Dimolybdenum Tetraacetate

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Abstract. The structure of this compound, previously reported in part by Lawton & Mason [*J. Amer. Chem. Soc.* (1965). **87**, 921–922] has been redetermined using more extensive, counter-diffractometer data. Crystals are triclinic, $P\bar{1}$, $a = 8 \cdot 418$ (2), $b = 5 \cdot 500$ (1), $c = 7 \cdot 529$ (1) Å, $\alpha = 84 \cdot 13$ (2), $\beta = 105 \cdot 24$ (2), $\gamma = 106 \cdot 00$ (2)°, 22 °C; $M = 428 \cdot 05$; $Z = 1$; $D_x = 2 \cdot 20$ g cm^{-3}. The Mo–Mo distance now obtained is $2 \cdot 0934$ (8) Å and the intermolecular O$\cdots$Mo contacts are $2 \cdot 645$ (4) Å.

Introduction. Dimolybdenum tetraacetate is a compound of unique significance in the field of metal-to-metal multiple bonds, since it is the precursor of nearly all of the known compounds containing Mo $\overset{4^\circ}{-}$ Mo (quadruple) bonds. Its partial structure was reported by Lawton & Mason (1965) nearly a decade ago, but many details were omitted and the accuracy was low by present standards. Two particularly important questions which remained unsettled by the published report are: (1) Is the Mo–Mo distance in this compound [reported as $2 \cdot 11$ (1) Å] really different from that [$2 \cdot 090$ (4) Å] in $Mo_2(O_2CCF_3)_4$ (Cotton & Norman 1971)? (2) Are the $Mo_2(O_2CCH_3)_4$ molecules packed so as to give slightly bonding intermolecular Mo$\cdots$O contacts, as in the case of $Mo_2(O_2CCF_3)_4$ where the distance is $2 \cdot 72$ (1) Å and in $K_4[Mo_2(SO_4)_4] \cdot 2H_2O$ where it is $2 \cdot 593$ Å (Angell, Cotton, Frenz & Webb, 1973)? A redetermination of the structure was undertaken to answer these questions and to provide a complete set of structural parameters.

A Syntex $P\bar{1}$ computer-controlled four-circle diffractometer equipped with a graphite-crystal monochromator in the incident beam was used for data collection. A needle-shaped crystal with dimensions $0 \cdot 045 \times 0 \cdot 025 \times 0 \cdot 021$ cm was selected and a triclinic unit cell, similar to that previously reported, was

obtained. Least-squares refinement of 15 reflections provided the orientation matrix for data collection and resulted in the following cell parameters: $a = 8 \cdot 418$ (2), $b = 5 \cdot 500$ (1), $c = 7 \cdot 529$ (1) Å, $\alpha = 84 \cdot 13$ (2), $\beta = 105 \cdot 24$ (2), $\gamma = 106 \cdot 00$ (2)° and $V = 323 \cdot 15$ (1) Å^3. For $Z = 1$ the calculated density is $2 \cdot 20$ g cm^{-3}, in good agreement with the experimental value of $2 \cdot 18$ g cm^{-3} determined by flotation in a mixture of bromoform and cyclohexane.

Data were collected in the range of $0° < 2\theta < 60°$ using Mo $K\alpha$ radiation. The $\theta/2\theta$ scan technique with variable scan rate from 4–24° min^{-1} has been used. The scan range was from 2θ(Mo $K\alpha_1$) $- 0 \cdot 9°$ to 2θ(Mo $K\alpha_2$) $+ 0 \cdot 9°$.

The stabilities of the crystal and the instrument were checked by periodic remeasurements of three standard reflections. No significant changes in these intensities were observed.

A total of 1909 reflections were collected and the usual data reduction procedures were applied.* The parameter 'p' used in the calculation of standard deviations of intensities $[\sigma(F_o^2)]$† was assigned the value $0 \cdot 07$.

