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$(C_{24}H_{20}P)_2[Mo_6Cl_{14}]$

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Abstract

The structure of bis(tetraphenylphosphonium) octa-μ_3-chloro-hexachlorohexamolybdate(2−) is reported. The structure consists of an $[Mo_6Cl_{14}]^{2-}$ cluster anion having a crystallographic center of inversion and two (inversion) symmetry-related tetraphenylphosphonium (TPP) cations. The molybdenum chloride cluster anion is a slightly distorted octahedron of Mo atoms surrounded by eight (μ_3) face-bridging and six axial Cl atoms, and is coordinated by ten nearest neighbor TPP molecules. The distorted cluster retains only inversion symmetry.

Comment

Molecular crystals containing the cluster anion $[Mo_6Cl_{14}]^{2-}$ are of interest for their optical properties. The cluster anion is luminescent with emission maximum, lifetime, and quantum yield of 805 nm, 180 µs, and 0.19, respectively, and has a broad absorption spectrum below 500 nm (Maverick, Najdzionek, Mackenzie, Nocera & Gray, 1983). The large quantum yield and moderately long lifetime makes the cluster ion a suitable candidate for electronic excited-state structure determination (Pressprich, White & Coppens, 1993) using modulated laser techniques.

The molybdenum chloride cluster anion in the title compound has slightly distorted octahedral symmetry. The distortion of the cluster is such as to remove all but inversion symmetry, with only the Mo2—Mo3, Mo1—Mo2^{i} and Mo2—Mo3^{i} nearest-neighbor bond lengths remaining equivalent at 2.606 (1) Å. The distortion may be viewed as a canting of the body diagonals (by about 0.2°). The molybdenum chloride cluster anion is nearly identical (to within 3σ in Mo—Mo bond lengths) to that reported in the tetramethyltetrathiafulvalene (TMTTF) complex $(TMTTF)_2[Mo_6Cl_{14}]$ (Ouhab, Battail, Perrin & Garragou-Lagrange, 1986).

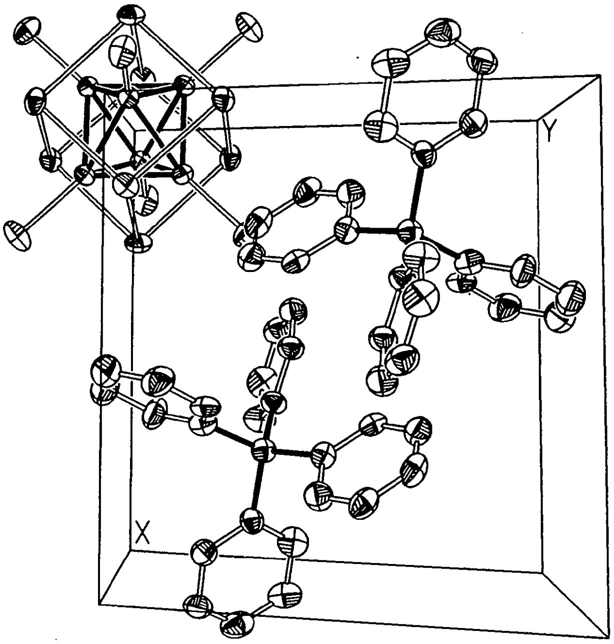

Fig. 1. The unit-cell packing diagram viewed along the *c* axis. The Mo—Cl bonds have been omitted and the adjacent bridging Cl atoms connected to show the geometry of the cluster. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

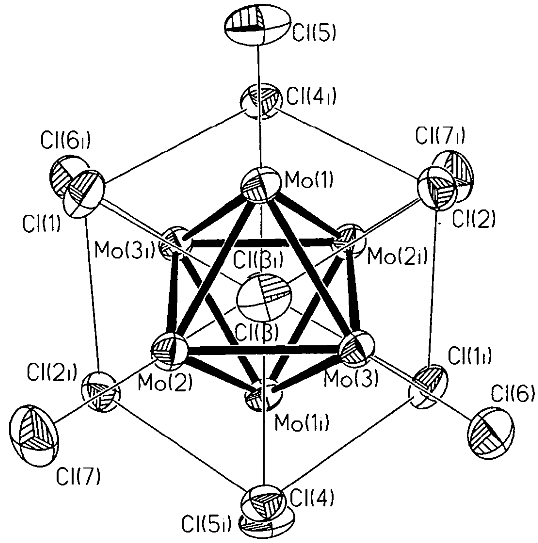

Fig. 2. The molybdenum chloride cluster anion showing the atomic labeling and the octahedral symmetry. The Mo—Cl bonds have been omitted and the adjacent bridging Cl atoms have been connected. Displacement ellipsoids are drawn at the 50% probability level.

