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Bis[bis(triphenylphosphine)iminium] Hexamolybdate

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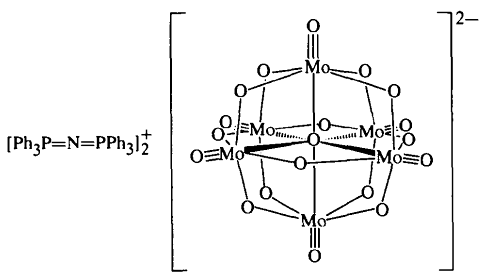
Abstract

The title compound, bis[bis(triphenylphosphorandiyl)-ammonium] nonadecaoxamolybdenum(VI), $(C_{36}H_{30}NP_2)_2[Mo_6O_{19}]$, crystallizes in the triclinic space group $P\bar{1}$. The hexamolybdate anion displays the typical overall octahedral geometry for the isopolyanion, with the central O atom, O11, residing on an inversion center.

Comment

The title compound, (I), was synthesized in an attempt to generate the hexamolybdate anion with cations allowing better solubility and crystallographic properties. Related compounds are bis(tetrabutylammonium) nonadecaoxahexamolybdenum(VI) (Dahlstrom, Zubieta, Neaves & Dilworth, 1982), bis(tetrabutylammonium) nonadecaoxahexamolybdenum(VI) (Rheingold, White, Haggerty & Maatta, 1993), bis(tetraphenylarsonium) hexamolybdate(VI) (Clegg, Sheldrick, Garner & Walton, 1982), hexakis(dimethylamino)cyclotriphosphazene hexamolybdate (Allcock, Bissell & Shawl, 1973).



(I)

Experimental

The synthesis of $[PPN]_2[Mo_6O_{19}]$, where [PPN] is bis(triphenylphosphine)iminium, was performed by a method similar to that of Che, Fournier & Launey (1979). $Na_2MoO_4.2H_2O$ (39 g) was dissolved in 50 ml of dimethylformamide (DMF), acetic anhydride (48 ml) was added slowly and the solution stirred for 10 min. The solution was then acidified with 16 ml of 12 *N* HCl which caused the solution to become hot, whereupon it was filtered. A 1 *M* solution of bis(triphenylphosphine)iminium chloride in 50 ml of DMF was added to the yellow filtrate and stirred. The resulting yellow precipitate was filtered and washed with ether. Crystals of $[PPN]_2[Mo_6O_{19}]$ were obtained by dissolving the yellow precipitate in hot acetonitrile, filtering and cooling to 263 K.

Crystal data

$(C_{36}H_{30}NP_2)_2[Mo_6O_{19}]$
$M_r = 1956.74$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

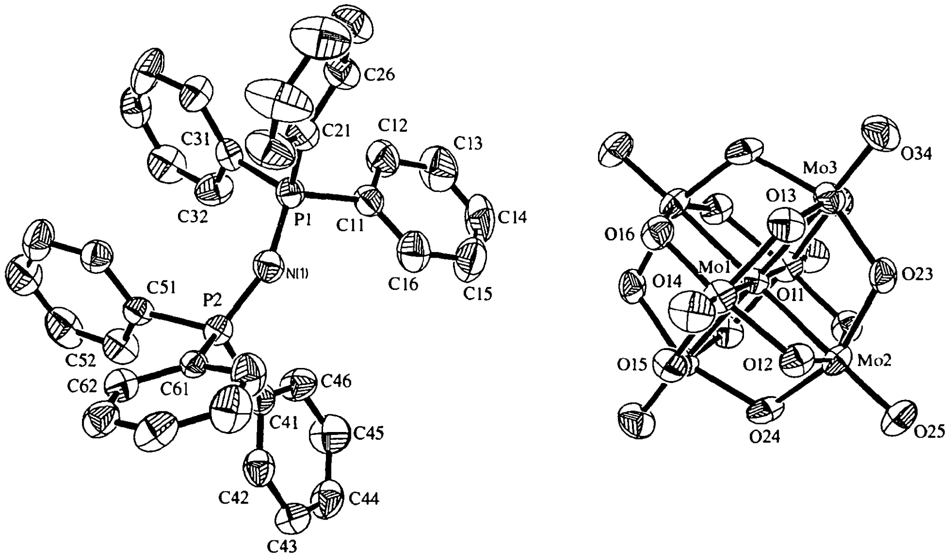


Fig. 1. View of the dianion and (unique) cation of $[PPN]_2[Mo_6O_{19}]$ showing the atomic labeling. The displacement ellipsoids are shown at the 50% probability level.

