

We thank Dr U. Klement for the collection of diffractometer data. The generous support given by the Fonds der Chemischen Industrie and the Degussa AG is gratefully acknowledged.

#### References

BAUR, W. H. & WENNINGER, G. (1969). *SADIAN*. Program for calculation of atomic distances and angles in crystal structures. Univ. of Illinois, Chicago, USA.

HOARD, J. L. (1933). *Z. Kristallogr.* **84**, 231–255.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)  
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 RANGE, K.-J., KÜHNEL, S. & ZABEL, M. (1989). *Acta Cryst.* **C45**, 1419–1420.  
 ROSENZWEIG, A. & CROMER, D. T. (1959). *Acta Cryst.* **12**, 709–712.  
 SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.

*Acta Cryst.* (1989). **C45**, 1621–1623

## A Carbonato(optically active cyclen)cobalt(III) Complex\*

BY SEI TSUBOYAMA,† SHIGERU MIKI, KIMIKO KOBAYASHI AND KAORU TSUBOYAMA

*The Institute of Physical and Chemical Research, Wako, Saitama 351–01, Japan*

AND TOSIO SAKURAI

*Faculty of Education, Shinshu University, Nishinagano, Nagano 380, Japan*

(Received 20 April 1989; accepted 7 June 1989)

**Abstract.** *cis*-(SSSR)- $\beta_1$ -Carbonato[(2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]cobalt(III) perchlorate trihydrate, [Co(CO<sub>3</sub>)-(C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>)]ClO<sub>4</sub>·3H<sub>2</sub>O,  $M_r = 556.93$ , monoclinic,  $P2_1$ ,  $a = 18.936$  (3),  $b = 13.768$  (5),  $c = 9.419$  (2) Å,  $\beta = 100.70$  (2)°,  $V = 2413$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.536$ ,  $D_x = 1.534$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.88$  mm<sup>-1</sup>,  $F(000) = 1184$ ,  $T = 296$  K, final  $R = 0.057$  for 3710 unique reflections with  $|F_o| > 3\sigma(|F_o|)$ . The asymmetric unit contains two virtually identical molecules. The Co<sup>III</sup> ion is surrounded by four N atoms of the macrocycle, and two O atoms of the bidentate carbonate group. The Co—O and Co—N distances agree with those found in related *cis*-carbonato(tetramine) complexes.

**Experimental.** During the reaction of racemic tyrosine and the optically active complex *cis*-(SSSR)-bromo(dibromo-aqua)[(2*R*,5*R*,8*R*,11*R*)-2,5,8,11-tetraethyl-1,4,7,10-tetraazacyclododecane]cobalt(III) (1) (Sakurai, Tsuboyama & Tsuboyama, 1980) under atmospheric conditions, the title compound (2) was obtained as a by-product. The reaction conditions are similar to those for the preparation of an (amino acidato) (chiral cyclen) complex (Tsuboyama, Sakurai & Tsuboyama, 1987). The characterization of complex (2) will be reported separately. The same crystal was obtained from an aqueous solution of (1)

when the pH was adjusted with Na<sub>2</sub>CO<sub>3</sub> to pH 8.0. The density was measured by flotation in CCl<sub>4</sub>-benzene. Crystals of the title compound are red plates. Unit-cell parameters by least-squares fit of 20 reflections in the range  $20 < 2\theta < 25^\circ$ . Crystal  $0.72 \times 0.30 \times 0.09$  mm, Rigaku AFC automated four-circle diffractometer, graphite-monochromatized Mo  $K\alpha$  radiation,  $\omega$  and  $\omega - 2\theta$  ( $2\theta > 30^\circ$ ) scan mode at a scan rate of  $4.0^\circ \text{ min}^{-1}$ , 4420 reflections measured in the range  $2\theta < 55^\circ$ ,  $hkl$  range:  $h - 24-24$ ,  $k 0-17$ ,  $l 0-12$ , 3710 unique reflections with  $|F_o| > 3\sigma(|F_o|)$ ; three standard reflections (212, 751 and 0.10.0) remeasured after every 150 reflections did not show any significant change in intensity during data collection. Lorentz-polarization correction, none for absorption. Structure solved by direct methods with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Calculations performed using the program system *UNICSIII* (Sakurai & Kobayashi, 1979) on a FACOM M-780. The two independent molecules are labelled *A* and *B*. The H-atom coordinates were calculated assuming ideal geometry. Refinement was carried out using block-diagonal least-squares procedure with anisotropic thermal parameters for all non-H atoms and isotropic for H atoms. The absolute configurations of the complex cations were assigned from the known configurations of the ligand as an internal reference (Sakurai *et al.*, 1980). Scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974).  $R = 0.057$ ,  $wR = 0.066$  (unit weight),  $S = 2.42$  for 856 refined

