

Refinement

Refinement on F^2
 $R = 0.0548$
 $wR = 0.0631$
 $S = 2.08$
 3016 reflections
 235 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0001F^2]$
 $(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.72 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.79 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1990)

Crystallography was performed at the National Single Crystal Diffractometer Facility, IACS, Calcutta. Financial assistance received from the Council of Scientific and Industrial Research, New Delhi, is acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ru(1)	1.1315 (1)	0.1159 (1)	0.3002 (1)	0.028 (1)
Ru(2)	0.8836 (1)	-0.0082 (1)	0.2250 (1)	0.027 (1)
Cl(1)	1.2465 (3)	0.1669 (2)	0.2029 (2)	0.047 (1)
Cl(2)	1.0001 (2)	0.0506 (2)	0.3805 (2)	0.032 (1)
Cl(3)	1.1010 (2)	-0.0256 (2)	0.2215 (2)	0.034 (1)
Cl(4)	0.9191 (2)	0.1376 (2)	0.1774 (2)	0.037 (1)
S(1)	1.1268 (3)	0.2441 (2)	0.3630 (2)	0.035 (1)
S(2)	1.3171 (2)	0.0757 (2)	0.4064 (2)	0.035 (1)
S(3)	0.7985 (3)	-0.0597 (2)	0.0768 (2)	0.036 (1)
S(4)	0.6848 (2)	0.0261 (2)	0.2261 (2)	0.036 (1)
S(5)	0.8849 (3)	-0.1382 (2)	0.2920 (2)	0.034 (1)
O(1)	1.2232 (8)	0.2675 (5)	0.4535 (6)	0.058 (3)
O(2)	1.3137 (8)	0.0351 (6)	0.4927 (5)	0.050 (3)
O(3)	0.6631 (7)	-0.0845 (6)	0.0427 (6)	0.054 (3)
O(4)	0.5945 (7)	-0.0428 (5)	0.2260 (6)	0.048 (3)
O(5)	0.8319 (9)	-0.2122 (5)	0.2319 (5)	0.051 (3)
C(1)	1.1260 (14)	0.3264 (8)	0.2825 (11)	0.060 (6)
C(2)	0.9776 (12)	0.2634 (8)	0.3756 (9)	0.048 (5)
C(3)	1.4380 (11)	0.1551 (9)	0.4377 (9)	0.052 (5)
C(4)	1.3958 (11)	0.0011 (8)	0.3554 (8)	0.047 (4)
C(5)	0.8183 (13)	0.0145 (8)	-0.0061 (8)	0.049 (4)
C(6)	0.8880 (13)	-0.1479 (8)	0.0556 (9)	0.051 (5)
C(7)	0.6027 (11)	0.0946 (8)	0.1328 (10)	0.055 (5)
C(8)	0.6925 (11)	0.0935 (7)	0.3220 (9)	0.048 (5)
C(9)	1.0454 (12)	-0.1670 (8)	0.3611 (10)	0.056 (5)
C(10)	0.8147 (13)	-0.1362 (7)	0.3811 (8)	0.049 (5)

Table 2. Selected geometric parameters (Å , $^\circ$)

