The Structure of *cis*-Dioxobis-(2-hydroxyethyl-1-oxo)molybdenum(VI)*

By F. A. Schröder† and J. Scherle

Lehrstuhl I für Anorganische Chemie der Universität, D-7800 Freiburg i. Br., Albertstrasse 21, *Germany* (*BRD*)

and Rita G. Hazell

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

The crystal structure of $MoO_2(OC_2H_4OH)_2$, the first known alkoxide of Mo^{VI}, without a halide atom, has been determined from counter data. The compound is tetragonal, space group $P4_1$ ($P4_3$), with $a=$ 9·555, $c=17·398$ Å, $Z=8$. The structure was solved by Patterson methods and refined to $R=0·049$ for 1940 independent reflexions. The crystal contains isolated molecules connected by hydrogen bonds. The Mo is coordinated by six O atoms with two short, two medium and two long Mo–O bonds. Two MoO_2C_2 five-membered rings exist in each molecule.

Introduction

The preparation of the title compound by reaction of MoO_3 with ethylene glycol has been described by Schröder & Scherle (1973). Solutions in water showed a *p*H of 2–3. In order to discover whether there are acidic C–OH groups or Mo–OH groups (not yet known to exist), both of which were possible according to other information, we investigated the crystal structure. Further results from this compound are given elsewhere (Schröder & Scherle, 1975). The structure of the different (in formula and structure) W alkoxide of ethylene glycol has also been determined (Scherle & Schröder, 1974).

Experimental

The crystals were obtained as colourless tetragonal unequal bipyramids by recrystallization from ethanol. Precise lattice parameters were determined from a Guinier powder photograph by least-squares calculations. The crystal data are: $MoO_2(OCH_2CH_2OH)_2$; M.W. 250·06; m.p. (under N_2) 179–181 °C (dec.). Tetragonal; $Z=8$; $D_m=2·06$; $D_x=2·09$ g cm^{-3}. $a=9·555$ (2), $c=17·398$ (6) Å, $V=1588$ (1) Å^3, μ for Mo $K\alpha$ ($\lambda=0·7107$ Å) radiation $=16·1$ cm^{-1}. Space group: $P4_1(P4_3)$. $F(000)=$ 1184. Crystal faces: general faces $\{hkl\}$ of the tetragonal pyramid and $\{100\}$ of the tetragonal prism. A single crystal of dimensions $0·1 \times 0·1 \times 0·2$ mm, sealed in a glass capillary, was selected. Intensities were measured on a two-circle diffractometer of the Arndt–Phillips design. Monochromatized (graphite) Mo $K\alpha$ radiation was used with a scintillation detector and pulse-height discrimination. In each layer a reference reflexion was monitored and showed no significant variation. By remeasuring the reference reflexions of the 0th layer several times during the collection of the intensities of the higher layers, all data were scaled to

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Table 1. *Final atomic parameters*

Standard deviations with respect to the last digit are given in parentheses. The labelling of the atoms in molecule 1 is according to Fig. 1; that in molecule 2 is analogous.

(*a*) Fractional coordinates. The estimated errors of the H atoms are: $x/a \simeq 0·03$, $x/b \simeq 0·03$, $x/c \simeq 0·02$.

	x/a	y/b	z/c
Mo(1)	0·1866 (1)	0·2362 (1)	0·0
O(11)	0·3295 (9)	0·2358 (11)	0·0603 (8)
O(12)	0·2429 (9)	0·2933 (10)	−0·0887 (8)
O(13)	0·1775 (8)	0·0373 (8)	−0·0318 (7)
O(14)	0·1058 (9)	0·4112 (9)	0·0427 (7)
O(15)	0·0494 (10)	0·1297 (9)	0·0861 (7)
O(16)	−0·0418 (9)	0·2537 (8)	−0·0525 (7)
C(11)	0·1429 (12)	−0·0686 (14)	0·0254 (9)
C(12)	0·0194 (15)	−0·0132 (14)	0·0716 (9)
C(13)	−0·0028 (16)	0·4769 (13)	0·0017 (11)
C(14)	−0·1141 (15)	0·3699 (13)	−0·0159 (8)
H(10)	0·072	0·217	0·311
H(11)	0·158	0·164	0·276
H(12)	0·072	−0·016	0·350
H(13)	0·012	−0·028	0·303
H(14)	−0·024	−0·400	0·005
H(15)	−0·006	0·570	0·009
H(16)	0·340	0·171	0·768
H(17)	0·411	0·211	0·700
H(18)	0·064	0·138	0·068
H(19)	0·240	0·104	0·706
Mo(2)	0·3187 (1)	0·2585 (1)	0·4972 (3)
O(21)	0·1642 (10)	0·2314 (11)	0·4497 (8)
O(22)	0·2765 (10)	0·3523 (10)	0·5776 (8)
O(23)	0·3357 (9)	0·0736 (8)	0·5543 (7)
O(24)	0·3943 (9)	0·3952 (9)	0·4258 (7)
O(25)	0·4381 (9)	0·1062 (9)	0·4179 (7)
O(26)	0·5507 (9)	0·2873 (8)	0·5379 (7)
C(21)	0·3634 (15)	−0·0542 (19)	0·5111 (11)
C(22)	0·4726 (13)	−0·0244 (15)	0·4523 (10)
C(23)	0·5130 (18)	0·4750 (17)	0·4480 (10)
C(24)	0·6226 (15)	0·3787 (14)	0·4827 (8)
H(20)	0·087	0·261	0·730
H(21)	0·128	0·396	0·800
H(22)	−0·049	0·542	0·739
H(23)	0·093	0·493	0·670
H(24)	0·567	0·500	0·231
H(25)	0·531	0·447	0·166
H(26)	0·301	0·327	0·202
H(27)	0·407	0·307	0·247
H(28)	0·495	0·129	0·389
H(29)	0·270	0·376	0·269

