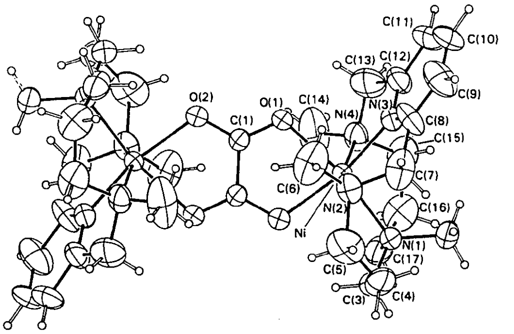

Fig. 1. View of the cation showing the atomic numbering. There is a centre of symmetry at the centre of the oxalate group.

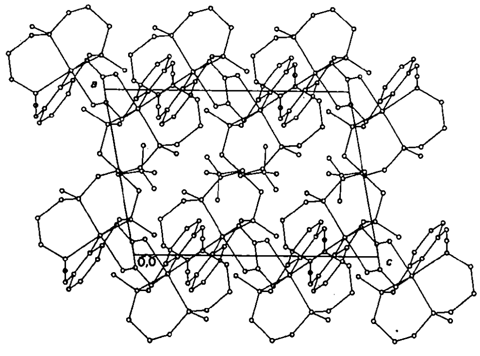

Fig. 2. Structure projected down **b**.

relatively unusual folded macrocycle; this ligand more often takes up the apex and three basal positions of a square pyramid (Alcock, Moore & Omar, 1987). Indeed, it is evident from the *trans* angle [N(2)—Ni—N(4)] of only 158·2 (3)° that the ligand is unable to accommodate the present geometry entirely satisfactorily. Another distortion arises from the 78·9° angle between the oxygen atoms, which is controlled by the bite of the oxalate ion. Ni—N and Ni—O distances are standard for high-spin Ni; as is normal, the Ni—N(3) (pyridine) distance is shorter than the others.

Tetradentate oxalate ions are rare, but not unknown (Davis, Einstein & Willis, 1982), and are generally planar, as here, forming five-membered chelate rings (rather than four-membered rings) with the metal ion.

In the crystal (Fig. 2), the cations are arranged in layers in the *bc* plane, with anions between the layers.

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Structure of μ-Oxo-bis[(2,3,7,8,12,13,17,18-octaethylporphyrinato)oxomolybdenum(V)] Diethanol Solvate

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Abstract. $[Mo_2(C_{36}H_{44}N_4)_2O_3].2C_2H_6O$, $M_r = 1397·6$, tetragonal, $P4/nnc$ (D_{4h}^4), $a = 13·796$ (5), $c = 17·021$ (6) Å, $V = 3239$ (3) Å^3, $Z = 2$, $D_x = 1·43$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7093$ Å, $\mu = 4·3$ cm^{-1}, $F(000) = 1448·7$ (including anomalous dispersion), $T = 123$ K, $R(F^2) = 0·078$ for 1414 reflections. The Mo dimer has crystallographically imposed 422 symmetry with a linear O=Mo—O—Mo=O arrangement along a fourfold axis. The Mo=O and Mo—O bond lengths are 1·721 (6) and 1·951 (1) Å, respectively. The two porphyrin rings, interplanar distance 3·54 Å, are twisted by 22·3° with respect to one another. The ethanol solvent molecule lies on a fourfold axis and is disordered.

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Introduction. Metal–metal bonded Mo^{II} porphyrin dimers have been prepared to study the rotational barrier about the Mo—Mo quadruple bonds (Collman & Woo, 1984). In an attempt to crystallize one of these dimers, $[Mo(oep)]_2$ (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato), we accidentally obtained the title compound, presumably as a result of air oxidation of the parent complex. Here we report its molecular structure and compare it with that of the corresponding tpp complex (tpp = 5,10,15,20-tetraphenylporphyrinato) (Johnson & Scheidt, 1978).

Experimental. Dark-blue crystals of the title compound were obtained accidentally by slow diffusion of pentane

Table 1. *Positional parameters and* B_{eq}(Å^2) *for* [{O=Mo(*oep*)}$_2$O].2C$_2$H$_5$OH

The origin is at $\bar{1}$. $B_{eq} = \frac{8}{3}\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Mo	$\frac{1}{4}$	$\frac{1}{4}$	0·135380 (37)	1·09 (1)
O(1)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1·3 (1)
O(2)	$\frac{1}{4}$	$\frac{1}{4}$	0·03426 (33)	3·2 (1)
S(1)†	$-\frac{1}{4}$	$-\frac{1}{4}$	0·16910 (55)	2·6 (1)
N	0·37682 (26)	0·16493 (28)	0·14273 (21)	1·57 (9)
C(1)	0·46810 (32)	0·19930 (38)	0·14563 (30)	1·9 (1)
C(2)	0·53325 (40)	0·11687 (43)	0·14987 (32)	3·0 (2)
C(3)	0·48046 (35)	0·03653 (38)	0·14757 (25)	2·3 (1)
C(4)	0·37938 (34)	0·06591 (36)	0·14475 (26)	1·8 (1)
C(5)	0·29782 (41)	0·00562 (33)	0·14621 (33)	2·1 (1)
C(6)	0·64427 (46)	0·12553 (49)	0·16030 (38)	4·2 (2)
C(7)	0·69233 (54)	0·13291 (64)	0·08367 (46)	5·9 (3)
C(8)	0·51468 (45)	−0·06713 (45)	0·14684 (33)	3·5 (2)
C(9)	0·53680 (50)	−0·10556 (46)	0·06482 (36)	4·0 (2)
S(2)†	−0·16076 (69)	−0·25148 (87)	0·20878 (54)	4·1 (3)

† S(1) is the central atom, and S(2) is one-half O + one-half terminal C atom of the disordered ethanol solvate molecule.