Ru(1)—Cl(1)	2.394 (4)	Ru(2)—Cl(2)	2.454 (3)
Ru(1)—Cl(2)	2.421 (3)	Ru(2)—Cl(3)	2.446 (3)
Ru(1)—Cl(3)	2.490 (3)	Ru(2)—Cl(4)	2.470 (3)
Ru(1)—Cl(4)	2.483 (3)	Ru(2)—S(3)	2.271 (3)
Ru(1)—S(1)	2.234 (3)	Ru(2)—S(4)	2.276 (3)
Ru(1)—S(2)	2.232 (3)	Ru(2)—S(5)	2.277 (3)
Cl(1)—Ru(1)—Cl(2)	171.9 (1)	Cl(2)—Ru(2)—Cl(3)	82.0 (1)
Cl(1)—Ru(1)—Cl(3)	90.9 (1)	Cl(2)—Ru(2)—Cl(4)	81.3 (1)
Cl(1)—Ru(1)—Cl(4)	93.5 (1)	Cl(2)—Ru(2)—S(3)	172.8 (1)
Cl(1)—Ru(1)—S(1)	93.2 (1)	Cl(2)—Ru(2)—S(4)	95.7 (1)
Cl(1)—Ru(1)—S(2)	89.2 (1)	Cl(2)—Ru(2)—S(5)	89.2 (1)
Cl(2)—Ru(1)—Cl(3)	81.8 (1)	Cl(3)—Ru(2)—Cl(4)	80.9 (1)
Cl(2)—Ru(1)—Cl(4)	81.7 (1)	Cl(3)—Ru(2)—S(3)	91.2 (1)
Cl(2)—Ru(1)—S(1)	93.5 (1)	Cl(3)—Ru(2)—S(4)	172.7 (1)
Cl(2)—Ru(1)—S(2)	94.7 (1)	Cl(3)—Ru(2)—S(5)	93.0 (1)
Cl(3)—Ru(1)—Cl(4)	79.8 (1)	Cl(4)—Ru(2)—S(3)	95.4 (1)
Cl(3)—Ru(1)—S(1)	171.4 (1)	Cl(4)—Ru(2)—S(4)	92.0 (1)
Cl(3)—Ru(1)—S(2)	92.1 (1)	Cl(4)—Ru(2)—S(5)	169.3 (1)
Cl(4)—Ru(1)—S(1)	92.5 (1)	S(3)—Ru(2)—S(4)	90.7 (1)
Cl(4)—Ru(1)—S(2)	171.5 (1)	S(3)—Ru(2)—S(5)	93.5 (1)
S(1)—Ru(1)—S(2)	95.5 (1)	S(4)—Ru(2)—S(5)	93.9 (1)

H atoms were fixed at ideal positions with fixed isotropic displacement parameters ($U_{iso} = 0.08 \text{ Å}^2$). Structure solution and refinement used *SHELXTL-Plus* (Sheldrick, 1990) on a MicroVAX II computer.

References

- Allesio, E., Balducci, G., Calligaris, M., Costa, G., Attia, W. M. & Mestroni, G. (1991). *Inorg. Chem.* **30**, 609–618, and references therein.
 Allesio, E., Mestroni, G., Nardin, G., Attia, W. M., Calligaris, M., Sava, G. & Zorzet, S. (1988). *Inorg. Chem.* **27**, 4099–4106.
 Davies, A. R., Einstein, F. W. B., Farrell, N. P., James, B. R. & McMillan, R. S. (1978). *Inorg. Chem.* **17**, 1965–1969.
 Heath, G. A., Lindsay, A. J. & Stephenson, T. A. (1982). *J. Chem. Soc. Dalton Trans.* pp. 2429–2432.
 Hudali, H. A., Kingston, J. V. & Tayim, H. A. (1979). *Inorg. Chem.* **18**, 1391–1394.
 Sheldrick, G. M. (1990). *SHELXTL-Plus. Structure Determination Software Programs*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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(2,3,7,8,12,13,17,18-Octaethylporphinato)-perchloratomanganese(III)

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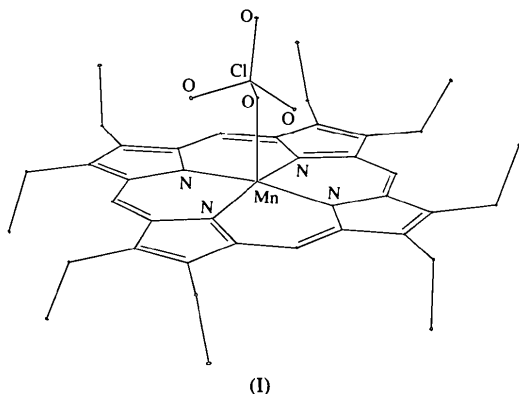
Abstract

The crystal structure of $[\text{Mn}(\text{OEP})(\text{OClO}_3)]$ (where OEP = $\text{C}_{36}\text{H}_{44}\text{N}_4$) has been determined. The axial Mn—O bond length is 2.183 (2) Å and the equatorial Mn—N_p bond lengths have an average value of 2.000 (5) Å . The molecules form weak dimers in the solid state with interring distances of 3.49 Å and a lateral shift of 3.27 Å . The compound is found to be isomorphous with the iron derivative $[\text{Fe}(\text{OEP})(\text{OClO}_3)]$. A brief comparison of the structural parameters for the two molecules is given.

Comment

The structure determination of the title compound, (I), was undertaken to identify the reaction intermediate

which leads to the novel singly hydroxo-bridged metalloporphyrin complex $\{[Mn(OEP)}_2OH\}ClO_4$, analogous to the reported compound $\{[Fe(OEP)}_2OH\}ClO_4$ (Scheidt *et al.*, 1992).



