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# *cis*-Dioxo[2,2′-oxydiethanolato(2—)-*O*,*O*′,*O*′′]molybdenum(VI), [Mo($C_4H_8O_3$)$O_2$]

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**Abstract.** $M_r = 232\cdot0$, orthorhombic, $Pmn2_1$, $a = 10\cdot487\,(4)$, $b = 4\cdot109\,(1)$, $c = 7\cdot655\,(3)$ Å, $V = 329\cdot86$ Å$^3$, $D_m$ (flotation) $= 2\cdot34$, $D_x = 2\cdot34$ Mg m$^{-3}$, $Z = 2$, $\mu$(Mo $K\alpha$) $= 1\cdot916$ mm$^{-1}$, $\lambda$(Mo $K\alpha$) $= 0\cdot7107$ Å, $T = 298$ K, $R = 0\cdot088$ for 299 observed reflections. This complex consists of a *cis*-dioxomolybdenum(VI) core with a doubly deprotonated *mer*-coordinated tridentate oxydiethanolato ligand. The sixth Mo coordination position is filled through a long-range interaction with a terminal O atom of an adjacent molecular unit.

**Introduction.** The title compound is formed through the Schultheis condensation of 2,2′-oxydiethanol (digol), $HOCH_2CH_2OCH_2CH_2OH$, with molybdenum trioxide. Elemental analyses were consistent with a composition $MoO_2(C_4H_8O_3)$, but the infrared spectrum did not indicate the structure of the compound (Knobler, Penfold, Robinson, Wilkins & Yong, 1980). If the ligand were tridentate through formation of two five-membered chelate rings (a structure which would normally preclude bridging by ligand O), it is not clear how the Mo might attain its preferred six-coordination. There is a strong infrared band at 847 cm$^{-1}$ which is typical neither of the usual *cis*-dioxo core (890–940 cm$^{-1}$) nor of a symmetrical Mo—O—Mo core-oxygen bridge (750–790 cm$^{-1}$). The crystal structure determination was made to resolve the question.

**Experimental.** The compound was recrystallized by slow cooling (from 433 K) of a solution in the ligand. Systematic absences in the precession photographs could not distinguish between space groups $Pmn2_1$ and *Pmmn*, but the alternative chosen was the noncentrosymmetric $Pmn2_1$ (*a*) because intensity statistics did not indicate the presence of a centre of inversion and (*b*) because *Pmmn* would have required the Mo atoms to be on sites of *mm* symmetry and coordinated with a planar ligand, a highly unlikely chemical situation. The choice of space group was confirmed by the successful structure refinement without anomalies. Crystal used for intensity measurements was pyramidal with sides 0·18 mm and height 0·08 mm, Hilger & Watts four-circle diffractometer, Zr-filtered Mo $K\alpha$ radiation, $\theta$–$2\theta$ scans, 364 reflections recorded, $0 < 2\theta < 46°$, 299 with $I > 3\sigma(I)$ used in the analysis; detailed procedures for data collection and assignment of errors were as described by Countryman & Penfold (1972); corrections for absorption not applied, since correction coefficients fell within the narrow range 1·20–1·25; the position of the Mo atom obtained from the Patterson function and used for initial phasing; the nine remaining non-hydrogen atoms located from subsequent electron density maps; least-squares refinement carried out with anisotropic temperature factors for the C atoms, with inclusion of methylene H atoms as members of rigid groups at C—H = 1·0 Å; the *R* value from minimization of the function $\sum w||F_o| - |F_c||^2$ was 0·088 for 35 parameters based on 299 reflections; unit weights; $F(000) = 228$; scattering factors for Mo, C and O from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections from Cromer & Liberman (1970); structure solution and refinement calculations carried out with *SHELX* (Sheldrick, 1976).

**Discussion.** Positional and isotropic thermal parameters are listed in Table 1, and interatomic distances and angles in Table 2.† The structure analysis has shown the complex to be of formula $MoO_2(C_4H_8O_3)$, with *mer* coordination of the tridentate ligand which develops two equivalent buckled five-membered rings (Fig. 1). The rings are related by a mirror plane which also contains O(1) and O(2) of the *cis*-dioxo core. The sixth Mo coordination position is satisfied by a long-range [2·38 (2) Å] linear-bridging interaction with the core oxygen O(1*) (Fig. 1) of the corresponding 'molecule' in an adjacent unit cell. In the extended structure the molecular units are linked through such bridges into columns parallel to the *b* axis of the cell (Fig. 2). This bridging by a 'terminal' O atom ($O_t$) of the *cis*-dioxo core modifies the Mo—$O_t$ bond lengths; Mo—O(2) has a value of 1·63 (4), but Mo—O(1) is increased to 1·73 (2) Å.