Table 1. *Positional and anisotropic thermal parameters for non-hydrogen atoms*

The numbers in parentheses in this and the other tables are the estimated standard deviations in the least significant digits. The anisotropic temperature parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	0·04395 (6)	0·16735 (8)	0·07307 (6)	0·01016 (8)	0·01295 (16)	0·01091 (9)	0·00340 (8)	0·00134 (6)	−0·00261 (8)
O(1)	−0·1754 (6)	0·0809 (8)	0·1772 (6)	0·0128 (7)	0·0240 (15)	0·0146 (8)	0·0051 (8)	0·0045 (6)	−0·0038 (9)
O(2)	−0·0766 (5)	0·3644 (7)	−0·1600 (6)	0·0127 (7)	0·0166 (13)	0·0125 (8)	0·0046 (8)	0·0015 (6)	−0·0020 (8)
O(3)	0·2687 (6)	0·2754 (8)	−0·0214 (7)	0·0115 (7)	0·0221 (15)	0·0166 (9)	0·0018 (8)	0·0028 (6)	−0·0028 (9)
O(4)	0·1697 (6)	−0·0069 (8)	0·3127 (6)	0·0152 (8)	0·0180 (14)	0·0128 (8)	0·0068 (8)	0·0003 (6)	−0·0041 (8)
C(1)	−0·2869 (8)	−0·1273 (13)	0·1296 (9)	0·0119 (10)	0·0292 (23)	0·0157 (12)	0·0083 (13)	0·0028 (9)	0·0019 (13)
C(2)	−0·1561 (8)	0·2426 (11)	−0·3077 (8)	0·0122 (9)	0·0233 (20)	0·0123 (10)	0·0059 (11)	0·0034 (8)	−0·0019 (11)
C(3)	−0·4438 (9)	0·1974 (17)	0·2040 (11)	0·013 (1)	0·046 (3)	0·022 (2)	0·005 (2)	0·009 (1)	−0·001 (2)
C(4)	−0·2329 (10)	0·3802 (14)	−0·4760 (9)	0·021 (1)	0·029 (2)	0·012 (1)	0·012 (1)	0·000 (1)	−0·001 (1)

Since the linear absorption coefficient was relatively low ($\mu = 19 \cdot 17$ cm^{-1}, Mo $K\alpha$) absorption corrections were omitted.

A three-dimensional Patterson function was calculated and from this (assuming space group $P\bar{1}$) one Mo and four oxygen atoms were immediately located.
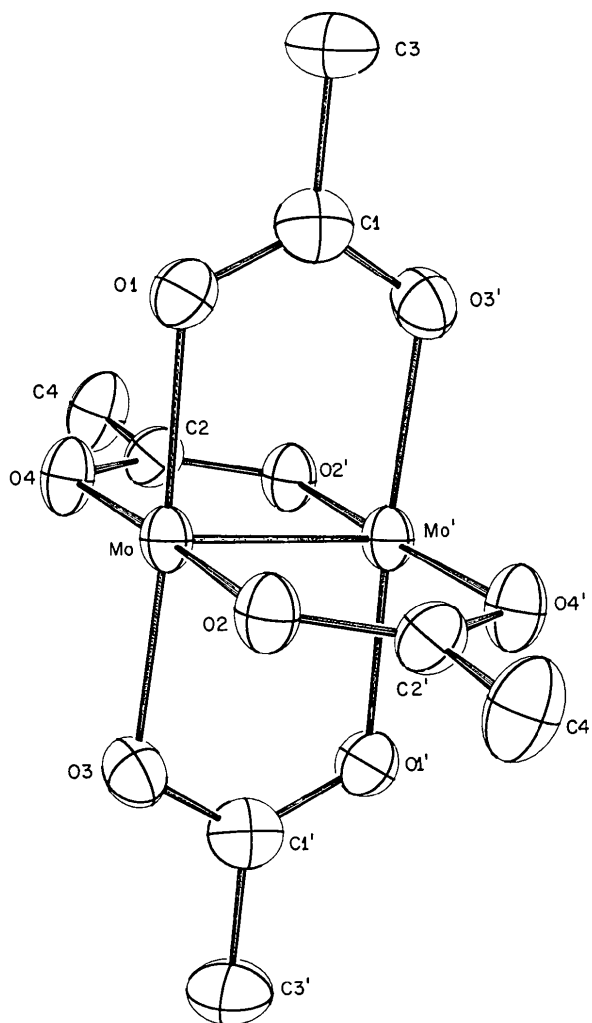

Fig. 1. An *ORTEP* drawing of the Mo$_2$(O$_2$CCH$_3$)$_4$ structure. Each atom is represented by its ellipsoid of thermal motion drawn to enclose 30 % of the electron density. The molecule has a center of inversion, $\bar{1}$, and the primed and corresponding unprimed numbers are related by $\bar{1}$.