An ORTEPII (Johnson, 1976) diagram with labeling scheme for this molecule is shown in Fig. 1. The average values for the unique chemical classes of distances and angles in the porphinato core, and the perpendicular displacements of each atom from the mean plane of the 24-atom core are given in Fig. 3. The agreement between chemically equivalent bond distances and angles is quite satisfactory.

The structure is isomorphous with that of the iron derivative $[Fe(OEP)(OCIO_3)]$ reported by Masuda *et al.* (1980) and thus shows strong similarities in all important structural features. The average Mn—N_p bond length of 2.000 (5) Å is very similar, within experimental error, to that of 1.994 (10) Å found for $[Fe(OEP)(OCIO_3)]$. An increase in the axial M—O bond length in the Mn derivative relative to the Fe derivative [from 2.067 (9) to 2.183 (2) Å] is associated with a decrease in metal-center displacements (from 0.26 to 0.18 Å). Compared with five-coordinate high-spin

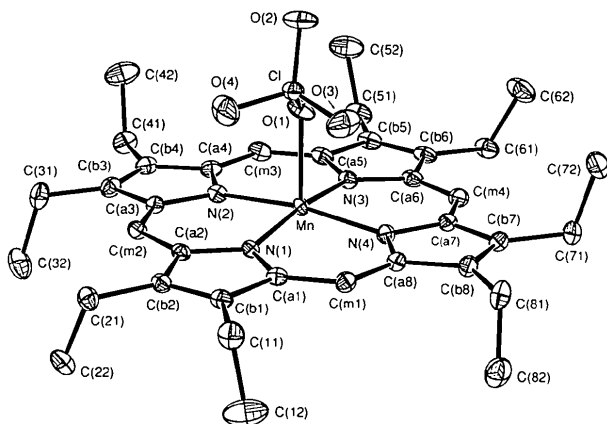


Fig. 1. ORTEPII diagram of the $[Mn(OEP)(OCIO_3)]$ molecule with labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity.

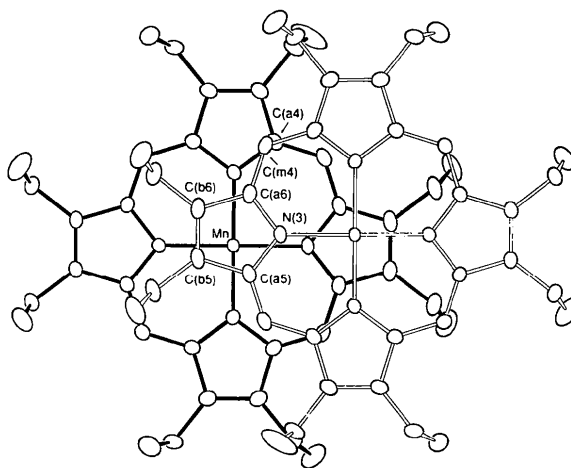


Fig. 2. Topview of a pair of $[Mn(OEP)(OCIO_3)]$ molecules, showing the close face-to-face contact and lateral shift between two porphyrin rings. Displacement ellipsoids are drawn at the 50% probability level. The perchlorato ligands and porphyrin H atoms are omitted for clarity.

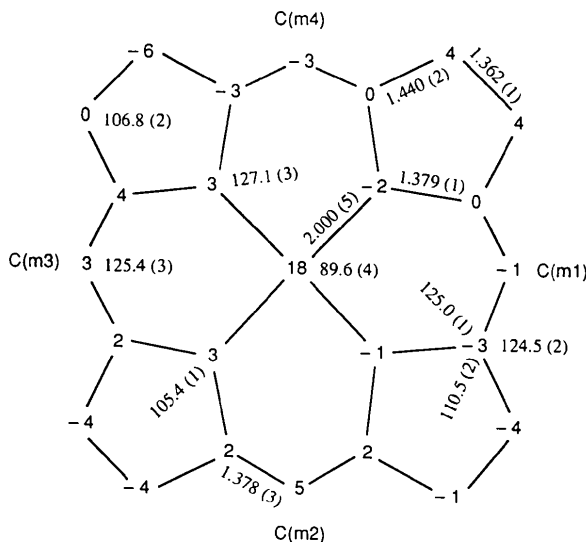


Fig. 3. Formal diagram of the porphinato core of $[Mn(OEP)(OCIO_3)]$, displaying the average values of the bond parameters. The numbers in parentheses are the estimated standard deviations calculated on the assumption that the average values were all drawn from the same population. Also displayed are the perpendicular displacements, in units of 0.01 Å, of each atom from the 24-atom mean plane of the core.