Table 1 (*cont.*)

(*b*) Thermal parameters in the form exp $[-2\pi^2(U_{11}h^2a^{*2}+\ldots+2U_{12}hka^*b^*+\ldots)\times10^3]$. The B values are those before the anisotropic refinement.

	B	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	1·48 (3)	22 (2)	24 (2)	12 (2)	1·5 (3)	−0·4 (4)	−5·0 (4)
O(11)	2·6 (4)	26 (5)	51 (6)	23 (5)	4 (4)	−11 (3)	−6 (4)
O(12)	2·2 (4)	29 (5)	36 (5)	20 (5)	−6 (4)	7 (3)	0 (4)
O(13)	1·6 (4)	23 (4)	21 (4)	14 (4)	2 (3)	0 (3)	−4 (3)
O(14)	1·9 (4)	25 (4)	30 (4)	19 (4)	12 (3)	−5 (3)	−15 (3)
O(15)	2·4 (4)	43 (5)	28 (5)	19 (5)	3 (4)	9 (4)	−3 (3)
O(16)	1·7 (4)	26 (4)	26 (4)	14 (4)	−2 (3)	−2 (3)	3 (3)
C(11)	2·2 (6)	24 (5)	37 (7)	24 (6)	−7 (5)	2 (4)	6 (5)
C(12)	2·6 (6)	36 (7)	34 (7)	29 (7)	2 (6)	3 (5)	11 (5)
C(13)	2·8 (6)	51 (7)	34 (6)	21 (6)	15 (5)	2 (6)	0 (6)
C(14)	2·4 (6)	50 (7)	25 (6)	18 (6)	−8 (5)	−4 (5)	4 (4)
Mo(2)	1·47 (3)	21 (2)	24 (1)	11 (2)	2·5 (4)	−0·5 (4)	0·3 (4)
O(21)	2·4 (4)	27 (5)	46 (6)	21 (5)	2 (4)	−5 (4)	2 (4)
O(22)	2·5 (4)	37 (5)	41 (5)	19 (5)	7 (4)	5 (4)	−4 (4)
O(23)	1·8 (4)	30 (4)	22 (4)	17 (4)	−1 (3)	6 (3)	5 (3)
O(24)	2·1 (4)	32 (5)	28 (5)	18 (4)	−5 (4)	−4 (3)	7 (3)
O(25)	2·0 (4)	39 (5)	26 (4)	11 (4)	5 (4)	12 (3)	5 (3)
O(26)	1·7 (4)	29 (5)	20 (4)	19 (4)	1 (3)	0 (3)	1 (3)
C(21)	3·2 (6)	34 (7)	66 (9)	37 (9)	−5 (7)	−9 (6)	18 (8)
C(22)	2·7 (6)	26 (6)	49 (8)	29 (7)	−3 (6)	−8 (5)	13 (6)
C(23)	3·1 (6)	33 (9)	54 (7)	29 (7)	14 (6)	5 (6)	13 (7)
C(24)	2·7 (6)	39 (7)	32 (6)	31 (7)	19 (6)	7 (5)	6 (5)

give one set. By ω-scanning, 2207 independent reflexions were measured within the range $6°\le2\theta\le68°$. Of these, 1940 had $I\ge3\sigma(I)$ and were classed as observed. Corrections were made for Lp factors but not for absorption.