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† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38210 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (× 10³) *and isotropic thermal parameters* (× 10³)

| | *x* | *y* | *z* | *U*(Å²)* |
|---|---|---|---|---|
| Mo | 0 | 176 (1) | 0 | 32 (1)† |
| O(1) | 0 | −245 (6) | 4 (9) | 39 (9)† |
| O(2) | 0 | 243 (8) | −209 (6) | 50 (17)† |
| O(3) | 164 (2) | 263 (5) | 59 (2) | 50 (8)† |
| O(4) | 0 | 198 (8) | 291 (4) | 40 (12)† |
| C(1) | 213 (3) | 234 (7) | 245 (4) | 36 (8) |
| C(2) | 113 (3) | 331 (9) | 364 (4) | 45 (8) |

* *U* values are mean-square amplitudes of vibration.

† Equivalent isotropic values for atoms refined anisotropically.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

O(1*) is in the adjacent unit cell along the *b* axis.

| | | | |
|---|---|---|---|
| Mo—O(1) | 1·73 (2) | Mo—O(1*) | 2·38 (2) |
| Mo—O(2) | 1·63 (4) | O(3)—C(1) | 1·52 (3) |
| Mo—O(3) | 1·82 (2) | C(1)—C(2) | 1·44 (4) |
| Mo—O(4) | 2·23 (3) | C(2)—O(4) | 1·42 (4) |
| O(1)—Mo—O(1*) | 178 (1) | O(3)—Mo—O(3′) | 143·2 (6) |
| O(1)—Mo—O(2) | 101 (3) | O(3)—Mo—O(4) | 75·3 (6) |
| O(1)—Mo—O(3) | 101 (1) | C(1)—O(3)—Mo | 122 (2) |
| O(1)—Mo—O(4) | 91 (2) | C(2)—C(1)—O(3) | 109 (2) |
| O(2)—Mo—O(3) | 102 (2) | O(4)—C(2)—C(1) | 105 (3) |
| O(2)—Mo—O(4) | 168 (1) | C(2)—O(4)—C(2′) | 114 (3) |

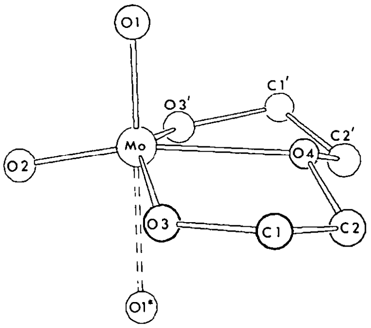

Fig. 1. The molecular unit showing the symmetry *m* and the bridging.

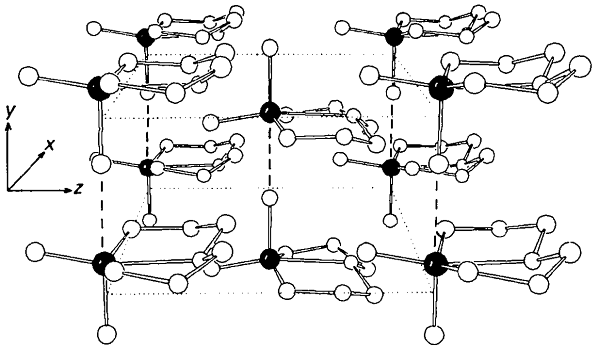

Fig. 2. The packing within the crystal, with the edges of the unit cell dotted. The Mo—O(1*) interactions between molecular units are dashed.

This type of asymmetric bridging is uncommon in complexes, but occurs in $MoO_2Cl_2.H_2O$ (Schröder & Christensen 1972) and it has recently been suggested by Rajan & Chakravorty (1981) specifically with reference to *mer*-coordinated ligands. It occurs also in crystalline molybdenum trioxide (Kihlborg, 1963). Here the chain-forming octahedra are linked laterally through asymmetric bridges, with *l*(Mo—O) values 1·73 (2) and 2·25 (2) Å, to form layers.

The present complex shows the usual long bonding *trans* to $O_t$. Thus the bond Mo—O(4) in the *trans* position linking the ether group is 2·23 (3) Å, while the *cis* Mo—O(3) bond to the alkoxide oxygen ($O_a$) is only 1·82 (2) Å. The latter bond may be compared with that of a corresponding bond of length 1·86 (1) Å formed *cis* to Mo—$O_t$ in the (pinacolato)molybdenum(VI) complex $Mo_2O_3(C_6H_{12}O_2)_2(C_6H_{13}O_2)_2$ with symmetrical core-oxygen bridging (Matheson & Penfold, 1979). The digolato and pinacolato complexes bear the formal analogy of both having only one non-bridging '$O_t$' atom per Mo. For *cis*-dioxo diolato complexes, $MoO_2L_2$, without bridging, Mo—$O_a$ lengths in the range 1·93–1·98 Å have been reported (Schröder, 1975; Schröder, Scherle & Hazell, 1975; Butcher, Penfold & Sinn, 1979). The shorter Mo—$O_a$ bonds in the bridged digolato and pinacolato compounds presumably result from an increase in the $\pi$ character of these bonds due to decreased competition by the core O atoms for the available $d\pi$ metal orbitals, and also from the absence of hydrogen bonding which would produce counter-lengthening.

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