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Bis[bis(triphenylphosphine)iminium] Decacarbonyldimolybdenum(*Mo—Mo*)

By Robert E. Bachman and Kenton H. Whitmire

Department of Chemistry, Rice University, PO Box 1892, *Houston, Texas* 77251, *USA*

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Abstract. $[C_{36}H_{30}NP_2]_2[Mo_2(CO)_{10}]$, $M_r = 1549.16$, triclinic, $P\bar{1}$, $a = 13.00\,(2)$, $b = 15.420\,(3)$, $c = 20.281\,(8)$ Å, $\alpha = 94.39\,(3)$, $\beta = 89.91\,(4)$, $\gamma = 114.65\,(4)$°, $V = 3683$ Å^3, $Z = 2$, $D_x = 1.397$ Mg m^{-3}, Mo $K\alpha$ radiation (graphite-crystal monochromator), $\lambda = 0.71069$ Å, $\mu = 1.19$ mm^{-1}, $F(000) = 1580.0$, $T = 193$ K, final conventional R factor = 0.054 for 5483 'observed' reflections and 901 variables. The title compound has been reported earlier in a solvated form which is monoclinic (No. 15). This sample, which was recrystallized from CH_3CN, contains no solvent of crystallization. The bis(triphenylphosphine)iminium, $[PPN]^+$, cations are as found in other structures. The structure shows $[PPN]^+$ cations and $[Mo_2(CO)_{10}]^{2-}$ anions in a 2:1 ratio. The metal–carbonyl anion contains a metal–metal bond of 3.153 (2) Å. The carbonyl ligands are arranged in a staggered conformation giving an approximate overall symmetry of D_{4d} for the anion.

Table 1. *Selected atomic coordinates and equivalent isotropic displacement parameters* (Å$^2 \times 10^2$) *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mo(1)	0.03423 (7)	0.12643 (6)	0.74333 (4)	2.58 (4)
Mo(2)	−0.07288 (7)	−0.09895 (6)	0.73926 (4)	2.72 (4)
O(11)	−0.1838 (7)	0.1114 (7)	0.8199 (4)	7.5 (5)
O(12)	0.1355 (6)	0.1067 (5)	0.8803 (3)	4.4 (3)
O(13)	0.2441 (6)	0.1045 (5)	0.6758 (3)	4.5 (3)
O(14)	−0.0978 (7)	0.1007 (5)	0.6066 (4)	5.6 (4)
O(15)	0.1648 (6)	0.3474 (5)	0.7425 (4)	5.1 (4)
O(21)	−0.3014 (6)	−0.0926 (6)	0.6907 (4)	5.7 (4)
O(22)	−0.1403 (7)	−0.0666 (6)	0.8872 (4)	5.6 (4)
O(23)	0.1786 (6)	−0.0556 (4)	0.7858 (3)	3.5 (3)
O(24)	0.0094 (6)	−0.0877 (5)	0.5914 (4)	5.1 (4)
O(25)	−0.1530 (6)	−0.3189 (5)	0.7455 (4)	5.8 (4)
C(11)	−0.107 (1)	0.1166 (8)	0.7929 (6)	4.6 (5)
C(12)	0.0989 (8)	0.1138 (6)	0.8302 (5)	2.9 (4)
C(13)	0.1669 (9)	0.1110 (7)	0.6968 (5)	3.3 (4)
C(14)	−0.0485 (9)	0.1092 (7)	0.6560 (5)	3.5 (5)
C(15)	0.1124 (8)	0.2650 (7)	0.7438 (5)	3.1 (4)
C(21)	−0.2187 (9)	−0.0949 (7)	0.7077 (5)	3.8 (5)
C(22)	−0.1154 (8)	−0.0783 (7)	0.8333 (6)	3.8 (5)
C(23)	0.0872 (9)	−0.0720 (6)	0.7691 (4)	2.6 (4)
C(24)	−0.0207 (8)	−0.0928 (7)	0.6454 (5)	3.2 (4)
C(25)	−0.1248 (8)	−0.2367 (8)	0.7428 (5)	4.0 (5)