The structure was solved and refined by the usual combination of least-squares refinements and difference-Fourier syntheses. In the least-squares refinement, in which $\sum w(|F_o| - |F_c|)^2$ was minimized, only those 1526 reflections were employed for which $F_o^2 > 3\sigma(F_o^2)$. Three cycles of least-squares refinement using isotropic temperature parameters of one molybdenum and four oxygen atoms resulted in $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0 \cdot 159$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w F_o^2]^{1/2} = 0 \cdot 215$. A difference Fourier synthesis then provided the locations of the carbon atoms. Five cycles of refinement using anisotropic temperature factors on all non-hydrogen atoms resulted in full convergence and gave $R_1 = 0 \cdot 047$ and $R_2 = 0 \cdot 062$. Parameter changes in the last cycle were all less than 0·05 times the estimated standard deviation of that parameter. There were only three pairs of parameters [all between the scale factor and β_{11}(Mo), β_{22}(Mo) and β_{33}(Mo)] where the correlation coefficients slightly exceeded 0·5. The standard deviation in an observation of unit weight was 1·18.

Of the 1526 reflections used in the least-squares refinement there were only 40 for which $||F_o| - |F_c||$ slightly exceeded $3\sigma(F_o^2)$. The $12\bar{1}$ reflection suffered from extinction.

In the final difference Fourier map the heighest peak had a density of 1·67 e Å^{-3} and there were four other peaks, with densities exceeding 1 e Å^{-3}. These five peaks appeared at distances of 0·8 to 1·2 Å from the

Table 2. *Interatomic distances and angles*

Intramolecular distances (Å)		Bond angles (°)	
Mo –Mo	2·0934 (8)	Mo'—Mo—O(1)	91·7 (1)
Mo –O(1)	2·110 (4)	Mo'—Mo—O(2)	90·4 (1)
Mo –O(2)	2·137 (4)	Mo'—Mo—O(3)	92·0 (1)
Mo –O(3)	2·107 (5)	Mo'—Mo—O(4)	93·2 (1)
Mo –O(4)	2·121 (4)	O(1)—Mo—O(3)	176·3 (2)
C(1)–O(1)	1·279 (8)	O(2)—Mo—O(4)	176·5 (2)
C(1)–O(3')	1·272 (8)	O(1)—Mo—O(2)	90·9 (2)
C(2)–O(4)	1·273 (7)	O(1)—Mo—O(4)	89·2 (2)
C(2)–O(2')	1·284 (7)	O(2)—Mo—O(3)	89·1 (2)
C(1)–C(3)	1·507 (9)	O(3)—Mo—O(4)	90·6 (2)
C(2)–C(4)	1·496 (9)	Mo—O(1)–C(1)	117·2 (4)
		Mo—O(2)–C(2')	118·5 (4)
Intermolecular distance (Å)		Mo—O(3)–C(1')	117·3 (4)
Mo –O(2)	2·645 (4)	Mo—O(4)–O(2)	117·1 (4)
		O(1)—C(1)–O(3')	121·8 (6)
		O(4)—C(2)–O(2')	120·8 (5)
		O(1)—C(1)–C(3)	118·7 (6)
		O(2')—C(2)–C(4)	119·4 (5)
		O(3')—C(1)–C(3)	119·5 (5)
		O(4)—C(2)–C(4)	119·4 (5)

Table 3. *Least-squares planes*

(a) Equations of planes

x, y and z are fractional triclinic coordinates.

