FLOMER, W. A., O'NEAL, S. C., KOLIS, J. W., JETER, D. & CORDES, A. W. (1988). *Inorg. Chem.* **27**, 969–971.
FRENZ, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.
GINSBERG, A. P., OSBORNE, J. H. & SPRINKLE, C. R. (1983). *Inorg. Chem.* **22**, 1781–1790.
HAUSHALTER, R. C. (1985*a*). *Angew. Chem. Int. Ed. Engl.* **24**, 432–433.
HAUSHALTER, R. C. (1985*b*). *Angew. Chem. Int. Ed. Engl.* **24**, 433–435.
HAUSHALTER, R. C. (1985*c*). *Inorg. Chim. Acta*, **102**, L37-L38.
KANATZIDIS, M. G. (1988). 196th Am. Chem. Soc. Natl Meet., Los Angeles, Abstract INOR 469.
MÜLLER, A., KRICKEMEYER, E., BÖGGE, H., CLEGG, W. & SHELDRICK G. M. (1983). *Angew. Chem. Int. Ed. Engl.* **22**, 1006–1007.
SHELDRICK G. M. (1985). *SHELXS86. Crystallographic Computing* 3; edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD. pp. 175–189. Oxford Univ. Press.

*Acta Cryst.* (1991). C**47**, 1196–1198

# Structure of [(*R*)-1,2-Dimethoxycarbonylethyl]bis(dimethylglyoximato)-[(*S*)-1-phenylethylamine]cobalt(III)

BY YOSHII SAKAI, TAKAYUKI TAMURA, AKIRA UCHIDA AND YUJI OHASHI†

*Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo* 152, *Japan*

AND EMIKO HASEGAWA, YOSHIFUSA ARAI AND YOSHIAKI OHGO

*Niigata College of Pharmacy*, 5829 *Kamishinei-cho, Niigata* 950-21, *Japan*

(*Received* 29 *October* 1990; *accepted* 10 *December* 1990)

**Abstract.** $C_{22}H_{34}CoN_5O_8$, $M_r = 555{\cdot}5$, trigonal, $P3_2$, $a = 14{\cdot}942\,(2)$, $c = 10{\cdot}174\,(3)$ Å, $V = 1967{\cdot}9\,(7)$ Å$^3$, $Z = 3$, $D_x = 1{\cdot}407$ g cm$^{-3}$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 6{\cdot}54$ cm$^{-1}$, $F(000) = 879$, $T = 298$ K, final $R = 0{\cdot}041$ for 3216 independent reflections. The crystal shows no change on exposure to X-rays at 298 K. The 1,2-dimethoxycarbonylethyl group takes an L-shape conformation.

**Introduction.** In the serial studies of crystalline-state racemization of bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes, two kinds of chiral reactive groups bonded to the Co atom [1-cyanoethyl (ce) group, $-C^*H(CH_3)CN$ and 1-methoxycarbonylethyl (mce) group, $-C^*H(CH_3)CO_2CH_3$] have been found to be racemized on exposure to X-rays (Ohashi, 1988; Kurihara, Ohashi, Sasada & Ohgo, 1983; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984). Recently it was reported that a cobaloxime complex, with the bulkier chiral group 1,2-dimethoxycarbonylethyl (dmce), was racemized in a cyclohexanone solution and that the racemization rate was not so different from those of the cobaloxime complexes with reactive ce and mce groups (Ohgo, Orisaku, Hasegawa & Takeuchi, 1986). This work was undertaken to ascertain if the crystalline-state racemization is observed for such a bulky chiral group and to determine the structure of the dmce group.

**Experimental.** The complex was prepared as reported by Ohgo, Orisaku, Hasegawa & Takeuchi (1986). Orange plate-like crystals obtained from an aqueous methanol solution; crystal dimensions 0·5 × 0·5 × 0·5 mm; Rigaku AFC-4 diffractometer with graphite-crystal-monochromated Mo $K\alpha$ radiation; systematic absences $00l$ $l \neq 3n$; cell parameters refined by least-squares method on 15 independent $2\theta$ values with $19 < 2\theta < 27°$; intensity measurement performed up to $2\theta = 55°$; range of $hkl$: 0 to 10, 0 to 16, −13 to 13; $\omega$–$2\theta$ scan technique; scan speed 4° min$^{-1}$; scan width $(1{\cdot}0 + 0{\cdot}35\tan\theta)°$; background 5 s before and after each scan. Three standard reflections monitored every 100 reflections; no significant variation in intensities; 3381 reflections measured, 3216 with $|F_o| > 3\sigma(F_o)$ considered observed and used for structure determination; corrections for Lorentz and polarization, absorption ignored. Direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference Fourier calculations; full-matrix least squares on $F$ (*SHELX*76; Sheldrick, 1976) with anisotropic thermal parameters for non-H atoms; H atoms derived geometrically (C—H 1·00 Å) and refined with isotropic thermal parameters;

---

† To whom correspondence should be addressed.