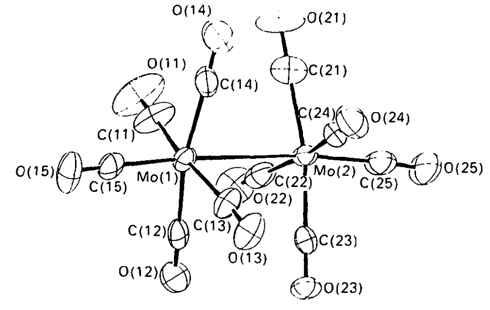

Fig. 1. *ORTEP*II (Johnson, 1976) representation showing the metal dimer and the atomic numbering scheme.

Experimental. The material was obtained from the reaction of $Mo(CO)_6$ with a mixture of sodium and bismuth in liquid ammonia and was recrystallized from a concentrated solution of CH_3CN held at 253 K for several days. An orange cut wedge, 0.30 × 0.20 × 0.20 mm, mounted on a glass fiber, was used for data collection with a Rigaku AFC-5*S* single-crystal diffractometer, Mo $K\alpha$ radiation and graphite-crystal monochromator. Unit-cell dimensions were determined from angular settings of 25 reflections with 2θ between 7 and 15°. The space group was determined to be $P\bar{1}$ from the lack of systematic absences and subsequent structure solution and refinement. 10041 reflections were measured ($0 < h < 36$, $-17 < k < 17$, $-26 < l < 26$; $4.0 < 2\theta < 55.0$°), of which 9530 were unique ($R_{int} = 4.9\%$) and 5483 were classified as observed with $I > 3\sigma(I)$. ω–2θ scans were employed with an 8.0° min^{-1} scan rate. Weak reflections [$I < 10\sigma(I)$] were rescanned (maximum two rescans) and the counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. Crystal and diffractometer stability were checked by monitoring three standard reflections every 150 reflections. Only random deviations (±0.6%) were observed over the course of data collection. No decay correction was applied. Empirical absorption correction, based on ψ scans, was applied with correction factors ranging from 0.78 to 1.00. The data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods and Fourier synthesis using

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the *TEXSAN*2.0 program package (Molecular Structure Corporation, 1989).

During the final stages of refinement the positional and anisotropic thermal parameters of all non-H atoms were refined. All H atoms were included in calculated positions. The final conventional agreement factors were $R = 0.054$, $wR = 0.058$ and $S = 1.57$ for the 5483 observed reflections and 901 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/\sigma^2(F_o)$ and $\sigma(F_o)$ from counting statistics. The maximum shift/e.s.d. in the last full-matrix least-squares cycle was less than 0.0008. The final difference Fourier map showed no peaks higher than 0.73 or deeper than -0.75 e Å^{-3}. All programs used in the structure solution and refinement are contained in the *TEXSAN*2.0 package. The plot was made using *ORTEP*II (Johnson, 1976). The atomic scattering factors included with the software package are from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final positional and displacement parameters for the metal anion are provided in Table 1.[*] Table 2 contains selected bond metricals. Fig. 1 illustrates the metal coordination and the numbering scheme. Fig. 2 shows the unit-cell packing.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Mo(1)—Mo(2)	3.153 (2)	O(11)—C(11)	1.12 (1)
Mo(1)—C(11)	2.05 (1)	O(12)—C(12)	1.15 (1)
Mo(1)—C(12)	2.01 (1)	O(13)—C(13)	1.13 (1)
Mo(1)—C(13)	2.06 (1)	O(14)—C(14)	1.16 (1)
Mo(1)—C(14)	2.02 (1)	O(15)—C(15)	1.17 (1)
Mo(1)—C(15)	1.94 (1)	O(21)—C(21)	1.15 (1)
Mo(2)—C(21)	2.03 (1)	O(22)—C(22)	1.16 (1)
Mo(2)—C(22)	2.02 (1)	O(23)—C(23)	1.15 (1)
Mo(2)—C(23)	2.03 (1)	O(24)—C(24)	1.16 (1)
Mo(2)—C(24)	2.01 (1)	O(25)—C(25)	1.17 (1)
Mo(2)—C(25)	1.95 (1)		