iron(III) porphyrinate complexes, the shorter equatorial Mn—N_p bond length and smaller Mn-atom displacement found in this molecule is consistent with its d^4 high-spin electronic structure (Scheidt & Reed, 1981). The molecules in the lattice form weak dimers (see Fig. 2), as observed for $[Fe(OEP)(OCIO_3)]$. The mean planes of the two porphinato cores with close 'face-to-face' contact have an interplanar distance of 3.49 Å and a lateral shift of 3.27 Å, consistent with its four-up/four-

down peripheral ethyl group orientation (Scheidt & Lee, 1987). Within such a dimeric unit, the Mn atom of one molecule is located just below the pyrrole ring of another molecule, with a distance of 3.60 Å from the Mn atom to the pyrrole least-squares plane. The shortest inter-ring distance of 3.50 Å is found between C(a4) of one ring and C(m2) of another ring. These structural parameters suggest that the Mn atom has a pseudo six-coordinate environment and that the pair of porphyrin units have overlapping π orbitals.

Experimental

The title compound was synthesized by the reaction of [Mn(OEP)Cl] in dichloromethane solution with an excess amount of aqueous perchloric acid (2%) and crystallized from distilled dichloromethane and hexanes.

Crystal data

[Mn(C₃₆H₄₄N₄)(ClO₄)]

$M_r = 687.14$

Monoclinic

$P2_1/c$

$a = 13.457(1) \text{ \AA}$

$b = 14.082(2) \text{ \AA}$

$c = 18.845(1) \text{ \AA}$

$\beta = 105.86(1)^\circ$

$V = 3435.2(6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.329 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 250 reflections

$\theta = 5.1\text{--}20.8^\circ$

$\mu = 0.506 \text{ mm}^{-1}$

$T = 127(2) \text{ K}$

Square bipyramid

$0.40 \times 0.25 \times 0.15 \text{ mm}$

Black

Data collection

Enraf–Nonius FAST area-detector diffractometer

Ellipsoid-mask fitting

Absorption correction:

refined from ΔF

(DIFABS; Walker & Stuart, 1983)

$T_{\min} = 0.675$, $T_{\max} =$

0.773

25492 measured reflections

8588 independent reflections

7058 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0459$

$\theta_{\text{max}} = 29.75^\circ$

$h = -16 \rightarrow 18$

$k = -10 \rightarrow 19$

$l = -26 \rightarrow 21$

Refinement

Refinement on F^2

$R(F) = 0.0463$

$wR(F^2) = 0.1090$

$S = 1.101$

8588 reflections

423 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 3.4902P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.966 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.755 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Mn	0.35410(2)	-0.01179(2)	0.05945(2)	0.01205(8)
N(1)	0.23946(12)	-0.10679(11)	0.03400(9)	0.0128(3)
N(2)	0.26936(13)	0.07572(11)	-0.01715(9)	0.0138(3)