0108-2701/91/061196-03$03.00

Table 1. *Positional parameters* (Co × $10^5$, *others* × $10^4$) *and* $B_{eq}$ *values* (Å$^2$)

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Co | 70821 (4) | 92678 (4) | 6273 | 2·5 (0) |
| N(1) | 5740 (3) | 8766 (3) | 1300 (3) | 3·1 (1) |
| N(2) | 7074 (3) | 8301 (3) | 1819 (3) | 3·0 (1) |
| N(3) | 8439 (3) | 9800 (3) | − 37 (3) | 3·0 (1) |
| N(4) | 7114 (3) | 10259 (3) | − 559 (3) | 3·1 (1) |
| O(1) | 5143 (2) | 9152 (3) | 934 (3) | 4·3 (1) |
| O(2) | 7897 (2) | 8192 (2) | 2035 (3) | 3·9 (1) |
| O(3) | 9094 (2) | 9495 (3) | 419 (3) | 4·0 (1) |
| O(4) | 6311 (3) | 10430 (3) | − 714 (3) | 4·2 (1) |
| C(1) | 5423 (3) | 8033 (4) | 2166 (4) | 3·5 (1) |
| C(2) | 6220 (3) | 7767 (3) | 2486 (4) | 3·5 (1) |
| C(3) | 8757 (3) | 10543 (3) | − 880 (4) | 3·3 (1) |
| C(4) | 7956 (4) | 10802 (3) | − 1202 (4) | 3·4 (1) |
| C(5) | 4379 (4) | 7528 (5) | 2788 (6) | 5·4 (2) |
| C(6) | 6093 (5) | 6987 (5) | 3520 (7) | 6·2 (2) |
| C(7) | 9836 (4) | 11108 (4) | − 1393 (6) | 4·7 (2) |
| C(8) | 8113 (5) | 11619 (5) | − 2167 (6) | 5·8 (2) |
| C(9) | 6477 (3) | 8096 (3) | − 747 (4) | 3·0 (1) |
| C(10) | 6115 (3) | 8403 (3) | − 1941 (4) | 3·4 (1) |
| O(5) | 6611 (3) | 8740 (3) | − 2924 (3) | 5·1 (1) |
| O(6) | 5148 (3) | 8224 (3) | − 1808 (3) | 4·6 (1) |
| C(11) | 4767 (6) | 8570 (7) | − 2890 (7) | 6·7 (3) |
| C(12) | 7236 (4) | 7745 (4) | − 1108 (5) | 4·0 (2) |
| C(13) | 6852 (4) | 6843 (4) | − 1998 (5) | 4·4 (2) |
| O(7) | 7398 (4) | 6644 (4) | − 2674 (4) | 6·1 (2) |
| O(8) | 5834 (3) | 6246 (3) | − 1996 (4) | 5·7 (2) |
| C(14) | 5458 (6) | 5368 (6) | − 2827 (9) | 8·5 (3) |
| N(5) | 7798 (3) | 10433 (3) | 2011 (3) | 3·0 (1) |
| C(15) | 7226 (4) | 10592 (4) | 3137 (4) | 3·8 (2) |
| C(16) | 7506 (4) | 11708 (4) | 3230 (4) | 3·9 (2) |
| C(17) | 8241 (4) | 12391 (4) | 4124 (5) | 5·2 (2) |
| C(18) | 8489 (7) | 13411 (6) | 4162 (9) | 8·7 (3) |
| C(19) | 8019 (12) | 13752 (7) | 3288 (14) | 11·7 (7) |
| C(20) | 7325 (10) | 13108 (10) | 2435 (11) | 10·6 (7) |
| C(21) | 7061 (5) | 12078 (6) | 2379 (6) | 6·6 (3) |
| C(22) | 7397 (7) | 10132 (5) | 4381 (5) | 6·9 (3) |