The coordinates of the two independent Mo atoms were obtained from a Patterson map. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). That for Mo was corrected for the real part of the anomalous dispersion. By Fourier methods the O and C atoms were located. Full-matrix least-squares refinement with unit weights gave $R=$ 0·083 $(R=\sum||F_o|-|F_c||/|F_o|)$ after three isotropic cycles. After two more anisotropic cycles R was 0·056. Inclusion of the H atoms, which had been located on a difference map, with $B=4·0$ $(U=5·1)$ Å², gave a final R of 0·049. A last cycle, including all 2207 reflexions resulted in no significant changes in any of the non-hydrogen atom parameters. Table 1 lists atomic coordinates and thermal parameters.* The data reduction was performed with our own programs on a GIER computer in Aarhus. For solving the structure, the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970) was used on the 1108 UNIVAC computer in Freiburg.

Results and discussion

Molecular structure

A schematic drawing of one of the two independent

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30705 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

molecules is given in Fig. 1. Table 2 shows bond lengths, bond angles and some contact distances. Table 3 gives details of various least-squares planes. The Mo–O distances are typical of a $2+2+2$ coordinated Mo atom: two close terminal O atoms (O_t), two medium Mo–O distances and two long ones. This coordination has been considered in detail by Schröder (1975). The Mo–O_t lengths suggest a bond order (b.o.) of 1·8. The same diagram gives a b.o. of 0·66 for the Mo–O(13) *etc.* bonds.

The Mo–O(13) *etc.* distance of 1·98 Å found here is 0·03 Å (corresponding to 3σ) longer than the sum of the ionic radii, according to Shannon & Prewitt (1969). This highlights the problems associated with
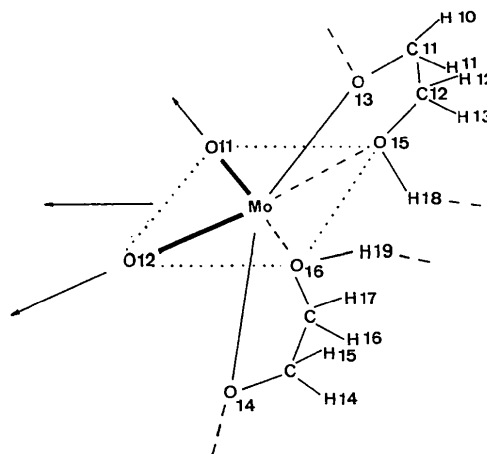
Fig. 1. Molecular structure of $MoO_2(OC_2H_4OH)_2$ shown schematically. The atoms are labelled as in molecule 1. The labelling in molecule 2 is analogous; O(13) corresponds to O(23) *etc.* The pseudosymmetry axes of chirality of the molecule are indicated by arrows.

the values given for those radii. There is a difference of 0·112 Å between the mean values of Mo–O(15)/ O(25) and Mo–O(16)/O(26) which corresponds to 12σ. The hydrogen bridges in which these two different O atoms, say O(15) and O(16), are involved are also given in Table 2. O(15), closer to Mo, is involved in the shorter hydrogen bond. The difference between the

mean O···O distances of these two types is 0·097 Å, corresponding to 8·5σ. As the hydrogen bonds are formed between symmetry-related donor and acceptor O atoms [e.g. O(15)···O(13)] and non-symmetry-related O atoms [e.g. O(16)···O(23); cf. Table 2] as well, unlike O···O distances of the hydrogen bonds are to be expected. The physical reason for this is ob-

Table 2. *Bond distances* (Å) *and angles* (°)

Standard deviations with respect to the last digit are given in parentheses. Symmetry-related atoms according to the following transformations: (i) $\bar{y},x,\frac{1}{4}+z$; (ii) $\bar{y},x,-\frac{3}{4}+z$; (iii) $1-y,x,\frac{1}{4}+z$.