N(3)	0.47628(13)	0.07420(11)	0.07083(9)	0.0152(3)
N(4)	0.44663(12)	-0.10843(11)	0.12172(9)	0.0145(3)
C(a1)	0.23893(15)	-0.19570(12)	0.06487(10)	0.0138(4)
C(a2)	0.14080(15)	-0.09344(13)	-0.01113(10)	0.0135(4)
C(a3)	0.1677(2)	0.06444(13)	-0.05711(10)	0.0147(4)
C(a4)	0.2984(2)	0.16315(13)	-0.03769(11)	0.0160(4)
C(a5)	0.4771(2)	0.16276(13)	0.03977(11)	0.0164(4)
C(a6)	0.57557(15)	0.06001(14)	0.11459(11)	0.0159(4)
C(a7)	0.5480(2)	-0.09686(13)	0.16193(11)	0.0164(4)
C(a8)	0.4179(2)	-0.19587(13)	0.14225(11)	0.0157(4)
C(b1)	0.1390(2)	-0.23915(13)	0.03743(11)	0.0153(4)
C(b2)	0.07795(15)	-0.17587(13)	-0.00965(11)	0.0146(4)
C(b3)	0.1332(2)	0.14501(14)	-0.10467(11)	0.0180(4)
C(b4)	0.2146(2)	0.20628(13)	-0.09232(11)	0.0179(4)
C(b5)	0.5782(2)	0.20466(14)	0.06464(11)	0.0188(4)
C(b6)	0.6396(2)	0.14064(14)	0.11037(11)	0.0181(4)
C(b7)	0.5832(2)	-0.17798(14)	0.20882(11)	0.0175(4)
C(b8)	0.5021(2)	-0.23937(14)	0.19658(11)	0.0179(4)
C(m1)	0.3216(2)	-0.23623(13)	0.11549(11)	0.0160(4)
C(m2)	0.10688(15)	-0.01341(13)	-0.05264(10)	0.0151(4)
C(m3)	0.3944(2)	0.20371(13)	-0.01070(11)	0.0182(4)
C(m4)	0.60877(15)	-0.01929(14)	0.15708(11)	0.0175(4)
C(11)	0.1107(2)	-0.33633(14)	0.05781(13)	0.0227(4)
C(21)	-0.0308(2)	-0.18841(15)	-0.05566(12)	0.0197(4)
C(31)	0.0297(2)	0.1548(2)	-0.15903(13)	0.0244(5)
C(41)	0.2196(2)	0.30122(14)	-0.12685(12)	0.0218(4)
C(51)	0.6064(2)	0.30176(15)	0.04332(13)	0.0246(5)
C(61)	0.7524(2)	0.1493(2)	0.14909(12)	0.0231(4)
C(71)	0.6873(2)	-0.1882(2)	0.26288(12)	0.0225(4)
C(81)	0.4979(2)	-0.3345(2)	0.23104(12)	0.0230(4)
C(12)	0.1443(3)	-0.4155(2)	0.04147(2)	0.0456(7)
C(22)	-0.0353(2)	-0.2187(2)	-0.13468(14)	0.0318(5)
C(32)	0.0175(2)	0.0923(2)	-0.22732(13)	0.0325(5)
C(42)	0.2039(2)	0.3839(2)	-0.0787(2)	0.0369(6)
C(52)	0.5729(2)	0.3812(2)	0.0869(2)	0.0383(6)
C(62)	0.7750(2)	0.1833(2)	0.22853(14)	0.0352(6)
C(72)	0.6932(2)	-0.1423(3)	0.3372(2)	0.0532(9)
C(82)	0.5026(2)	-0.4173(2)	0.18025(15)	0.0304(5)
Cl	0.24208(4)	0.00980(3)	0.19261(3)	0.01641(10)
O(1)	0.30622(12)	0.05260(10)	0.15020(8)	0.0216(3)
O(2)	0.23653(14)	0.07623(12)	0.24836(9)	0.0305(4)
O(3)	0.2872(2)	-0.07667(12)	0.22398(10)	0.0366(4)
O(4)	0.14254(12)	-0.00647(14)	0.14352(10)	0.0351(4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Mn—N(1)	1.999(2)	C(a7)—C(m4)	1.382(3)
Mn—N(2)	2.001(2)	C(a8)—C(m1)	1.379(3)
Mn—N(3)	2.006(2)	C(b1)—C(b2)	1.363(3)
Mn—N(4)	1.995(2)	C(b3)—C(b4)	1.363(3)
Mn—O(1)	2.183(2)	C(b5)—C(b6)	1.360(3)
N(1)—C(a1)	1.381(2)	C(b7)—C(b8)	1.362(3)
N(1)—C(a2)	1.380(2)	C(b1)—C(11)	1.498(3)
N(2)—C(a3)	1.379(2)	C(b2)—C(21)	1.493(3)
N(2)—C(a4)	1.379(2)	C(b3)—C(31)	1.493(3)
N(3)—C(a5)	1.379(2)	C(b4)—C(41)	1.496(3)
N(3)—C(a6)	1.380(2)	C(b5)—C(51)	1.503(3)
N(4)—C(a7)	1.378(2)	C(b6)—C(61)	1.499(3)
N(4)—C(a8)	1.377(2)	C(b7)—C(71)	1.496(3)
C(a1)—C(b1)	1.439(3)	C(b8)—C(81)	1.496(3)
C(a2)—C(b2)	1.441(3)	C(11)—C(12)	1.519(3)
C(a3)—C(b3)	1.442(3)	C(21)—C(22)	1.534(3)
C(a4)—C(b4)	1.438(3)	C(31)—C(32)	1.531(3)
C(a5)—C(b5)	1.439(3)	C(41)—C(42)	1.526(3)
C(a6)—C(b6)	1.440(3)	C(51)—C(52)	1.527(3)
C(a7)—C(b7)	1.443(3)	C(61)—C(62)	1.521(3)
C(a8)—C(b8)	1.440(3)	C(71)—C(72)	1.525(3)
C(a1)—C(m1)	1.376(3)	C(81)—C(82)	1.521(3)
C(a2)—C(m2)	1.377(3)	Cl—O(1)	1.457(2)
C(a3)—C(m2)	1.384(3)	Cl—O(2)	1.424(2)
C(a4)—C(m3)	1.376(3)	Cl—O(3)	1.416(2)
C(a5)—C(m3)	1.377(3)	Cl—O(4)	1.423(2)
C(a6)—C(m4)	1.375(3)		
N(1)—Mn—N(2)	89.36(6)	C(m1)—C(a8)—C(b8)	124.3(2)
N(1)—Mn—N(3)	170.44(7)	C(b2)—C(b1)—C(a1)	107.1(2)
N(1)—Mn—N(4)	90.07(7)	C(b1)—C(b2)—C(a2)	106.7(2)
N(2)—Mn—N(3)	89.67(7)	C(b4)—C(b3)—C(a3)	106.5(2)