Mo(2)—Mo(1)—C(11)	85.4 (3)	C(21)—Mo(2)—C(22)	88.4 (4)
Mo(2)—Mo(1)—C(12)	81.6 (3)	C(21)—Mo(2)—C(23)	167.6 (4)
Mo(2)—Mo(1)—C(13)	84.6 (3)	C(21)—Mo(2)—C(24)	89.8 (4)
Mo(2)—Mo(1)—C(14)	86.5 (3)	C(21)—Mo(2)—C(25)	99.7 (4)
Mo(2)—Mo(1)—C(15)	175.1 (3)	C(22)—Mo(2)—C(23)	91.6 (4)
C(11)—Mo(1)—C(12)	87.3 (4)	C(22)—Mo(2)—C(24)	169.2 (4)
C(11)—Mo(1)—C(13)	169.7 (4)	C(22)—Mo(2)—C(25)	93.8 (4)
C(11)—Mo(1)—C(14)	90.5 (4)	C(23)—Mo(2)—C(24)	87.9 (4)
C(11)—Mo(1)—C(15)	99.3 (4)	C(23)—Mo(2)—C(25)	92.7 (4)
C(12)—Mo(1)—C(13)	88.9 (4)	C(24)—Mo(2)—C(25)	97.0 (4)
C(12)—Mo(1)—C(14)	168.0 (4)	Mo(1)—C(11)—O(11)	180 (1)
C(12)—Mo(1)—C(15)	97.3 (4)	Mo(1)—C(12)—O(12)	179.4 (8)
C(13)—Mo(1)—C(14)	91.3 (4)	Mo(1)—C(13)—O(13)	174.8 (9)
C(13)—Mo(1)—C(15)	90.7 (4)	Mo(1)—C(14)—O(14)	178.0 (9)
C(14)—Mo(1)—C(15)	94.7 (4)	Mo(1)—C(15)—O(15)	176.0 (8)
Mo(1)—Mo(2)—C(21)	86.4 (3)	Mo(2)—C(21)—O(21)	179.1 (9)
Mo(1)—Mo(2)—C(22)	84.6 (3)	Mo(2)—C(22)—O(22)	179.7 (9)
Mo(1)—Mo(2)—C(23)	81.3 (3)	Mo(2)—C(23)—O(23)	179.1 (8)
Mo(1)—Mo(2)—C(24)	84.7 (3)	Mo(2)—C(24)—O(24)	178.9 (9)
Mo(1)—Mo(2)—C(25)	173.7 (3)	Mo(2)—C(25)—O(25)	178.2 (9)

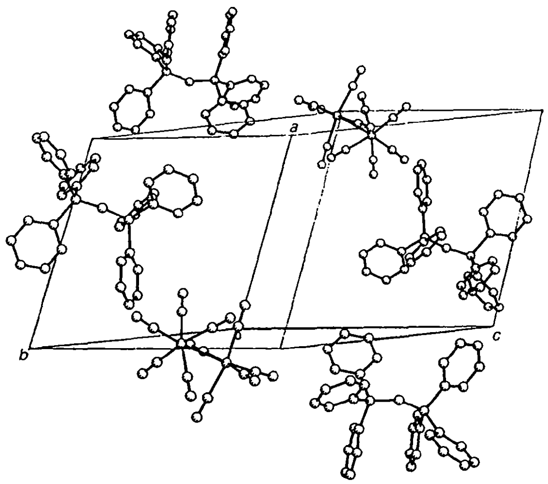

Fig. 2. Packing diagram of the unit cell.

Related literature. A previous report of the CH_2Cl_2-solvated structure has appeared (Handy, Ruff & Dahl, 1970).

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[*] Lists of all atom coordinates, anisotropic displacement parameters, complete bond distances and angles, and observed and calculated structure factors, as well as *ORTEP*II (Johnson, 1976) plots of the countercations, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55523 (94 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0598]