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Experimental

The method of Sheldon (1962) was used to produce $MoCl_2$ by disproportionation of $MoCl_3$ (Alfa Products). The crude light green $MoCl_2$ was dissolved in hot 6*M* HCl and was filtered, yielding a light yellow solution. Addition of excess PPh_4Cl (Aldrich Chemicals) in 6*M* HCl immediately precipitated $(PPh_4)_2[Mo_6Cl_{14}]$, which was subsequently recrystallized from CH_3CN.

Crystal data

$(C_{24}H_{20}P)_2[Mo_6Cl_{14}]$
$M_r = 1750$
Triclinic
$P\bar{1}$
$a = 11.024$ (1) Å
$b = 11.526$ (2) Å
$c = 12.770$ (2) Å
$\alpha = 63.48$ (1)°
$\beta = 82.30$ (1)°
$\gamma = 86.33$ (1)°
$V = 1439$ (9) Å^3
$Z = 1$
$D_x = 2.02$ (1) Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 10$–27°
$\mu = 1.99$ (1) mm^{-1}
$T = 293$ K
Irregular
$0.14 \times 0.12 \times 0.07$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: analytical
$T_{min} = 0.74$, $T_{max} = 0.85$
6593 measured reflections
6593 independent reflections
3886 observed reflections $[I > 3\sigma(I)]$

$\theta_{max} = 27°$
$h = 0 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 12$
4 standard reflections
frequency: 60 min
intensity variation: −2.6%

Refinement

Refinement on F
$R = 0.041$
$wR = 0.048$
$S = 1.150$
3886 reflections
317 parameters
H-atom parameters not refined
Calculated weights $w = 1/\sigma^2(F)$, where $\sigma(F) = \sigma(F^2)/2F$ and $\sigma(F^2) = [\sigma^2_{counting} + (0.04|F|^2)^2]^{1/2}$

$\Delta\rho_{max} = 1.24$ e Å^{-3}
$\Delta\rho_{min} = -1.26$ e Å^{-3}
Extinction correction: $I_c = I_o(1 + 2gI_c)$
Extinction coefficient: $g = 1.02 \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo1	0.11209 (5)	−0.12665 (5)	0.07343 (4)	0.0293 (2)
Mo2	0.10767 (5)	0.12626 (5)	−0.01925 (4)	0.0294 (2)
Mo3	−0.06596 (5)	−0.00719 (5)	0.14297 (4)	0.0285 (1)
Cl1	0.2708 (2)	0.0072 (2)	−0.0843 (1)	0.0415 (5)
Cl2	−0.0561 (2)	−0.2461 (2)	0.2238 (1)	0.0399 (5)
Cl3	0.1438 (2)	−0.0083 (2)	0.1880 (1)	0.0390 (4)
Cl4	−0.0651 (2)	0.2329 (1)	0.0469 (1)	0.0369 (4)
Cl5	0.2592 (2)	−0.2960 (2)	0.1642 (2)	0.0527 (6)
Cl6	−0.1551 (2)	−0.0109 (2)	0.3281 (1)	0.0521 (6)
Cl7	0.2486 (2)	0.2936 (2)	−0.0455 (2)	0.0553 (6)
P	0.2684 (2)	0.6610 (2)	0.6015 (1)	0.0333 (5)
C1	0.2635 (6)	0.5248 (6)	0.5691 (5)	0.036 (2)
C2	0.3304 (6)	0.4097 (6)	0.6239 (6)	0.039 (2)
C3	0.3195 (7)	0.3123 (6)	0.5914 (6)	0.048 (2)
C4	0.2449 (7)	0.3262 (6)	0.5087 (5)	0.046 (2)
C5	0.1773 (7)	0.4385 (6)	0.4564 (6)	0.047 (2)
C6	0.1864 (7)	0.5361 (6)	0.4877 (6)	0.045 (2)
C7	0.3296 (6)	0.7983 (6)	0.4700 (5)	0.036 (2)
C8	0.3683 (6)	0.7901 (7)	0.3663 (6)	0.039 (2)
C9	0.4227 (7)	0.8965 (7)	0.2683 (6)	0.052 (3)
C10	0.4400 (7)	1.0081 (7)	0.2752 (7)	0.059 (3)
C11	0.4013 (8)	1.0177 (7)	0.3783 (7)	0.059 (3)
C12	0.3471 (7)	0.9134 (6)	0.4760 (7)	0.052 (2)
C13	0.1135 (6)	0.6879 (6)	0.6527 (5)	0.034 (2)
C14	0.0471 (6)	0.7985 (6)	0.5875 (6)	0.040 (2)
C15	−0.0701 (7)	0.8138 (6)	0.6332 (6)	0.049 (2)
C16	−0.1200 (7)	0.7235 (7)	0.7410 (6)	0.055 (2)
C17	−0.0551 (7)	0.6112 (7)	0.8034 (6)	0.053 (3)
C18	0.0621 (7)	0.5935 (7)	0.7603 (6)	0.046 (2)
C19	0.3670 (6)	0.6373 (6)	0.7111 (5)	0.034 (2)
C20	0.4865 (6)	0.5987 (6)	0.6983 (6)	0.040 (2)
C21	0.5639 (7)	0.5929 (6)	0.7761 (6)	0.046 (2)
C22	0.5249 (7)	0.6266 (7)	0.8652 (6)	0.048 (2)
C23	0.4057 (7)	0.6646 (7)	0.8797 (6)	0.051 (2)
C24	0.3259 (7)	0.6706 (6)	0.8025 (5)	0.046 (2)