	Molecule 1	Molecule 2	Mean
Mo—O(11)/O(12)/O(21)/O(22)	1·723 (10)	1·704 (10)	1·723
	1·729 (10)	1·737 (11)	
Mo—O(13)/O(14)/O(23)/O(24)	1·977 (8)	1·984 (9)	1·979
	1·983 (9)	1·973 (9)	
Mo—O(15)/O(25)	2·225 (10)	2·271 (9)	2·248
Mo—O(16)/O(26)	2·368 (9)	2·352 (8)	2·360
C(11)–O(13)	1·457 (16)		⎫
C(13)–O(14)	1·411 (18)		⎬ 1·434
C(21)–O(23)		1·445 (18)	⎪
C(23)–O(24)		1·421 (18)	⎭
C(12)–O(15)	1·419 (19)		⎫
C(14)–O(16)	1·449 (16)		⎬ 1·437
C(22)–O(25)		1·420 (16)	⎪
C(24)–O(26)		1·460 (16)	⎭
C(11)/O(21)–C(12)/C(22)	1·497 (20)	1·487 (22)	1·500
C(13)/O(23)–C(14)/C(24)	1·500 (20)	1·514 (20)	
O(11)/O(21)–Mo—O(12)/O(22)	107·6 (5)	104·6 (5)	106·1
O(11)/O(21)–Mo—O(13)/O(23)	101·7 (4)	102·1 (5)	101·9
O(11)/O(21)–Mo—O(14)/O(24)	94·4 (5)	95·3 (5)	94·8
O(11)/O(21)–Mo—O(15)/O(25)	93·2 (4)	93·8 (4)	93·5
O(11)/O(21)–Mo—O(16)/O(26)	164·5 (4)	168·4 (4)	166·4
O(12)/O(22)–Mo—O(13)/O(23)	93·8 (4)	95·0 (4)	94·4
O(12)/O(22)–Mo—O(14)/O(24)	101·3 (4)	102·6 (4)	102·0
O(12)/O(22)–Mo—O(15)/O(25)	157·9 (4)	160·5 (4)	159·2
O(12)/O(22)–Mo—O(16)/O(26)	85·5 (4)	84·5 (4)	85·0
O(13)/O(23)–Mo—O(14)/O(24)	153·4 (4)	151·3 (4)	152·4
O(13)/O(23)–Mo—O(15)/O(25)	74·0 (3)	74·5 (3)	74·2
O(13)/O(23)–Mo—O(16)/O(26)	85·3 (3)	84·0 (3)	84·6
O(14)/O(24)–Mo—O(15)/O(25)	84·3 (4)	81·8 (4)	83·0
O(14)/O(24)–Mo—O(16)/O(26)	74·3 (3)	75·4 (3)	74·8
O(15)/O(25)–Mo—O(16)/O(26)	75·3 (3)	78·2 (3)	76·8
Mo—O(13)/O(23)-C(11)/C(21)	118·8 (7)	118·7 (8)	118·8
Mo—O(14)/O(24)-C(13)/C(23)	117·9 (8)	119·7 (8)	118·8
Mo—O(15)/O(25)-C(12)/C(22)	115·7 (8)	113·6 (8)	114·6
Mo—O(16)/O(26)-C(14)/C(24)	108·8 (7)	108·8 (7)	108·8
O(13)/O(23)–C(11)/C(21)–C(12)/C(22)	107 (1)	109 (1)	108
O(14)/O(24)–C(13)/C(23)–C(14)/C(24)	109 (1)	109 (1)	109
O(15)/O(25)–C(12)/C(22)–C(11)/C(21)	107 (1)	107 (1)	107
O(16)/O(26)–C(14)/C(24)–C(13)/C(23)	107 (1)	108 (1)	108
Hydrogen bonds			
O(15)/O(25)–O(13)/O(14) (i)	2·498 (13)	2·608 (13)	2·553
O(16)–O(23) (ii)	2·638 (12)		⎫ 2·662
O(26)–O(24) (iii)		2·662 (13)	⎭
O(15)/O(25)–H(18)/O(28)–O(13)/O(14) (i)	140 (15)	158 (15)	149
O(16)–H(19)–O(23) (ii)	161 (15)	153 (15)	157
Oxygen–oxygen contacts			
O(11)/O(21)–O(12)/O(22)	2·785 (15)	2·723 (15)	⎫
O(11)/O(21)–O(13)/O(23)	2·875 (14)	2·874 (14)	⎪
O(11)/O(21)–O(14)/O(24)	2·726 (14)	2·723 (14)	⎪
O(11)/O(21)–O(15)/O(25)	2·889 (14)	2·927 (14)	⎪
O(12)/O(22)–O(13)/O(23)	2·711 (13)	2·748 (14)	⎬ 2·826
O(12)/O(22)–O(14)/O(24)	2·875 (14)	2·900 (14)	⎪
O(12)/O(22)–O(16)/O(26)	2·819 (13)	2·788 (13)	⎪
O(13)/O(23)–O(16)/O(26)	2·959 (12)	2·914 (12)	⎪
O(14)/O(24)–O(15)/O(25)	2·829 (13)	2·789 (13)	⎭
O(13)/O(23)–O(15)/O(25)	2·537 (13)	2·585 (13)	⎫ 2·608
O(14)/O(24)–O(16)/O(26)	2·646 (13)	2·663 (13)	⎭

viously the opposite helical conformation along the bonds, *e.g.* Mo(1)–O(15)$\cdots$O(13')–Mo(1') and Mo(1)–O(16)$\cdots$O(23')–Mo(2'),* respectively. Somewhat surprising seems the large difference that is actually found, which obviously corresponds to unequal binding forces of, *e.g.* Mo–O(15) and Mo–O(16).

