 (6)	7831 (8)	73 (9)*	C(343)	3989	1120	6387	78 (9)
O(25')	198 (12)	2003 (6)	7416 (9)	81 (10)*	C(344)	3987	1357	6942	64 (7)
O(26')	-1189 (11)	2402 (6)	6732 (8)	76 (9)*	C(345)	3242	1422	7075	64 (7)
O(34')	-156 (10)	3725 (5)	7607 (8)	60 (8)*	C(346)	2499	1251	6653	53 (6)
O(36')	-1373 (10)	3245 (6)	6814 (7)	67 (8)*	C(341)	2501	1014	6097	44 (6)
O(45')	1379 (9)	2990 (5)	7208 (8)	59 (7)*	C(412)	4654 (8)	4016 (5)	4754 (7)	65 (7)
O(46')	-39 (10)	3366 (5)	6518 (7)	59 (7)*	C(413)	5361	4277	4998	47 (6)
O(56')	154 (11)	2539 (5)	6426 (8)	69 (8)*	C(414)	6083	4105	5448	59 (7)
C(112)	5667 (8)	816 (5)	5499 (7)	57 (7)	C(415)	6099	3673	5654	62 (7)
C(113)	4966	548	5268	82 (9)	C(416)	5392	3411	5411	79 (9)
C(114)	4246	705	4799	82 (9)	C(411)	4669	3583	4961	44 (6)
C(115)	4225	1130	4561	78 (8)	C(422)	3573 (9)	3192 (4)	5918 (7)	51 (6)
C(116)	4925	1398	4791	60 (7)	C(423)	3311	3014	6417	81 (9)
C(111)	5646	1240	5261	49 (6)	C(424)	2998	2589	6357	76 (8)
C(122)	6746 (8)	1621 (3)	4335 (7)	48 (6)	C(425)	2947	2343	5797	63 (7)
C(123)	6995	1781	3818	58 (7)	C(426)	3209	2522	5298	60 (7)
C(124)	7281	2209	3837	46 (6)	C(421)	3522	2947	5358	43 (6)
C(125)	7319	2477	4372	51 (6)	C(432)	2023 (10)	3414 (5)	4244 (6)	58 (7)
C(126)	7070	2316	4889	58 (7)	C(433)	1287	3605	3844	74 (8)
C(121)	6784	1888	4871	47 (6)	C(434)	1298	3869	3316	73 (8)
C(132)	8255 (10)	1380 (5)	5977 (6)	58 (7)	C(435)	2044	3941	3188	70 (8)
C(133)	8977	1175	6374	78 (9)	C(436)	2780	3750	3588	69 (8)
C(134)	8958	933	6921	70 (8)	C(431)	2770	3486	4116	48 (6)
C(135)	8218	897	7071	57 (7)	C(442)	3374 (7)	2516 (5)	3688 (7)	48 (6)
C(136)	7497	1102	6674	63 (7)	C(443)	3554	2206	3276	64 (7)
C(131)	7515	1344	6127	51 (6)	C(444)	4366	2162	3258	75 (8)
C(142)	6828 (7)	2351 (5)	6500 (7)	47 (6)	C(445)	4999	2428	3653	61 (7)
C(143)	6617	2643	6920	50 (6)	C(446)	4819	2738	4065	60 (7)
C(144)	5818	2636	6974	62 (7)	C(441)	4007	2782	4082	51 (6)

* $U_{\text{eq}} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} matrix).

respectively. The two crystallographically independent anions are insignificantly different.

Introduction. The title compound was obtained as one product of the hydrolysis and oxidation of $[\text{Ph}_4\text{As}]_2[\text{Mo}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4]$, which contains a Mo—Mo quadruple bond (Clegg, Garner, Parkes & Walton, 1979; Garner & Walton, 1982, unpublished results). The crystal structure was determined in order to identify this product.