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *for* [{O=Mo(*oep*)}$_2$O].2C$_2$H$_5$OH

Mo–O(1)	1·951 (1)	C(1)–C(5′)	1·407 (7)
Mo–O(2)	1·721 (6)	C(4)–C(5)	1·400 (8)
Mo–N	2·111 (4)	C(2)–C(6)	1·547 (8)
N–C(1)	1·346 (6)	C(3)–C(8)	1·506 (8)
N–C(4)	1·367 (6)	C(6)–C(7)	1·468 (9)
C(1)–C(2)	1·451 (7)	C(8)–C(9)	1·524 (8)
C(3)–C(4)	1·453 (6)	S(1)–S(2)*	1·404 (10)
C(2)–C(3)	1·327 (8)		

O(1)–Mo–O(2)	180·0	C(1)–C(2)–C(3)	108·2 (5)
O(1)–Mo–N	86·6 (1)	C(1)–C(2)–C(6)	124·0 (5)
O(2)–Mo–N	93·4 (1)	C(3)–C(2)–C(6)	127·7 (5)
N–Mo–N′	89·8 (1)	C(2)–C(3)–C(4)	107·1 (5)
N–Mo–N″	173·2 (2)	C(2)–C(3)–C(8)	128·4 (5)
Mo–O–Mo	180·0	C(4)–C(3)–C(8)	124·4 (5)
C(1)–N–C(4)	109·1 (4)	N–C(4)–C(3)	107·7 (4)
C(1)–N–Mo	125·6 (3)	N–C(4)–C(5)	125·0 (4)
C(4)–N–Mo	125·4 (3)	C(3)–C(4)–C(5)	127·3 (5)
N–C(1)–C(2)	107·8 (5)	C(4)–C(5)–C(1′)	128·6 (4)
N–C(1)–C(5)	125·6 (4)	C(2)–C(6)–C(7)	110·5 (5)
C(2)–C(1)–C(5)	126·7 (4)	C(3)–C(8)–C(9)	113·6 (5)
		S(2)–S(1)–S(2)*	122·5 (10)

* Disordered ethanol solvate molecule; see the footnote of Table 1.

into an air-exposed C_6D_6 solution of [Mo(oep)]$_2$ (Collman & Woo, 1984). An ^{1}H NMR spectrum indicates the presence of ethanol solvate molecules in the powder sample of [Mo(oep)]$_2$. Plate-shaped crystal, 0·1 × 0·3 × 0·3 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; 25 reflections ($12 \leq 2\theta \leq 35°$) used for measuring lattice parameters at 123 K; analytical absorption correction applied with a transmission-factor range of 0·888–0·965; ω scan; max. $\lambda^{-1}\sin\theta = 0{\cdot}5946$ Å^{-1}; $+h$ (0 to 16), $+k$ (0 to 16), $+l$ (0 to 20); six standard reflections measured after every 2 h of data collection showed no significant decay in intensities; 3255 measured, averaged ($R_{\rm int} = 5{\cdot}2\%$) to 1414 unique data; solution by Patterson and Fourier techniques; full-matrix least-squares refinement on F and final refinement cycles on F^2; positions of H atoms of methyl groups located on difference electron density maps and idealized by a least-squares procedure; other H-atom positions derived with the assumption of idealized geometries (C—H = 0·95 Å); all non-H atoms refined anisotropically; 111 refined parameters; $w = 1/\sigma^2(F^2)$; $R(F^2) = 0{\cdot}078$; $wR(F^2) = 0{\cdot}124$; $S(F^2) = 1{\cdot}68$; $R(F) = 0{\cdot}050$ based on 998 reflections with $F^2 > 3\sigma(F^2)$; max. $\Delta/\sigma = 0{\cdot}32$ in final cycle of refinement; in final difference electron density synthesis max. and min. heights 1·1 (2) and −0·8 (2) e Å^{-3}; atomic scattering factors for non-H atoms and anomalous-dispersion correction terms for Mo are from Cromer & Waber (1974); scattering factor for H from Stewart, Davidson & Simpson (1965); all calculations were performed on a Harris 1000 computer with methods and programs standard for this laboratory (Waters & Ibers, 1977).

Discussion. Positional and equivalent isotropic thermal parameters are given in Table 1 and bond lengths and angles in Table 2.* A perspective view of the molecule is shown in Fig. 1.