\* Metal Complexes of Chiral Cyclen. 13. Part 12: Tsuboyama, Miki, Chijimatsu, Tsuboyama & Sakurai (1989).

† To whom correspondence should be addressed.

Table 1. Atomic parameters

Positional parameters are multiplied by 10<sup>4</sup>. The equivalent isotropic temperature factor is defined by  $B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)$ .

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co(A)	426 (1)	0*	4880 (1)	1.9
N(1A)	505 (4)	273 (6)	2892 (9)	2.3
C(2A)	938 (6)	1209 (8)	2817 (12)	3.1
C(3A)	917 (6)	1803 (8)	4207 (13)	3.1
N(4A)	1026 (5)	1105 (6)	5451 (9)	2.5
C(5A)	870 (6)	1503 (9)	6868 (13)	3.2
C(6A)	784 (7)	599 (9)	7728 (12)	3.2
N(7A)	259 (4)	-77 (7)	6856 (8)	2.6
C(8A)	-522 (5)	144 (8)	6879 (10)	2.4
C(9A)	-941 (5)	124 (8)	5327 (11)	2.5
N(10A)	-488 (4)	690 (6)	4494 (9)	2.1
C(11A)	-738 (6)	864 (7)	2870 (11)	2.3
C(12A)	-239 (6)	291 (9)	2098 (11)	3.0
C(21A)	1697 (6)	915 (10)	2652 (13)	3.5
C(22A)	2188 (7)	1771 (13)	2541 (17)	5.2
C(51A)	1448 (7)	2209 (11)	7568 (15)	4.6
C(52A)	1287 (10)	2708 (11)	8841 (16)	5.9
C(81A)	-827 (7)	-575 (9)	7851 (14)	3.7
C(82A)	-1586 (8)	-341 (13)	7996 (15)	5.5
C(111A)	-1528 (7)	638 (11)	2297 (13)	3.9
C(112A)	-2046 (7)	1391 (12)	2691 (15)	4.7
O(16A)	53 (4)	-1285 (5)	4405 (8)	2.6
O(17A)	1171 (4)	-954 (5)	5145 (8)	3.0
C(18A)	705 (6)	-1644 (8)	4721 (12)	2.6
O(19A)	860 (5)	-2506 (5)	4583 (10)	3.6
Co(B)	4584 (1)	-179 (1)	4756 (1)	1.8
N(1B)	4412 (4)	-426 (6)	2699 (8)	2.1
C(2B)	4010 (6)	-1374 (8)	2361 (11)	2.6
C(3B)	4125 (6)	-1996 (8)	3719 (11)	2.5
N(4B)	4068 (4)	-1346 (6)	4965 (9)	2.0
C(5B)	4315 (6)	-1762 (8)	6458 (12)	2.7
C(6B)	4389 (6)	-850 (8)	7443 (12)	2.6
N(7B)	4839 (4)	-141 (6)	6849 (8)	2.1
C(8B)	5648 (5)	-299 (8)	7320 (11)	2.7
C(9B)	5987 (5)	-242 (8)	5971 (10)	2.5
N(10B)	5519 (4)	-803 (6)	4854 (9)	2.1
C(11B)	5704 (6)	-898 (8)	3354 (11)	2.4
C(12B)	5140 (6)	-362 (8)	2283 (11)	2.8
C(21B)	3206 (7)	-1169 (11)	1809 (14)	4.4
C(22B)	3034 (9)	-698 (13)	349 (16)	5.7
C(51B)	3790 (7)	-2507 (9)	6843 (12)	3.3
C(52B)	4032 (7)	-2912 (9)	8371 (14)	3.7
C(81B)	5972 (7)	387 (11)	8509 (12)	4.1
C(82B)	6768 (7)	238 (17)	9023 (16)	7.4
C(111B)	6461 (7)	-594 (9)	3230 (12)	3.3
C(112B)	7067 (7)	-1277 (11)	3877 (15)	4.2
O(16B)	4888 (4)	1133 (5)	4520 (7)	2.4
O(17B)	3798 (4)	703 (5)	4652 (8)	2.2
C(18B)	4220 (6)	1460 (7)	4498 (11)	2.4
O(19B)	4032 (4)	2295 (5)	4392 (9)	3.4
Cl(1)	875 (2)	-2082 (2)	114 (4)	4.4
O(11)	387 (9)	-2764 (15)	271 (22)	13.1
O(12)	793 (10)	-1251 (11)	858 (16)	11.1
O(13)	1550 (8)	-2519 (13)	527 (18)	10.3
O(14)	763 (10)	-1927 (10)	-1371 (13)	10.2
Cl(2)	-3990 (2)	-3080 (3)	540 (4)	4.5
O(21)	-4187 (8)	-3724 (12)	-618 (19)	12.8
O(22)	-4341 (9)	-3332 (11)	1658 (17)	10.1
O(23)	-4193 (7)	-2146 (8)	161 (14)	7.1
O(24)	-3239 (6)	-3148 (11)	1007 (14)	7.9
O(W)	7897 (7)	-8002 (11)	6478 (15)	8.3
O(W2)	2659 (6)	908 (8)	6094 (11)	5.5
O(W3)	2605 (7)	-1102 (13)	5013 (20)	11.2