Table 3 contains details of the three best planes formed by the Mo and four of the O atoms of each molecule. It can be seen that all atoms depart by a maximum of 1σ from their planes. The 'equatorial' planes A, B (Fig. 1) containing the two O_t atoms, fit the Mo atoms better, while the others (F, G, I, L) fit the O atoms better. This can also be seen from the fact that for planes $A–D$ the coefficients of the planes are practically unaltered by defining the plane with and without the Mo atom. This is supported by the results obtained from the two corresponding kinds of planes (F, H, K, M), calculated only from the positions of the O atoms although the relatively poor fit of plane M can-

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* Primes denote generally equivalent atoms of the family.

not be explained. The last two kinds of planes $(E–M)$ are essentially planes of the O atoms. This is also expressed by the sums of the *cis* O–Mo–O angles, $361\cdot6$ $(16)°$ in plane A and $361\cdot1$ $(16)°$ in plane C of the second molecule. The values in the other planes are I: $355\cdot7$ (15); L: $355\cdot9$ (16); E: $353\cdot4$ (16); G: $353\cdot9$ $(16)°$, thus deviating more than 3σ from the ideal value of $360°$. By extrapolation of the results obtained by Schröder (1974), only Mo–O(11)/O(21) and Mo–O(12)/O(22) contain contributions of π bonding. Thus it seems that the fit of the plane containing these two bonds is mainly influenced by this π bonding interaction.

There are pseudosymmetry (chiral) elements in the molecules which are indicated in Fig. 1. One twofold axis, bisecting the angle O(11)–Mo(1)–O(12) and lying in plane A, is valid for the whole molecule, as the values of Table 3 show. Two more twofold axes lying in the planes E (G) and I (L) run roughly along the directions O(12)–Mo–O(15) and O(11)–Mo–O(16) and are only valid with respect to the O atoms.

Table 3. *Least-squares planes*

The planes are given in the form $px + qy + rz = s$ in direct space, where x, y and z are the fractional atomic coordinates.

(a) Planes defined by Mo and O atoms or O atoms alone.

Plane	Atoms defining the planes	p	q	r	s	σ(plane)
A	Mo(1), O(11), O(12), O(15), O(16)	$-1\cdot5548$	$8\cdot7412$	$6\cdot4304$	$1\cdot7767$	$0\cdot164$
B	O(11), O(12), O(15), O(16)	$-1\cdot5557$	$8\cdot7410$	$6\cdot4305$	$1\cdot7770$	$0\cdot190$
C	Mo(2), O(21), O(22), O(25), O(26)	$-1\cdot2720$	$-7\cdot5537$	$10\cdot3997$	$2\cdot8567$	$0\cdot136$
D	O(21), O(22), O(25), O(26)	$-1\cdot2721$	$-7\cdot5537$	$10\cdot3997$	$2\cdot8566$	$0\cdot157$
E	Mo(1), O(12), O(13), O(14), O(15)	$8\cdot1702$	$-0\cdot2703$	$9\cdot0078$	$1\cdot2014$	$0\cdot147$
F	O(12), O(13), O(14), O(15)	$8\cdot2123$	$-0\cdot2126$	$8\cdot8851$	$1\cdot1551$	$0\cdot015$
G	Mo(2), O(22), O(23), O(24), O(25)	$8\cdot6389$	$1\cdot2750$	$7\cdot0618$	$6\cdot8370$	$0\cdot141$
H	O(22), O(23), O(24), O(25)	$8\cdot6748$	$1\cdot1998$	$6\cdot9590$	$6\cdot8444$	$0\cdot012$
I	Mo(1), O(11), O(13), O(14), O(16)	$-4\cdot3408$	$-3\cdot6287$	$14\cdot0201$	$-1\cdot4546$	$0\cdot131$
K	O(11), O(13), O(14), O(16)	$-4\cdot4138$	$-3\cdot6082$	$13\cdot9620$	$-1\cdot4073$	$0\cdot061$
L	Mo(2), O(21), O(23), O(24), O(26)	$-3\cdot5667$	$5\cdot6083$	$12\cdot4994$	$6\cdot2931$	$0\cdot156$
M	O(21), O(23), O(24), O(26)	$-3\cdot6405$	$5\cdot5864$	$12\cdot4612$	$6\cdot1919$	$0\cdot123$

(b) Planes defined by the ring atoms Mo–O–C

Plane	Atoms defining the planes	p	q	r	s	σ(plane)
N	Mo(1), O(13), C(11), C(12), O(15)	$7\cdot3991$	$-0\cdot7926$	$10\cdot9133$	$1\cdot1371$	$0\cdot192$
O	Mo(2), O(23), C(21), C(22), O(25)	$8\cdot0561$	$2\cdot2501$	$8\cdot4103$	$7\cdot3565$	$0\cdot183$
P	Mo(1), O(14), C(13), C(14), O(16)	$-3\cdot4007$	$-3\cdot8579$	$14\cdot6630$	$-1\cdot5103$	$0\cdot215$
Q	Mo(2), O(24), C(23), C(24), O(26)	$-2\cdot7870$	$6\cdot2049$	$12\cdot2186$	$6\cdot7250$	$0\cdot193$