Experimental. Large pale-yellow crystals were formed directly in the reaction. A block $ca\ 0.37 \times 0.33 \times 0.27$ mm was cut from one and sealed in a Lindemann-glass capillary. Measurements were made on a Stoe—Siemens AED diffractometer (Clegg, 1981). Cell dimensions were derived from 2θ values ($20 < 2\theta < 25^\circ$) of 50 reflexions. Data were collected to $2\theta_{\text{max}} = 45^\circ$. Because of the large asymmetric unit (150 non-H atoms), data were collected at very high speed (Hope & Nichols, 1981), 13 796 intensities being measured in two days. Three standard reflexions showed no significant intensity variation in this time. Azimuthal scan measurements indicated that absorption effects were negligible; no correction was applied.

7656 unique data with $F > 4\sigma(F)$ were used for structure solution (by automatic direct methods) and refinement (to a minimum of $\sum w\Delta^2$; $\Delta = |F_o| - |F_c|$). C atoms were assigned isotropic, other non-H atoms anisotropic thermal parameters. To reduce the computing requirements, phenyl groups were refined as rigid regular hexagons ($\text{C—C} = 1.395 \text{ \AA}$) with fixed C—H ($= 0.96 \text{ \AA}$) bisecting C—C—C angles externally.

Final refinement: 489 refined parameters, $wR = 0.078$, $w^{-1} = \sigma^2(F) + 0.0002F^2$; secondary-extinction parameter $x = 1.6(1) \times 10^{-8}$ [$F'_c = F_c(1 - xF_c^2/\sin\theta)$]. Mean shift/e.s.d. = 0.01, max. = 0.10; max. difference peak = 0.96, max. trough = 0.99 $e \text{ \AA}^{-3}$; variance independent of $\sin\theta$, F_o and indices.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974); computer programs were written by WC (diffractometer control) and GMS (*SHELX 76* and *SHELXTL*).

Discussion. Atomic coordinates are given in Table 1. Fig. 1 shows one anion, Fig. 2 the crystal packing. Mean bond lengths and angles of various types within the anions are given in Table 2, together with

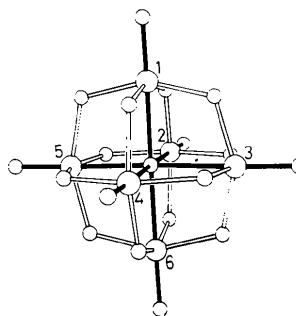


Fig. 1. One of the independent $[\text{Mo}_6\text{O}_{19}]^{2-}$ anions, showing the numbering of the Mo atoms. Terminal O atoms bear the same numbers, bridging O atoms bear the numbers of both bonded Mo atoms [e.g. O(13) bridges Mo(1) and Mo(3)], the central O atom is O(7). The other anion is numbered in the same way, with primes.

Table 2. Bond lengths (\AA) and angles ($^\circ$) in the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion

Mean values are given for each type of bond length or angle, with the range in parentheses.

Cation Reference	$\text{HN}_3\text{P}_3(\text{NMe}_2)_6^+$ (1)	(18-crown-6) K^+ (2)	$\text{Mo}(\text{S}_2\text{CNEt}_2)_4^+$ (3)	Ph_4As^+ (4)
Mo—O(terminal)	1.677 (1.676–1.678)	1.674 (1.670–1.683)	1.686 (1.673–1.698)	1.683 (1.644–1.723)
Mo—O(central)	2.319 (2.312–2.324)	2.320 (2.305–2.335)	2.315 (2.303–2.323)	2.313 (2.283–2.347)
Mo—O(bridging)	1.928 (1.855–2.005)	1.926 (1.890–1.959)	1.916 (1.881–1.948)	1.923 (1.859–1.961)
O(c)—Mo—O(t)	177.3 (176.4–179.7)	178.7 (178.2–179.5)	178.4 (177.5–179.0)	178.5 (176.9–179.4)
O(c)—Mo—O(b)	76.7 (75.2–77.9)	76.6 (75.8–77.6)	76.4 (75.3–77.2)	76.7 (74.4–78.1)
O(t)—Mo—O(b)	103.3 (101.9–105.0)	103.4 (101.8–106.0)	103.6 (102.1–105.4)	103.3 (100.2–106.1)
O(b)—Mo—O(b)	{ 85.3 (82.7–91.3)	{ 86.9 (84.3–88.9)	{ 86.8 (84.6–89.1)	{ 87.0 (84.5–89.7)
	{ 153.1 (152.3–153.6)	{ 153.1 (152.2–153.7)	{ 152.7 (151.5–153.5)	{ 153.4 (150.5–154.9)
Mo—O(c)—Mo	{ 90.0 (89.4–90.6)	{ 90.0 (89.4–90.6)	{ 90.0 (89.8–90.2)	{ 90.0 (88.3–91.5)
	{ 180.0*	{ 179.2 (178.7–179.6)	{ 180.0*	{ 178.5 (177.8–179.9)
Mo—O(b)—Mo	116.5 (116.3–116.7)	116.9 (116.2–118.0)	117.2 (116.1–118.2)	116.5 (114.3–118.4)