\* This parameter was used to define the unit-cell origin along z and is listed without an e.s.d.

parameters, max. shift/e.s.d. in final cycle = 0.24. Final difference peak 0.7 e  $\text{\AA}^{-3}$ . The atomic parameters are given in Table 1,\* selected bond lengths and

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51994 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ), and torsion angles ( $^\circ$ ) for molecule A

Co—N(1)	1.942 (9)	Co—O(17)	1.910 (8)
Co—N(4)	1.915 (9)	O(16)—C(18)	1.311 (13)
Co—N(7)	1.947 (8)	O(17)—C(18)	1.308 (13)
Co—N(10)	1.948 (8)	C(18)—O(19)	1.236 (13)
Co—O(16)	1.926 (7)		
N(1)—Co—N(4)	88.3 (4)	N(7)—Co—O(16)	93.2 (4)
N(1)—Co—N(7)	170.7 (4)	N(7)—Co—O(17)	94.8 (4)
N(1)—Co—N(10)	87.1 (4)	N(10)—Co—O(16)	97.5 (3)
N(1)—Co—O(16)	92.5 (3)	N(10)—Co—O(17)	165.7 (3)
N(1)—Co—O(17)	94.2 (4)	O(16)—Co—O(17)	68.2 (3)
N(4)—Co—N(7)	88.1 (4)	Co—O(16)—C(18)	90.3 (6)
N(4)—Co—N(10)	97.2 (4)	Co—O(17)—C(18)	91.1 (6)
N(4)—Co—O(16)	165.3 (3)	O(16)—C(18)—O(17)	110.4 (9)
N(4)—Co—O(17)	97.2 (3)	O(17)—C(18)—O(19)	124.8 (10)
N(7)—Co—N(10)	84.8 (4)		
C(12)—N(1)—C(3)—C(3)	97.8 (10)	N(7)—C(8)—C(9)—N(10)	-45.8 (10)
N(1)—C(2)—C(3)—N(4)	42.6 (11)	C(8)—C(9)—N(10)—C(11)	-178.3 (8)
C(2)—C(3)—N(4)—C(5)	-167.9 (9)	C(9)—N(10)—C(11)—C(12)	-111.6 (10)
C(3)—N(4)—C(5)—C(6)	162.1 (9)	N(10)—C(11)—C(12)—N(1)	35.8 (11)
N(4)—C(5)—C(6)—N(7)	-51.4 (11)	C(2)—N(1)—C(12)—C(11)	-76.3 (11)
C(5)—C(6)—N(7)—C(8)	-83.1 (11)	C(18)—O(16)—O(17)—Co	179.5 (10)
C(6)—N(7)—C(8)—C(9)	132.2 (9)		