N(2)—Mn—N(4)	170.22 (7)	C(b3)—C(b4)—C(a4)	106.9 (2)
N(3)—Mn—N(4)	89.28 (7)	C(b6)—C(b5)—C(a5)	106.9 (2)
N(1)—Mn—O(1)	95.30 (6)	C(b5)—C(b6)—C(a6)	106.8 (2)
N(2)—Mn—O(1)	94.44 (6)	C(b8)—C(b7)—C(a7)	106.6 (2)
N(3)—Mn—O(1)	94.26 (6)	C(b7)—C(b8)—C(a8)	106.8 (2)
N(4)—Mn—O(1)	95.34 (6)	C(a1)—C(m1)—C(a8)	125.7 (2)
C(a1)—N(1)—Mn	126.73 (13)	C(a2)—C(m2)—C(a3)	125.0 (2)
C(a2)—N(1)—Mn	127.32 (12)	C(a4)—C(m3)—C(a5)	125.5 (2)
C(a3)—N(2)—Mn	127.44 (13)	C(a6)—C(m4)—C(a7)	125.2 (2)
C(a4)—N(2)—Mn	127.09 (13)	C(a1)—C(b1)—C(11)	125.0 (2)
C(a5)—N(3)—Mn	127.00 (14)	C(a2)—C(b2)—C(21)	124.8 (2)
C(a6)—N(3)—Mn	127.46 (13)	C(a3)—C(b3)—C(31)	125.5 (2)
C(a7)—N(4)—Mn	127.45 (13)	C(a4)—C(b4)—C(41)	124.7 (2)
C(a8)—N(4)—Mn	126.66 (13)	C(a5)—C(b5)—C(51)	124.8 (2)
C(a1)—N(1)—C(a2)	105.56 (15)	C(a6)—C(b6)—C(61)	125.3 (2)
C(a3)—N(2)—C(a4)	105.4 (2)	C(a7)—C(b7)—C(71)	125.6 (2)
C(a5)—N(3)—C(a6)	105.4 (2)	C(a8)—C(b8)—C(81)	125.0 (2)
C(a7)—N(4)—C(a8)	105.3 (2)	C(b2)—C(b1)—C(11)	127.9 (2)
N(1)—C(a1)—C(b1)	110.2 (2)	C(b1)—C(b2)—C(21)	128.4 (2)
N(1)—C(a2)—C(b2)	110.4 (2)	C(b4)—C(b3)—C(31)	127.9 (2)
N(2)—C(a3)—C(b3)	110.6 (2)	C(b3)—C(b4)—C(41)	128.4 (2)
N(2)—C(a4)—C(b4)	110.5 (2)	C(b6)—C(b5)—C(51)	128.2 (2)
N(3)—C(a5)—C(b5)	110.4 (2)	C(b5)—C(b6)—C(61)	127.9 (2)
N(3)—C(a6)—C(b6)	110.4 (2)	C(b8)—C(b7)—C(71)	127.7 (2)
N(4)—C(a7)—C(b7)	110.7 (2)	C(b7)—C(b8)—C(81)	128.2 (2)
N(4)—C(a8)—C(b8)	110.7 (2)	C(b1)—C(11)—C(12)	113.6 (2)
N(1)—C(a1)—C(m1)	124.9 (2)	C(b2)—C(21)—C(22)	111.7 (2)
N(1)—C(a2)—C(m2)	125.1 (2)	C(b3)—C(31)—C(32)	112.9 (2)
N(2)—C(a3)—C(m2)	125.0 (2)	C(b4)—C(41)—C(42)	113.2 (2)
N(2)—C(a4)—C(m3)	125.2 (2)	C(b5)—C(51)—C(52)	112.9 (2)
N(3)—C(a5)—C(m3)	125.0 (2)	C(b6)—C(61)—C(62)	114.1 (2)
N(3)—C(a6)—C(m4)	125.0 (2)	C(b7)—C(71)—C(72)	112.9 (2)
N(4)—C(a7)—C(m4)	124.9 (2)	C(b8)—C(81)—C(82)	113.6 (2)
N(4)—C(a8)—C(m1)	125.0 (2)	O(1)—Cl—O(2)	106.93 (9)
C(m1)—C(a1)—C(b1)	124.9 (2)	O(1)—Cl—O(3)	109.49 (11)
C(m2)—C(a2)—C(b2)	124.4 (2)	O(1)—Cl—O(4)	107.67 (10)
C(m2)—C(a3)—C(b3)	124.5 (2)	O(2)—Cl—O(3)	111.10 (11)
C(m3)—C(a4)—C(b4)	124.3 (2)	O(2)—Cl—O(4)	110.83 (11)
C(m3)—C(a5)—C(b5)	124.5 (2)	O(3)—Cl—O(4)	110.68 (12)
C(m4)—C(a6)—C(b6)	124.6 (2)	Cl—O(1)—Mn	127.13 (8)
C(m4)—C(a7)—C(b7)	124.4 (2)		