The Mo dimer has crystallographically imposed 422 symmetry with a linear O=Mo—O—Mo=O arrangement along a fourfold axis. A disordered ethanol molecule is found on a fourfold axis. The terminal Mo=O and the bridging Mo—O bond distances are 1·721 (6) and 1·951 (1) Å, respectively.

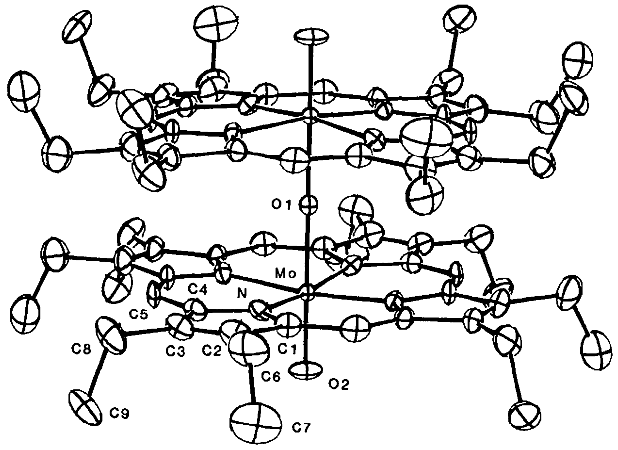

Fig. 1. Drawing of μ-oxo-bis[(2,3,7,8,12,13,17,18-octaethylporphyrinato)oxomolybdenum(V)] (50% probability thermal ellipsoids) along with the atom-numbering scheme. H atoms are omitted for clarity.

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44163 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Both are slightly longer than those of the corresponding tpp complex (Johnson & Scheidt, 1978). The Mo atom is displaced 0·13 Å out of the plane defined by the four porphyrinato N atoms toward the terminal oxo ligand. The Mo—N bond distance is 2·111 (4) Å, also slightly longer than the value found in the tpp complex.

The porphyrinato core is planar within 0·06 Å, but is slightly domed. The bond lengths and angles are normal compared with those reported for the planar porphyrins. The two porphyrin rings are twisted by 22·3° with respect to one another. The interplanar distance between mean nitrogen planes is 3·65 Å. The interplanar distance between the mean porphyrin planes is 3·54 Å, considerably shorter than that in the tpp complex (3·85 Å) where the approach of the two porphyrin cores is hindered by the bulky phenyl groups. As shown in Fig. 1, all peripheral ethyl groups are oriented outside, permitting better π–π interaction between the two porphyrin cores.

When we attempted to crystallize [Mo(oep)]$_2$ from toluene/heptane, the title compound crystallized in space group $C2/m$ (C_{2h}^3) of the monoclinic system with $a = 20{\cdot}13$ (8), $b = 14{\cdot}327$ (6), $c = 24{\cdot}155$ (10) Å, $\beta = 103{\cdot}54$ (1)°, $V = 6773$ Å^3. However, owing to severe disordering of solvent molecules, this structure did not refine well and was abandoned.

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Tris(2,6-dimethylphenyl)hydroxystibonium Iodide

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Abstract. [$Sb(C_8H_9)_3(OH)$]I, $M_r = 581{\cdot}14$, monoclinic, $P2_1/c$, $a = 10{\cdot}584$ (2), $b = 11{\cdot}184$ (3), $c = 19{\cdot}292$ (4) Å, $\beta = 94{\cdot}60$ (2)°, $V = 2276$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}70$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 25{\cdot}7$ cm^{-1}, $F(000) = 1136$, $T = 294$ K, $R = 0{\cdot}023$ for 4167 reflections with $I > 3\sigma(I)$. The structure contains discrete hydrogen-bonded units, $(Me_2C_6H_3)_3\overset{+}{Sb}$—O—H···I$^-$, with O···I 3·315 (2), Sb—O 1·907 (2), mean Sb—C 2·120 (3) Å, C—Sb—C 114·3–115·6 (1), O—Sb—C 97·4–106·9 (1)°. The infrared spectrum is also in accord with a stibonium salt structure. The coordination at Sb is distorted tetrahedral due to repulsions between the bulky 2,6-dimethylphenyl ligands and with the iodide ion.

Introduction. Whereas the products of partial hydrolysis of triaryl- and trialkylarsenic dihalides, the so-called 'hydroxyhalides' [*e.g.* $Ph_3AsOHCl$], have been structurally characterized (Ferguson & Macaulay, 1968), structural information on the corresponding antimony compounds is lacking and some doubt has been expressed about their existence (Long, Doak & Freedman, 1964; Doak, Long & Freedman, 1965). In this paper we report the first structure determination of an R_3SbOHI compound, namely tris(2,6-dimethylphenyl)hydroxystibonium iodide [$(Me_2C_6H_3)_3$Sb(OH)I].

Experimental. Tris(2,6-dimethylphenyl)hydroxystibonium iodide crystallized as orange plates from a solution of tris(2,6-dimethylphenyl)antimony diiodide dissolved in aqueous (10%) methanol, m.p. 487–489 K. (Found: C, 49·4; H, 4·8%. Calc. for $C_{24}H_{28}IOSb$: C, 49·6; H, 4·9%.) Accurate cell dimensions and crystal

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