Table 2. *Selected bond distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Co—N(1) | 1·884 (4) | C(9)—C(10) | 1·492 (7) |
| Co—N(2) | 1·881 (4) | C(9)—C(12) | 1·514 (7) |
| Co—N(3) | 1·894 (4) | C(10)—O(5) | 1·196 (7) |
| Co—N(4) | 1·893 (4) | C(10)—O(6) | 1·338 (7) |
| Co—C(9) | 2·062 (5) | O(6)—C(11) | 1·449 (11) |
| Co—N(5) | 2·074 (4) | C(12)—C(13) | 1·482 (8) |
| N(1)—O(1) | 1·336 (6) | C(13)—O(7) | 1·212 (8) |
| N(1)—C(1) | 1·296 (7) | C(13)—O(8) | 1·324 (8) |
| C(1)—C(2) | 1·468 (8) | O(8)—C(14) | 1·420 (10) |
| C(1)—C(5) | 1·493 (9) | | |
| | | | |
| N(1)—Co—N(2) | 82·1 (2) | O(1)—N(1)—C(1) | 120·9 (4) |
| N(1)—Co—N(3) | 178·8 (2) | N(1)—C(1)—C(2) | 112·1 (5) |
| N(1)—Co—N(4) | 98·5 (2) | N(1)—C(1)—C(5) | 124·3 (5) |
| N(1)—Co—C(9) | 88·9 (2) | C(2)—C(1)—C(5) | 123·6 (5) |
| N(1)—Co—N(5) | 95·0 (2) | Co—C(9)—C(10) | 111·4 (3) |
| N(2)—Co—N(3) | 98·5 (2) | Co—C(9)—C(12) | 111·8 (3) |
| N(2)—Co—N(4) | 179·0 (2) | C(10)—C(9)—C(12) | 111·0 (4) |
| N(2)—Co—C(9) | 87·4 (2) | C(9)—C(10)—O(5) | 124·6 (5) |
| N(2)—Co—N(5) | 90·5 (2) | C(9)—C(10)—O(6) | 112·2 (4) |
| N(3)—Co—N(4) | 80·8 (2) | O(5)—C(10)—O(6) | 123·2 (5) |
| N(3)—Co—C(9) | 92·1 (2) | C(10)—O(6)—C(11) | 115·5 (5) |
| N(3)—Co—N(5) | 84·0 (2) | C(9)—C(12)—C(13) | 116·5 (5) |
| N(4)—Co—C(9) | 93·4 (2) | C(12)—C(13)—O(7) | 124·6 (6) |
| N(4)—Co—N(5) | 88·6 (2) | C(12)—C(13)—O(8) | 113·8 (5) |
| C(9)—Co—N(5) | 175·3 (2) | O(7)—C(13)—O(8) | 121·6 (6) |
| Co—N(1)—O(1) | 122·3 (3) | C(13)—O(8)—C(14) | 114·3 (6) |
| Co—N(1)—C(1) | 116·7 (4) | | |

$\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma(F_o)^2 + 0{\cdot}000495F_o^2]^{-1}$; absolute configuration determined in the least-squares calculation including anomalous-dispersion terms; max.$(\Delta/\sigma)$ 0·30; final $R = 0{\cdot}041$ and $wR = 0{\cdot}041$; $\Delta\rho$ excursions in the final difference map $\pm 0{\cdot}5$ e Å$^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); calculations carried out on a HITAC M-280H computer at the computer center of this Institute.

**Discussion.** The final atomic parameters for non-H atoms are given in Table 1.* An *ORTEP* (Johnson, 1976) drawing of the molecule with atomic numbering is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. The crystal showed no change on exposure to X-rays at 298 K.

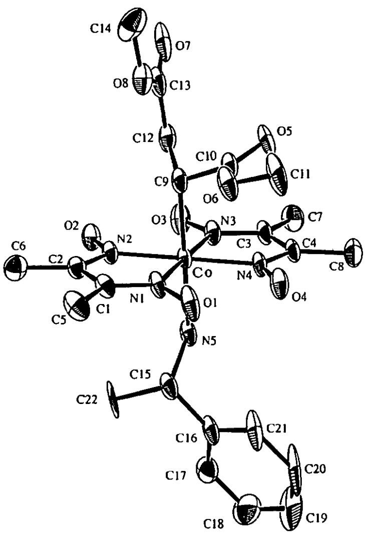

Fig. 1. *ORTEP* (Johnson, 1976) drawing of molecular structure (30% probability thermal ellipsoids) with the numbering of atoms.

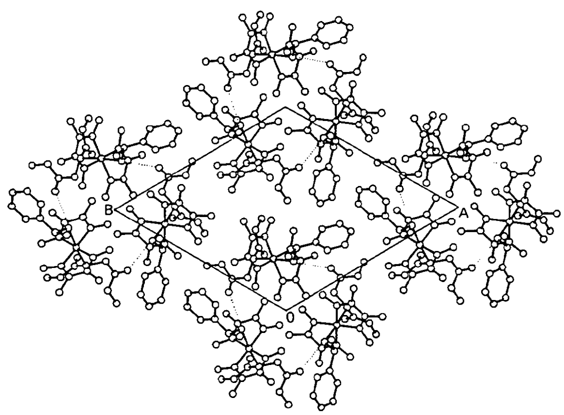

Fig. 2. Projection of the crystal structure along the $c$ axis. Hydrogen bonds are indicated by dotted lines.