Triclinic
$P\bar{1}$
$a = 11.368\,(2)$ Å
$b = 13.490\,(3)$ Å
$c = 13.573\,(3)$ Å
$\alpha = 61.62\,(3)°$
$\beta = 84.55\,(3)°$
$\gamma = 87.83\,(3)°$
$V = 1823.0\,(7)$ Å^3
$Z = 1$
$D_x = 1.782$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 3.72–9.84°$
$\mu = 1.161$ mm^{-1}
$T = 223\,(2)$ K
Block
0.30 × 0.20 × 0.20 mm
Yellow

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
5300 measured reflections
5026 independent reflections
3804 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0261$
$\theta_{\rm max} = 24°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 0$
$l = -14 \rightarrow 13$
3 standard reflections monitored every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0471$
$wR(F^2) = 0.1228$
$S = 1.046$
5026 reflections
466 parameters
H-atom parameters were calculated and refined as a riding model with fixed $U_{\rm iso}$ values

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.6372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.613$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.730$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
Mo1	0.44052 (6)	0.89479 (6)	0.19077 (5)	0.0387 (2)
Mo2	0.69070 (5)	1.00442 (6)	0.04168 (5)	0.0396 (2)
Mo3	0.45904 (6)	1.16522 (6)	0.00910 (6)	0.0399 (2)
O11	1/2	1	0	0.0282 (14)
O12	0.6084 (4)	0.9207 (4)	0.1870 (4)	0.0434 (13)
O13	0.4176 (4)	1.0455 (4)	0.1627 (4)	0.0443 (13)
O14	0.4013 (5)	0.8160 (5)	0.3281 (4)	0.058 (2)
O15	0.4944 (4)	0.7808 (4)	0.1458 (4)	0.0450 (13)
O16	0.3027 (4)	0.9051 (4)	0.1199 (4)	0.0435 (13)
O23	0.6173 (4)	1.1399 (4)	0.0420 (4)	0.0427 (12)
O24	0.6925 (4)	0.8759 (4)	0.0218 (4)	0.0472 (13)
O25	0.8293 (5)	1.0108 (5)	0.0701 (5)	0.058 (2)
O34	0.4212 (5)	1.2818 (5)	0.0181 (5)	0.0568 (15)
N1	−0.1022 (5)	0.3801 (5)	0.3802 (5)	0.041 (2)
P1	−0.1693 (2)	0.4895 (2)	0.30282 (15)	0.0332 (4)
P2	−0.0758 (2)	0.2527 (2)	0.42102 (15)	0.0311 (4)
C11	−0.0655 (6)	0.5887 (6)	0.1958 (6)	0.039 (2)
C12	−0.0987 (8)	0.6667 (7)	0.0920 (7)	0.055 (2)
C13	−0.0139 (10)	0.7384 (8)	0.0112 (8)	0.074 (3)
C14	0.1004 (9)	0.7318 (8)	0.0328 (9)	0.071 (3)
C15	0.1339 (8)	0.6575 (8)	0.1354 (9)	0.071 (3)
C16	0.0503 (8)	0.5852 (7)	0.2174 (7)	0.057 (2)
C21	−0.2354 (6)	0.5480 (6)	0.3883 (6)	0.037 (2)
C22	−0.2550 (8)	0.4797 (8)	0.5020 (7)	0.064 (3)
C23	−0.3080 (10)	0.5239 (9)	0.5695 (7)	0.085 (4)
C24	−0.3394 (9)	0.6330 (9)	0.5238 (8)	0.074 (3)
C25	−0.3216 (8)	0.7016 (7)	0.4122 (7)	0.056 (2)
C26	−0.2709 (7)	0.6593 (6)	0.3435 (7)	0.045 (2)
C31	−0.2828 (6)	0.4678 (6)	0.2316 (6)	0.036 (2)
C32	−0.2513 (7)	0.4231 (7)	0.1587 (7)	0.051 (2)
C33	−0.3383 (8)	0.3985 (7)	0.1078 (7)	0.056 (2)
C34	−0.4530 (8)	0.4199 (7)	0.1287 (7)	0.055 (2)
C35	−0.4854 (7)	0.4637 (8)	0.1977 (7)	0.060 (2)
C36	−0.4008 (7)	0.4896 (7)	0.2494 (7)	0.048 (2)
C41	0.0673 (6)	0.2370 (6)	0.3617 (6)	0.037 (2)
C42	0.1470 (6)	0.1593 (6)	0.4285 (7)	0.044 (2)
C43	0.2592 (7)	0.1487 (7)	0.3817 (7)	0.051 (2)
C44	0.2899 (7)	0.2171 (7)	0.2692 (8)	0.055 (2)
C45	0.2135 (8)	0.2957 (8)	0.2034 (8)	0.064 (3)
C46	0.1035 (7)	0.3060 (7)	0.2493 (7)	0.049 (2)
C51	−0.1841 (6)	0.1824 (6)	0.3866 (6)	0.033 (2)
C52	−0.1517 (7)	0.1272 (6)	0.3232 (6)	0.045 (2)
C53	−0.2391 (9)	0.0789 (7)	0.2947 (7)	0.058 (2)
C54	−0.3568 (8)	0.0860 (7)	0.3271 (8)	0.061 (2)
C55	−0.3865 (7)	0.1390 (7)	0.3905 (7)	0.055 (2)
C56	−0.3017 (6)	0.1879 (6)	0.4208 (6)	0.043 (2)
C61	−0.0719 (5)	0.1803 (5)	0.5699 (5)	0.0284 (15)
C62	−0.1249 (6)	0.0753 (6)	0.6356 (6)	0.037 (2)
C63	−0.1144 (6)	0.0171 (7)	0.7500 (6)	0.045 (2)
C64	−0.0517 (6)	0.0636 (7)	0.7988 (6)	0.047 (2)
C65	0.0010 (8)	0.1668 (8)	0.7364 (7)	0.056 (2)
C66	−0.0098 (7)	0.2265 (7)	0.6210 (7)	0.051 (2)