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

Mo1—Mo2	2.6106 (8)	C1—C2	1.406 (9)
Mo1—Mo2^{i}	2.6060 (8)	C1—C6	1.386 (9)
Mo1—Mo3	2.6098 (7)	C2—C3	1.376 (9)
Mo1—Mo3^{i}	2.5965 (8)	C3—C4	1.37 (1)
Mo1—Cl1	2.474 (2)	C4—C5	1.38 (1)
Mo1—Cl2	2.456 (2)	C5—C6	1.364 (9)
Mo1—Cl3	2.469 (2)	C7—C8	1.379 (9)
Mo1—Cl4^{i}	2.470 (2)	C7—C12	1.389 (9)
Mo1—Cl5	2.421 (2)	C8—C9	1.397 (9)
Mo2—Mo3	2.6054 (7)	C9—C10	1.35 (1)
Mo2—Mo3^{i}	2.6070 (7)	C10—C11	1.38 (1)
Mo2—Cl1	2.471 (2)	C11—C12	1.38 (1)
Mo2—Cl2^{i}	2.476 (2)	C13—C14	1.396 (9)
Mo2—Cl3	2.471 (2)	C13—C18	1.389 (9)
Mo2—Cl4	2.458 (2)	C14—C15	1.379 (9)
Mo2—Cl7	2.431 (2)	C15—C16	1.37 (1)
Mo3—Cl1^{i}	2.472 (2)	C16—C17	1.39 (1)
Mo3—Cl2	2.472 (2)	C17—C18	1.37 (1)
Mo3—Cl3	2.454 (2)	C19—C20	1.375 (9)
Mo3—Cl4	2.476 (2)	C19—C24	1.396 (9)
Mo3—Cl6	2.417 (2)	C20—C21	1.371 (9)
P—C1	1.798 (7)	C21—C22	1.37 (1)
P—C7	1.799 (7)	C22—C23	1.37 (1)
P—C13	1.803 (7)	C23—C24	1.38 (1)
P—C19	1.801 (6)		
Mo2—Mo1—Mo2^{i}	90.13 (2)	Mo1—Mo3—Cl4	117.86 (4)
Mo2—Mo1—Mo3	59.88 (2)	Mo1—Mo3—Cl6	136.56 (6)
Mo2—Mo1—Mo3^{i}	60.09 (2)	Mo1—Mo3^{i}—Mo2^{i}	60.13 (2)
Mo2—Mo1—Cl1	58.07 (4)	Mo1—Mo3^{i}—Mo2	60.22 (2)
Mo2—Mo1—Cl2	118.19 (5)	Mo1—Mo3^{i}—Cl1	58.37 (4)
Mo2—Mo1—Cl3	58.13 (4)	Mo1—Mo3^{i}—Cl2^{i}	118.47 (5)
Mo2—Mo1—Cl4^{i}	118.51 (5)	Mo1—Mo3^{i}—Cl3^{i}	118.49 (5)
Mo2—Mo1—Cl5	136.13 (6)	Mo1—Mo3^{i}—Cl4^{i}	58.21 (4)
Mo2—Mo1^{i}—Mo3^{i}	59.98 (2)	Mo1—Mo3^{i}—Cl6^{i}	133.34 (6)
Mo2—Mo1^{i}—Mo3	60.10 (2)	Mo2—Mo3—Mo2^{i}	90.22 (2)
Mo2—Mo1^{i}—Cl1^{i}	118.39 (5)	Mo2—Mo3—Cl1^{i}	118.47 (5)
Mo2—Mo1^{i}—Cl2^{i}	58.48 (5)	Mo2—Mo3—Cl2	117.78 (5)
Mo2—Mo1^{i}—Cl3^{i}	117.66 (5)	Mo2—Mo3—Cl3	58.38 (4)
Mo2—Mo1^{i}—Cl4	57.86 (4)	Mo2—Mo3—Cl4	57.80 (4)
Mo2—Mo1^{i}—Cl5^{i}	133.68 (6)	Mo2—Mo3—Cl6	134.35 (5)
Mo3—Mo1—Mo3^{i}	89.91 (2)	Mo2—Mo3^{i}—Cl1	58.14 (4)
Mo3—Mo1—Cl1	117.93 (5)	Mo2—Mo3^{i}—Cl2^{i}	58.28 (4)
Mo3—Mo1—Cl2	58.32 (4)	Mo2—Mo3^{i}—Cl3^{i}	118.21 (5)
Mo3—Mo1—Cl3	57.69 (4)	Mo2—Mo3^{i}—Cl4^{i}	118.40 (5)
Mo3—Mo1—Cl4^{i}	117.83 (5)	Mo2—Mo3^{i}—Cl6^{i}	135.39 (5)