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all the bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53815 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Co—C(9) and Co—N(5) distances, 2·062 (5) and 2·074 (4) Å, respectively, are approximately the same as the corresponding ones in the ce and mce complexes. The Co—C and Co—N distances in (*R*-ce)(*S*-1-phenylethylamine)cobaloxime (Ohashi, Sasada, Takeuchi & Ohgo, 1980*a*), (*S*-ce)(*S*-1-phenylethylamine)cobaloxime (Ohashi, Sasada, Takeuchi & Ohgo, 1980*b*), (*R*-mce)(*R*-1-phenylethylamine)cobaloxime (Ohashi & Sasada, 1977) and (*S*-mce)(*R*-1-phenylethylamine)cobaloxime (I) and (II) (Kurihara, Uchida, Ohashi & Sasada, 1984) are 2·036 (8) and 2·088 (8) Å, 2·070 (8) and 2·054 (5) Å, 2·067 (8) and 2·066 (6) Å, 2·080 (7) and 2·075 (5) Å, and 2·086 (5) and 2·074 (4) Å, respectively. Other bond distances are not significantly different from the corresponding ones of the related complexes. The torsion angle of C(10)—C(9)—C(12)—C(13) is 60·4 (4)°. This causes the dmce group to take an L-shape.

The crystal structure viewed along the *c* axis is shown in Fig. 2. The molecules are connected by a hydrogen bond N(5)—H(5)···O(7) and make a spiral chain along the *c* axis. The N(5)···O(7) and H(N1)···O(7) distances and N(5)—H(N1)···O(7) angle are 3·174 (7), 2·20 (5) Å and 166 (4)°, respectively. There are no unusually short contacts between the molecules except the hydrogen bonds.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

### References

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kurihara, T., Ohashi, Y., Sasada, Y. & Ohgo, Y. (1983). *Acta Cryst.* B**39**, 243–250.

Kurihara, T., Uchida, A., Ohashi, Y. & Sasada, Y. (1984). *Acta Cryst.* B**40**, 478–483.

Kurihara, T., Uchida, A., Ohashi, Y., Sasada, Y. & Ohgo, Y. (1984). *J. Am. Chem. Soc.* **106**, 5718–5724.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Ohashi, Y. (1988). *Acc. Chem. Res.* **21**, 268–274.

Ohashi, Y. & Sasada, Y. (1977). *Bull. Chem. Soc. Jpn*, **50**, 2863–2869.

Ohashi, Y., Sasada, Y., Takeuchi, S. & Ohgo, Y. (1980*a*). *Bull. Chem. Soc. Jpn*, **53**, 627–634.

Ohashi, Y., Sasada, Y., Takeuchi, S. & Ohgo, Y. (1980*b*). *Bull. Chem. Soc. Jpn*, **53**, 1501–1509.

Ohgo, Y., Orisaku, K., Hasegawa, E. & Takeuchi, S. (1986). *Chem. Lett.* pp. 27–30.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

---

*Acta Cryst.* (1991). C47, 1198–1202

# Structure of ($\eta^5$-Cyclopentadienyl)(1,2,3,4,4a,10a-$\eta^6$-2-methyldibenzo[*b*,*e*][1,4]dioxine)iron(II) Hexafluorophosphate at 163 K

By K. A. Abboud and S. H. Simonsen

*Department of Chemistry, University of Texas at Austin, Austin, TX* 78712, *USA*

and A. Piórko and R. G. Sutherland

*Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N* 0*W*0

(*Received* 7 *August* 1990; *accepted* 19 *December* 1990)

**Abstract.** $[C_{18}H_{15}FeO_2][PF_6]$ (I), $M_r = 464·13$, monoclinic, $P2_1/c$, $a = 7·976$ (1), $b = 8·959$ (3), $c = 24·936$ (8) Å, $\beta = 99·00$ (2)°, $V = 1760$ (1) Å$^3$, $Z = 4$, $D_x = 1·751$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 10·153$ cm$^{-1}$, $F(000) = 936$, $T = 163$ (2) K, full-matrix least-squares refinement of (I) converged to $R = 0·047$ and $wR = 0·044$ with 3103 reflections $[I > 3\sigma(I)]$ of 4065 total unique reflections. The dihedral angle between the arene rings of the dioxine ligand is 173·8 (1)°; the C—O bond distances to the coordinated ring are significantly shorter than those of the uncoordinated ring. Inclusion of electronegative atoms (*i.e.* N) in the arene rings of thianthrenes and complexation of iron cyclopentadienyl (FeCp) to the arene rings, resulted in flattening of the dihedral angle. The effect was similar, but more pronounced, in phenoxathiins. The effect of an electron-releasing group (methyl) substituent on the arene ring of a thianthrene FeCp complex was to decrease the dihedral angle; but, inconsistently, two methyl groups (in the 2 and 7 positions) increased the angle. Dibenzodioxine and other dibenzodioxines with varying numbers of chloro substituents are planar. The dihedral angle of the title compound is 173·8°. It

0108-2701/91/061198-05\$03.00