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

Mo1—O14	1.673 (5)	Mo3—O24^{i}	1.971 (5)
Mo1—O16	1.882 (5)	Mo3—O11	2.3177 (8)
Mo1—O13	1.894 (5)	O11—Mo2^{i}	2.3017 (8)
Mo1—O12	1.945 (5)	O11—Mo3^{i}	2.3177 (8)
Mo1—O15	1.965 (5)	O11—Mo1^{i}	2.3287 (11)
Mo1—O11	2.3287 (11)	O15—Mo3^{i}	1.896 (5)
Mo2—O25	1.673 (5)	O16—Mo2^{i}	1.933 (5)
Mo2—O24	1.876 (5)	O24—Mo3^{i}	1.971 (5)
Mo2—O12	1.911 (5)	N1—P2	1.562 (6)
Mo2—O16^{i}	1.933 (5)	N1—P1	1.567 (6)
Mo2—O23	1.981 (5)	P1—C21	1.787 (7)
Mo2—O11	2.3017 (8)	P1—C31	1.794 (7)
Mo3—O34	1.671 (5)	P1—C11	1.800 (7)
Mo3—O23	1.874 (5)	P2—C61	1.782 (7)
Mo3—O15^{i}	1.896 (5)	P2—C41	1.796 (7)
Mo3—O13	1.961 (5)	P2—C51	1.803 (7)