(c) Distances of atoms (Å); starred atoms do not define the planes

A Mo(1) $-0\cdot002$, O(11) $0\cdot164$, O(12) $-0\cdot166$, O(15) $-0\cdot161$, O(16) $0\cdot166$, O(13)* $-1\cdot926$, O(14)* $1\cdot925$, C(11)* $-2\cdot424$, C(12)* $-1\cdot464$, C(13)* $2\cdot404$, C(14)* $1\cdot527$

B O(11) $0\cdot163$, O(12) $-0\cdot167$, O(15) $-0\cdot161$, O(16) $0\cdot166$, Mo(1)* $-0\cdot003$, O(13)* $-1\cdot927$, O(14) $1\cdot927$, C(11)* $-2\cdot430$, C(12)* $-1\cdot465$, C(13)* $2\cdot404$, C(14)* $1\cdot527$

C Mo(2) $0\cdot0004$, O(21) $-0\cdot137$, O(22) $0\cdot144$, O(25) $0\cdot128$, O(26) $-0\cdot135$, O(23)* $1\cdot924$, O(24)* $1\cdot909$, C(21)* $2\cdot399$, C(22)* $1\cdot427$, C(23)* $-2\cdot441$, C(24)* $-1\cdot487$

D O(21) $-0\cdot137$, O(22) $0\cdot144$, O(25) $0\cdot128$, O(26) $-0\cdot135$, Mo(2) $0\cdot0004$, O(23)* $1\cdot925$, O(24)* $-1\cdot909$, C(21)* $2\cdot400$, C(22)* $1\cdot427$, C(23)* $-2\cdot440$, C(24)* $-1\cdot487$

E Mo(1) $0\cdot260$, O(12) $-0\cdot097$, O(13) $-0\cdot046$, O(14) $-0\cdot058$, O(15) $0\cdot048$, O(11)* $1\cdot972$, O(16)* $-2\cdot080$

F O(12) $-0\cdot013$, O(13) $0\cdot014$, O(14) $0\cdot012$, O(15) $-0\cdot014$, Mo(1)* $0\cdot328$, O(11)* $2\cdot038$, O(16)* $-2\cdot014$

G Mo(2) $-0\cdot250$, O(22) $0\cdot074$, O(23) $0\cdot069$, O(24) $0\cdot076$, O(25) $0\cdot032$, O(21)* $-1\cdot947$, O(26)* $2\cdot087$

H O(22) $-0\cdot010$, O(23) $0\cdot011$, O(24) $0\cdot010$, O(25) $-0\cdot011$, Mo(2)* $-0\cdot316$, O(21)* $-2\cdot013$, O(26)* $2\cdot022$

I Mo(1) $-0\cdot213$, O(11) $0\cdot017$, O(13) $0\cdot106$, O(14) $0\cdot106$, O(16) $-0\cdot017$, O(12)* $1\cdot965$, O(15)* $1\cdot965$

K O(11) $-0\cdot053$, O(13) $0\cdot048$, O(14) $0\cdot057$, O(16) $-0\cdot053$, Mo(1)* $-0\cdot269$, O(12)* $-1\cdot967$, O(15)* $1\cdot912$

L Mo(2) $0\cdot202$, O(21) $0\cdot039$, O(23) $-0\cdot152$, O(24) $-0\cdot162$, O(26) $0\cdot073$, O(22)* $1\cdot914$, O(25)* $-2\cdot036$

M O(21) $0\cdot106$, O(23) $-0\cdot098$, O(24) $-0\cdot115$, O(26) $0\cdot107$, Mo(2)* $0\cdot255$, O(22)* $1\cdot966$, O(25)* $-1\cdot986$

N Mo(1) $0\cdot057$, O(13) $-0\cdot198$, C(11) $0\cdot261$, C(12) $-0\cdot182$, O(15) $0\cdot062$

O Mo(2) $-0\cdot039$, O(23) $0\cdot172$, C(21) $-0\cdot248$, C(22) $0\cdot190$, O(25) $-0\cdot076$

P Mo(1) $-0\cdot036$, O(14) $0\cdot195$, C(13) $-0\cdot294$, C(14) $0\cdot226$, O(16) $-0\cdot092$

Q Mo(2) $0\cdot029$, O(24) $-0\cdot171$, C(23) $0\cdot259$, C(24) $-0\cdot209$, O(26) $0\cdot091$