Mo3—Mo1—Cl5	137.07 (5)
Mo3—Mo1^{i}—Cl1^{i}	58.30 (5)
Mo3—Mo1^{i}—Cl2^{i}	118.56 (5)
Mo3—Mo1^{i}—Cl3^{i}	118.18 (5)
Mo3—Mo1^{i}—Cl4	58.46 (4)
Mo3—Mo1^{i}—Cl5^{i}	133.00 (5)
Cl1—Mo1—Cl2	175.76 (6)
Cl1—Mo1—Cl3	90.12 (6)
Cl1—Mo1—Cl4^{i}	90.65 (6)
Cl1—Mo1—Cl5	91.71 (7)
Cl2—Mo1—Cl3	89.16 (6)
Cl2—Mo1—Cl4^{i}	89.71 (6)
Cl2—Mo1—Cl5	92.52 (7)
Cl3—Mo1—Cl4^{i}	175.10 (6)
Cl3—Mo1—Cl5	94.79 (6)
Cl4^{i}—Mo1—Cl5	90.02 (6)
Mo1—Mo2—Mo1^{i}	89.87 (2)
Mo1—Mo2—Mo3	60.05 (2)
Mo1—Mo2—Mo3^{i}	59.69 (2)
Mo1—Mo2—Cl1	58.19 (4)
Mo1—Mo2—Cl2^{i}	117.79 (5)
Mo1—Mo2—Cl3	58.08 (4)
Mo1—Mo2—Cl4	118.50 (5)
Mo1—Mo2—Cl7	135.48 (6)
Mo1—Mo2^{i}—Mo3^{i}	59.77 (2)
Mo1—Mo2^{i}—Mo3	60.08 (2)
Mo1—Mo2^{i}—Cl1^{i}	118.27 (5)
Mo1—Mo2^{i}—Cl2	57.72 (4)
Mo1—Mo2^{i}—Cl3^{i}	117.49 (5)
Mo1—Mo2^{i}—Cl4^{i}	58.29 (4)
Mo1—Mo2^{i}—Cl7^{i}	134.65 (6)
Mo3—Mo2—Mo3^{i}	89.78 (2)
Mo3—Mo2—Cl1	118.22 (5)
Mo3—Mo2—Cl2^{i}	117.47 (5)
Mo3—Mo2—Cl3	57.74 (4)
Mo3—Mo2—Cl4	58.47 (4)
Mo3—Mo2—Cl7	135.18 (5)
Mo3—Mo2^{i}—Cl1^{i}	58.20 (4)
Mo3—Mo2^{i}—Cl2	58.13 (4)
Mo3—Mo2^{i}—Cl3^{i}	117.73 (5)
Mo3—Mo2^{i}—Cl4^{i}	118.36 (5)
Mo3—Mo2^{i}—Cl7^{i}	135.05 (5)
Cl1—Mo2—Cl2^{i}	90.19 (6)
Cl1—Mo2—Cl3	90.17 (6)
Cl1—Mo2—Cl4	175.87 (6)
Cl1—Mo2—Cl7	92.40 (7)
Cl2^{i}—Mo2—Cl3	174.50 (6)
Cl2^{i}—Mo2—Cl4	89.50 (6)
Cl2^{i}—Mo2—Cl7	92.39 (7)
Cl3—Mo2—Cl4	89.75 (6)
Cl3—Mo2—Cl7	93.08 (7)
Cl1^{i}—Mo3—Cl2	90.24 (6)
Cl1^{i}—Mo3—Cl3	175.81 (6)
Cl1^{i}—Mo3—Cl4	90.54 (6)
Cl1^{i}—Mo3—Cl6	91.42 (7)
Cl2—Mo3—Cl3	89.15 (6)
Cl2—Mo3—Cl4	175.16 (6)
Cl2—Mo3—Cl6	93.83 (6)
Cl3—Mo3—Cl4	89.73 (6)
Cl3—Mo3—Cl6	92.77 (7)
Cl4—Mo3—Cl6	90.93 (6)
Mo1—Cl1—Mo2	63.74 (4)
Mo1—Cl1—Mo3^{i}	63.33 (4)
Mo2—Cl1—Mo3^{i}	63.66 (4)
Mo1—Cl2—Mo2^{i}	63.80 (4)
Mo1—Cl2—Mo3	63.96 (4)
Mo2^{i}—Cl2—Mo3	63.59 (4)