O14—Mo1—O16	104.9 (3)	Mo2—O11—Mo2^{i}	180.0
O14—Mo1—O13	104.9 (2)	Mo2—O11—Mo3^{i}	89.77 (4)
O16—Mo1—O13	89.0 (2)	Mo2^{i}—O11—Mo3^{i}	90.23 (4)
O14—Mo1—O12	102.9 (2)	Mo2—O11—Mo3	90.23 (4)
O16—Mo1—O12	152.0 (2)	Mo2^{i}—O11—Mo3	89.77 (4)
O13—Mo1—O12	87.0 (2)	Mo3^{i}—O11—Mo3	180.0
O14—Mo1—O15	102.2 (2)	Mo2—O11—Mo1^{i}	89.84 (4)
O16—Mo1—O15	86.8 (2)	Mo2^{i}—O11—Mo1^{i}	90.16 (4)
O13—Mo1—O15	152.7 (2)	Mo3^{i}—O11—Mo1^{i}	90.25 (4)
O12—Mo1—O15	84.2 (2)	Mo3—O11—Mo1^{i}	89.75 (4)
O14—Mo1—O11	178.1 (2)	Mo2—O11—Mo1	90.16 (4)
O16—Mo1—O11	76.14 (15)	Mo2^{i}—O11—Mo1	89.84 (4)
O13—Mo1—O11	76.69 (15)	Mo3^{i}—O11—Mo1	89.75 (4)
O12—Mo1—O11	76.02 (14)	Mo3—O11—Mo1	90.25 (4)
O15—Mo1—O11	76.13 (14)	Mo1^{i}—O11—Mo1	180.000 (1)
O25—Mo2—O24	102.8 (2)	Mo2—O12—Mo1	116.5 (2)
O25—Mo2—O12	103.5 (2)	Mo1—O13—Mo3	117.3 (2)
O24—Mo2—O12	89.8 (2)	Mo3^{i}—O15—Mo1	116.2 (2)
O25—Mo2—O16^{i}	103.2 (2)	Mo1—O16—Mo2^{i}	117.9 (2)
O24—Mo2—O16^{i}	88.1 (2)	Mo3—O23—Mo2	116.2 (2)
O12—Mo2—O16^{i}	153.0 (2)	Mo2—O24—Mo3^{i}	115.9 (2)
O25—Mo2—O23	103.0 (2)	P2—N1—P1	149.3 (4)
O24—Mo2—O23	154.2 (2)	N1—P1—C21	108.0 (3)
O12—Mo2—O23	86.2 (2)	N1—P1—C31	114.6 (3)
O16^{i}—Mo2—O23	84.1 (2)	C21—P1—C31	108.3 (3)
O25—Mo2—O11	178.7 (2)	N1—P1—C11	109.2 (3)
O24—Mo2—O11	78.22 (15)	C21—P1—C11	109.8 (3)
O12—Mo2—O11	77.32 (15)	C31—P1—C11	106.8 (3)

O16$^{\rm i}$—Mo2—O11	75.88 (15)	N1—P2—C61	109.9 (3)
O23—Mo2—O11	76.01 (14)	N1—P2—C41	110.0 (3)
O34—Mo3—O23	105.3 (2)	C61—P2—C41	106.9 (3)
O34—Mo3—O15$^{\rm i}$	103.8 (2)	N1—P2—C51	113.6 (3)
O23—Mo3—O15$^{\rm i}$	90.5 (2)	C61—P2—C51	107.4 (3)
O34—Mo3—O13	102.5 (2)	C41—P2—C51	108.8 (3)
O23—Mo3—O13	87.1 (2)	C16—C11—C12	119.0 (7)
O15$^{\rm i}$—Mo3—O13	153.2 (2)	C16—C11—P1	119.1 (6)
O34—Mo3—O24$^{\rm i}$	101.0 (2)	C12—C11—P1	121.9 (6)
O23—Mo3—O24$^{\rm i}$	153.5 (2)	C22—C21—P1	119.0 (6)
O15$^{\rm i}$—Mo3—O24$^{\rm i}$	86.3 (2)	C26—C21—P1	122.4 (6)
O13—Mo3—O24$^{\rm i}$	84.1 (2)	C36—C31—P1	122.5 (6)
O34—Mo3—O11	176.6 (2)	C32—C31—P1	118.5 (6)
O23—Mo3—O11	77.59 (15)	C46—C41—P2	121.1 (6)
O15$^{\rm i}$—Mo3—O11	77.7 (2)	C42—C41—P2	120.8 (6)
O13—Mo3—O11	75.75 (14)	C66—C61—P2	119.6 (5)
O24$^{\rm i}$—Mo3—O11	76.05 (15)	C62—C61—P2	121.5 (5)

Symmetry code: (i) $1 - x, 2 - y, -z$.

Data collection: *TEXSAN* (Molecular Structure Corporation, 1990). Cell refinement: *TEXSAN*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BS1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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