The five-membered MoO_2C_2 ring is drawn schematically in Fig. 2. While the C–C lengths seem to be slightly shortened compared with a $C(sp^3)$–$C(sp^3)$ single bond, the values of the O–C–C angles do not suggest strain in these rings. This is supported by the observation that the C–C length always seems to be slightly short, even in compounds where the $C_2H_4(OH)_2$ molecule as a whole is coordinated to metal atoms, e.g. $LiCl.2C_2H_4(OH)_2$: 1·515 Å (Dunitz & Meyer, 1974), $CaCl_2.4C_2H_4(OH)_2$: 1·359 Å (Dunitz & Steiner, 1974),* $Na(PhCOCHCOCH_3)$ $[C_2H_4(OH)_2]_2$: 1·506 (9) Å (Bright, Milburn & Truter, 1971).

The values of the best planes through the five-membered rings are included in Table 3. The deviations of the atoms, with a maximum somewhat more than 1σ, seem to indicate that the rings are not so strictly planar as they would be if there were π-bonding within the rings. Each ring shows a slight puckering (Table 3) so that there are two more chiral twofold rotation axes. They bisect the C–C bond and contain the Mo atom.

The disposition of the methylene hydrogen atoms with respect to the ring plane is shown schematically in Fig. 2 as well as that of the hydroxyl-group hydrogen atoms which is different for the two types of rings. H(18)/H(28) are 0·3 Å (mean) above the planes, while O(19)/O(29) are 0·75 Å (mean) above. This arrange-

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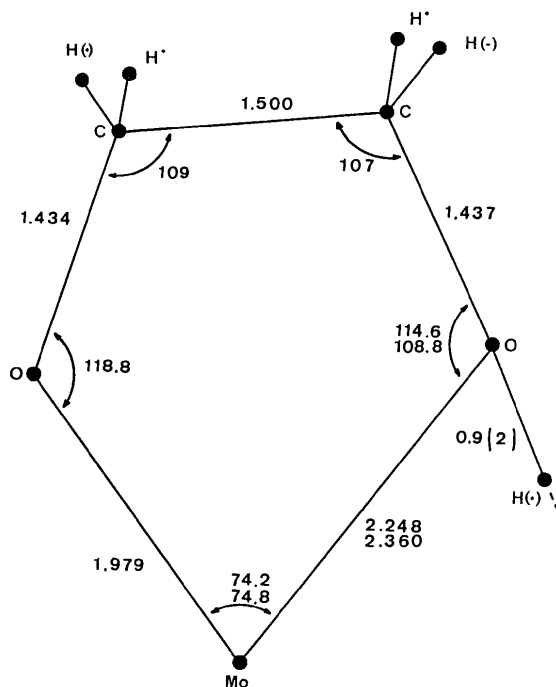* The investigators believe that this shortening is more apparent than real.

Fig. 2. Bond lengths (Å) and angles (°) in the MoO_2C_2 five-membered rings. The values given are the means (Table 2). H atoms with asterisks lie in the least-squares plane, H(+) and H(−) above and below.
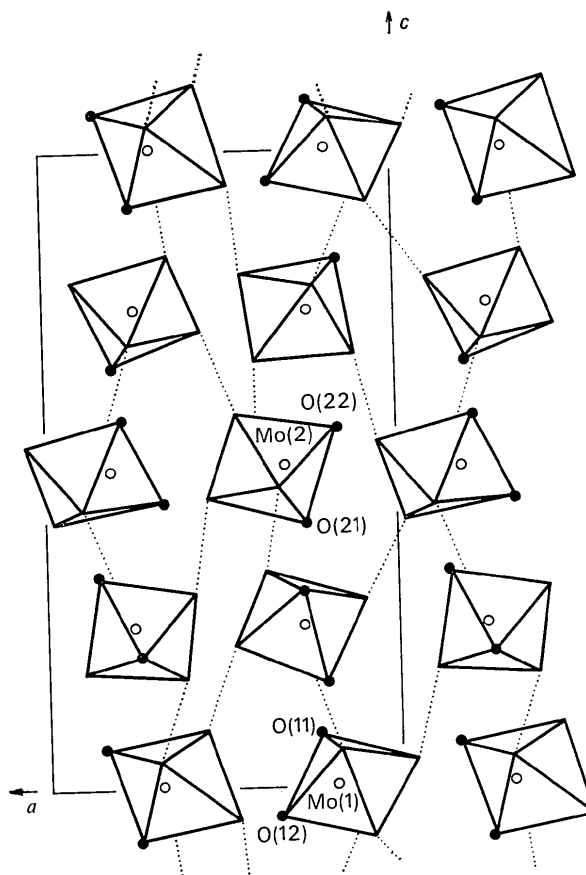