Mo1—Cl3—Mo2	63.80 (4)
Mo1—Cl3—Mo3	64.03 (4)
Mo2—Cl3—Mo3	63.88 (4)
Mo1—Cl4^{i}—Mo2^{i}	63.85 (4)
Mo1—Cl4^{i}—Mo3^{i}	63.33 (4)
Mo2—Cl4—Mo3	63.74 (4)
C1—P—C7	108.8 (3)
C1—P—C13	106.5 (3)
C1—P—C19	114.0 (3)
C7—P—C13	112.5 (3)
C7—P—C19	105.7 (3)
C13—P—C19	109.5 (3)
P—C1—C2	123.4 (5)
P—C1—C6	116.6 (5)
C2—C1—C6	120.0 (6)
C1—C2—C3	118.0 (7)
C2—C3—C4	121.2 (7)
C3—C4—C5	120.8 (7)
C4—C5—C6	118.9 (7)
C1—C6—C5	121.0 (7)
P—C7—C8	122.1 (5)
P—C7—C12	118.7 (5)
C8—C7—C12	118.9 (7)
C7—C8—C9	120.5 (7)
C8—C9—C10	120.2 (7)
C9—C10—C11	119.9 (7)
C10—C11—C12	120.6 (8)
C7—C12—C11	119.9 (7)
P—C13—C14	121.9 (5)
P—C13—C18	117.2 (5)
C14—C13—C18	120.9 (6)
C13—C14—C15	118.7 (7)
C14—C15—C16	120.8 (7)
C15—C16—C17	120.2 (7)
C16—C17—C18	120.3 (8)
Cl4—Mo2—Cl7	91.73 (6)
Mo1—Mo3—Mo1^{i}	90.09 (2)
Mo1—Mo3—Mo2	60.08 (2)
Mo1—Mo3—Mo2^{i}	59.94 (2)
Mo1—Mo3—Cl1^{i}	118.06 (5)
Mo1—Mo3—Cl2	57.72 (4)
Mo1—Mo3—Cl3	58.28 (4)
C22—C23—C24	119.6 (7)
C13—C18—C17	119.0 (7)
P—C19—C20	119.9 (5)
P—C19—C24	119.9 (5)
C20—C19—C24	119.9 (6)
C19—C20—C21	119.4 (7)
C20—C21—C22	121.2 (7)
C21—C22—C23	120.1 (7)
C19—C24—C23	119.8 (7)

Symmetry code: (i) $-x, -y, -z$.

The Mo atoms were located from Patterson maps and the remaining atomic positions were determined by difference Fourier synthesis and least-squares refinements using *SDP* (Enraf-Nonius, 1985). The H-atom positions were not refined, but were constrained to ride on the appropriate C atoms. Non-H atoms were refined anisotropically. Data collection and cell refinement were performed with *CAD*-4 *Software* (Enraf-Nonius, 1989). The structure was solved and refined using *SDP*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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