Cell-constants determination and intensity-data collection were performed on an Enraf-Nonius FAST area-detector diffractometer with an Mo rotating anode source. Our detailed methods and procedures for small molecule X-ray data collection with the FAST system have been described previously (Scheidt & Turowska-Tyrk, 1994). All H atoms were idealized with the standard methods in *SHELXL93* (Sheldrick, 1993) and included in the least-square process as fixed contributors (for methyl H atoms, the methyl group orientations were refined) using a riding model for CH (C—H = 0.95 Å), CH₂ (C—H = 0.99 Å) and CH₃ (C—H = 0.98 Å).

Data collection: *MADNES* (Messerschmitt & Pflugrath, 1987). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: JZ1011). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Masuda, H., Taga, T., Osaki, K., Sugimoto, H., Yoshida, Z.-I. & Ogoshi, H. (1980). *Inorg. Chem.* **19**, 950–955.
- Messerschmitt, A. & Pflugrath, J. W. (1987). *J. Appl. Cryst.* **20**, 306–315.
- Scheidt, W. R., Cheng, B., Safo, M. K., Cukiernik, F., Marchon, J.-C. & Debrunner, P. G. (1992). *J. Am. Chem. Soc.* **114**, 4420–4421.
- Scheidt, W. R. & Lee, Y. J. (1987). *Struct. Bonding*, **64**, 1–70.
- Scheidt, W. R. & Reed, C. A. (1981). *Chem. Rev.* **81**, 543–555.
- Scheidt, W. R. & Turowska-Tyrk, I. (1994). *Inorg. Chem.* **33**, 1314–1318.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

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[(R)-1,2-Diethoxycarbonyl ethyl]bis(dimethylglyoximato)(methyl diphenylphosphine)cobalt(III)

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Abstract

The crystal structure of the title compound, [Co(C₄H₇-N₂O₂)₂(C₈H₁₃O₄)(C₁₃H₁₃P)], has been determined in order to examine whether or not the chiral 1,2-diethoxycarbonyl ethyl group is racemized on exposure to either visible light or X-rays with retention of the single-crystal form. Although the reaction cavity of the chiral group is considerably large, the chiral group is isolated from the other chiral groups in the structure. The cooperative motion between the chiral groups necessary for the racemization of bulky groups may be impossible in such an isolated environment.

Comment

In the study of crystalline-state racemization of bis(dimethylglyoximato)cobalt(III) complexes, three kinds of chiral group bonded to the Co atom,