Fig. 3. Crystal structure of $MoO_2(OC_2H_4OH)_2$ shown schematically. Only Mo and O_t atoms (at the corners of the idealized octahedra) are drawn, C and H atoms are omitted for clarity. Dotted lines give the directions of H bonds.

ment corresponds to the two types of conformation of ethylene glycol expected to be present in dilute solutions (Matsuura & Miyazawa, 1967). With the nomenclature of these authors, the first type of ring [containing O(15)/O(25) and H(18)/H(28)] contains the ligand in the TGG' orientation, the second type [O(16)/O(26) and H(19)/H(29)] in the GGG' orientation. The effect of conformation on the vibration spectra will be discussed elsewhere (Schröder & Scherle, 1975).

Crystal structure

Fig. 3 shows the crystal structure. If the molecules are considered as spheres, the crystal structure corresponds approximately to a ccp structure. The H bonds run roughly along c. The values of the O–H···O angles deviate between 2 and 3σ from linearity (Table 2).

It has not been possible to measure the amount of rotatory polarization of the crystals of $MoO_2(OC_2H_4OH)_2$ since they lack any cleavage plane normal to [001]. Solutions of the compound in ethylene glycol did not show any rotatory power.

A comparison of $MoO_2(OC_2H_4OH)_2$ with three other

Table 4. *Selected distances (Å) and angles (°) in directly comparable* Mo *compounds*

Mo–O$_{br}$(I) labels the medium Mo–O distances, Mo–O$_{br}$(II) the long ones. Figures with an asterisk are averaged values.

	Mo–O$_t$	O$_t$–Mo–O$_t$	Mo–O$_{br}$(I)	O$_{br}$(I)–Mo–O$_{br}$(I)	Mo–O$_{br}$(II)	O$_t$–Mo–O$_{br}$(II)
(1) MoO$_2$(C$_9$H$_6$NO)$_2$	1·71*	104	1·98*		2·32*†	163*†
(2) H[MoO$_2$(OCH$_2$CH$_2$)$_3$N] = MoO$_2$[(OC$_2$H$_4$)$_2$ NOC$_2$H$_4$OH]	1·79 (4)*		1·94 (3)*		2·34 (3)* / 2·43 (4)*†	
(3) MoO$_2$(C$_{15}$H$_{11}$O$_2$)$_2$	1·696 (8)*	104·8 (4)	1·992 (8)*	159·6 (3)	2·166 (8)*	165·6 (3), 163·1 (3)
(4) MoO$_2$(OC$_2$H$_4$OH)$_2$	1·723 (10)*	106·1 (5)*	1·979 (9)*	152·4 (4)	2·304 (9)*	166·4 (4)*, 159·2 (4)*

† O$_{br}$(II) has to be replaced by N$_{br}$.

compounds is possible: (1) dioxo(bis-8-hydroxyquin-olinato)molybdenum(VI), MoO$_2$(C$_9$H$_6$NO)$_2$ (Atov-myan & Sokolova, 1969), (2) H[MoO$_2$(OCH$_2$CH$_2$)$_3$N] (Atovmyan & Krasochka, 1970) and (3) Dioxobis-(1,3-diphenylpropandionato)molybdenum(VI), MoO$_2$(C$_{15}$H$_{11}$O$_2$)$_2$ (Kojić-Prodić, Ružić-Toroš, Grden-ić & Golić, 1974). All these structures show the 2+2+2 coordination of Mo by two close O$_t$, two medium Mo–O and two long Mo–O distances. Either or both of these can be replaced by Mo–N as in (1) and (2). Unfortunately, the results given for (1) and (2) are poor. Nevertheless they permit a prediction concerning the formulation of (2). The long Mo–O distance of 2·34$_5$ Å suggests a coordinated C–O–H group as in the present compound. Thus (2) should probably be written as MoO$_2$[(OC$_2$H$_4$)$_2$NC$_2$H$_4$OH]. Table 4 gives the most outstanding structural results for compounds (1)–(4). If the results for the compounds (3) and (4) (also those which are not given in Table 4) are compared, the following conclusions can be drawn: (*a*) The Mo–O angles are much the same in both compounds. (Thus the greatest difference between corresponding angles is 7·2°.) (*b*) This does not explain why the dative Mo–O$_{br}$ in (3) is shorter (average 2·17 Å) than in (4) (average 2·30 Å), contrary what would be expected from a *trans* effect. For these bonds in (3) are *trans* to shorter Mo–O$_t$ (1·696 Å) and should therefore be longer than those in (4) where they are *trans* to longer Mo–O$_t$ (1·723 Å). This suggests that the findings concerning these results in compound (3) may be more in error than stated by the authors.

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