References: (1) Allcock, Bissell & Shawl (1973); e.s.d.'s for individual bond lengths and angles are 0.004 \AA and 0.2 $^\circ$. (2) Nagano & Sasaki (1979); e.s.d.'s: 0.011 \AA and 0.5 $^\circ$. (3) Garner, Howlader, Mabbs, McPhail, Miller & Onan (1978); e.s.d.'s: 0.009 \AA and 0.4 $^\circ$. (4) This work; e.s.d.'s: 0.018 \AA and 0.8 $^\circ$.

* Fixed by crystallographic symmetry.

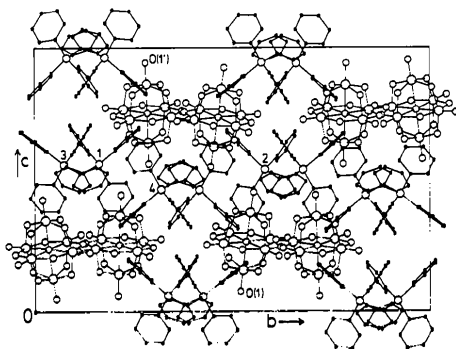


Fig. 2. The packing seen in parallel projection along the a axis. Labeled are O(1), O(1') and (by number only) the four independent As atoms.

corresponding values for other structures containing the hexamolybdate anion.*

Each Mo atom is coordinated by six O atoms in a distorted octahedral arrangement, the distortion consisting of a displacement of Mo towards the terminal O atoms. The six MoO_6 coordination octahedra in each anion share a common vertex at the central O atom. Each octahedron shares four edges with adjacent octahedra, but no faces are shared. The overall symmetry of the anion approximates closely to $m3m$ (O_h).

The geometry of the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion in this structure is in close agreement with those previously

* Detailed bond lengths and angles, H-atom coordinates, anisotropic thermal parameters and structure-factor lists have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36989 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

determined. As in the $(18\text{-crown-6})\text{K}^+$ and $\text{Mo}(\text{S}_2\text{CNEt}_2)_4^+$ complexes, and in contrast to the $\text{HN}_3\text{P}_3(\text{NMe}_2)_6^+$ complex, no significant asymmetry is observed in the Mo—O—Mo bridges. The marked asymmetry in the one single case has been attributed to interionic N—H \cdots O hydrogen bonding (Garner *et al.*, 1978).

Concerning the preparation of the complex, we note that the homologous hexatungstate anion, $[\text{W}_6\text{O}_{19}]^{2-}$, is produced, together with the $[\text{W}(\text{C}_4\text{H}_9\text{NC})_7]^+$ cation, when *tert*-butyl isocyanide reacts, in the presence of some water, with $\text{K}_3\text{W}_2\text{Cl}_9$; this starting material also contains a multiple metal-metal bond, in this case a triple W—W bond (LaRue, Liu & San Filippo, 1980).

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