(1)	O(1), O(3'), O(1'), O(3)	$3 \cdot 311x - 2 \cdot 873y + 4 \cdot 588z - 0 = 0$
(2)	O(2), O(4), O(2'), O(4')	$-7 \cdot 642x + 0 \cdot 216y + 4 \cdot 151z - 0 = 0$
(3)	O(1), O(2), O(3), O(4)	$-0 \cdot 321x + 4 \cdot 576y + 3 \cdot 762z - 1 \cdot 0916 = 0$

(b) Dihedral angles

Planes (1) and (2)	90·8°
Planes (1) and (3)	91·3
Planes (2) and (3)	89·7

Mo atom. Another difference Fourier map where all reflections beyond $\sin \theta/\lambda = 0.35$ were excluded provided densities less than 0.8 e Å^{-3}. In this map there were peaks at locations reasonable for hydrogen atoms, but attempts at refinement failed.

Atomic scattering factors for Mo, C and O were taken from Cromer (1974) and the anomalous dispersion corrections for Mo were obtained from Cromer & Liberman (1970).

The positional thermal parameters are reported in Table 1. Fig. 1 shows the structure and the atom numbering scheme. The bond distances (as well as the one important intermolecular contact) and the bond angles are listed in Table 2. The important least-squares planes are defined in Table 3. A table of structure factors is available.*

Discussion. The structure is in very close agreement with that of $Mo_2(O_2CCF_3)_4$. The two Mo–Mo distances, 2.093 (1) and 2.090 (4) Å are the same to within ± 0.005 Å, despite the difference in the basicities of the CH_3COO^- and CF_3COO^- ligands. The average values of the other principal dimensions of this structure, viz. Mo–O, 2.12 ± 0.01; C–O, 1.280 ± 0.005; C–C, 1.501 ± 0.005 Å; Mo–Mo–O, 91.8 ± 0.8; O–C–O, $121.3 \pm 0.5°$, all agree closely with the corresponding dimensions of the $Mo_2(O_2CCF_3)_4$ structure. These dimensions would be suitable for use in molecular-orbital calculations or vibrational analyses.

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30598 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The $Mo_2(O_2CCH_3)_4$ molecules are strung together in infinite chains in essentially the same way as the $Mo_2(O_2CCF_3)_4$ molecules. The oxygen atoms O(2) and O(2') each make a contact that is essentially coaxial with the Mo–Mo bond to the closest Mo atom of the adjacent molecule. The $O \cdots Mo$ distance in this case, 2.645 (4) Å, is similar to those in $Mo_2(O_2CCF_3)_4$, 2.71 (1) Å, and $K_4[Mo_2(SO_4)_4] . 2H_2O$, 2.593 Å.

The fact that the Mo–Mo distance in the two carboxylato compounds (2.092 Å) is significantly (in a statistical sense) shorter than that [2.110 (3) Å] in the $[Mo_2(SO_4)_4]^{4-}$ ion may be due to the smaller 'bite' of the RCO_2^- ligand as compared to that of the SO_4^{2-} ligand. On the other hand, since Mo–Mo distances in various salts of the $Mo_2Cl_8^{4-}$ ion vary over a range of ca. 0.02 Å, (cf. Angell et al., 1973), there may not be any such simple explanation.

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Benzidine–s-Trinitrobenzene Solvent-Free Molecular Complex

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Abstract. Orthorhombic, *Pbna*, $a = 14.767$ (6), $b = 17.574$ (7), $c = 7.087$ (2) Å, $C_{12}H_{12}N_2 . C_6H_3N_3O_6$, $Z = 4$, $D_x = 1.44$, $D_m = 1.44$ g cm^{-3}. Crystals were grown from a chloroform solution. Benzidine and s-trinitrobenzene are alternately stacked along **c** to form molecular columns. The two benzene rings in benzidine are twisted about the inter-ring bond. The nitro groups in s-trinitrobenzene are not in the plane of the benzene ring.

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Introduction. From the systematic absences in preliminary Weissenberg and precession photographs ($k = 2n + 1$ for $0kl$, $h + l = 2n + 1$ for $h0l$ and $h = 2n + 1$ for $hk0$) the space group was determined to be *Pbna*. Very weak diffuse streaks elongated along the a^* axis were observed around the 112, 212, 022, 122, 222, 024, 124, 134, 234, 044, 154, 136, 046, 146, 156 and 066 reflexions on the Weissenberg and precession photographs. These diffuse streaks were neglected in the structure analysis.

The precise cell constants and intensity data were measured on a Rigaku four-circle automatic diffractometer using Mo $K\alpha$ radiation. 700 independent