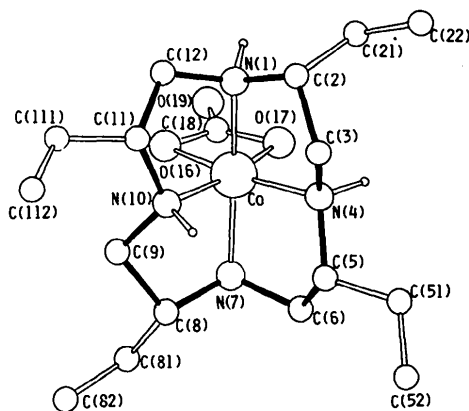


Fig. 1. Structure of molecule A with atom numbering. Only the H atoms attached to the asymmetric N atoms are shown for clarity.

angles for molecule A in Table 2. The structure of molecule A is shown in Fig. 1.

**Related literature.** For comparison with other cobalt(III) complexes containing cyclen see Giusti, Chimichi, Ciampolini, Sabat & Masi (1984) and Loehlin & Fleischer (1976). The bond distances and angles for a series of [Co<sup>III</sup>(CO<sub>3</sub>)N<sub>4</sub>] complexes (N<sub>4</sub> = tetraamine) have been compared in the literature (Niederhoffer, Martell, Rudolf & Clearfield, 1982; Healy, Kennard, Smith & White, 1981). The crystal structures of other complexes containing carbonate and tetraamine have also been determined (Gargallo, Mather, Duesler & Tapscott, 1983; Niederhoffer *et al.*, 1982; Schlemper, Gupta & Dasgupta, 1983; Snow, 1972).

This study was performed through Special Coordination Funds of the Science and Technology Agency of the Japanese Government.

### References

- GARGALLO, M. E., MATHER, D., DUESLER, E. N. & TAPSCOTT, R. E. (1983). *Inorg. Chem.* **22**, 2888–2891.
- GIUSTI, J., CHIMICHI, S., CIAMPOLINI, M., SABAT, M. & MASI, D. (1984). *Inorg. Chim. Acta*, **88**, 51–54.
- HEALY, P. C., KENNARD, C. H. L., SMITH, G. & WHITE, A. H. (1981). *Cryst. Struct. Commun.* **10**, 883–888.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- LOEHLIN, J. H. & FLEISCHER, E. B. (1976). *Acta Cryst.* **B32**, 3063–3066.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- NIEDERHOFFER, E. C., MARTELL, A. E., RUDOLF, P. & CLEARFIELD, A. (1982). *Inorg. Chem.* **21**, 3734–3741.
- SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.
- SAKURAI, T., TSUBOYAMA, S. & TSUBOYAMA, K. (1980). *Acta Cryst.* **B36**, 1797–1801.
- SCHLEMPER, E. O., GUPTA, K. S. & DASGUPTA, T. P. (1983). *Acta Cryst.* **C39**, 1012–1015.
- SNOW, M. R. (1972). *Aust. J. Chem.* **25**, 1307–1309.
- TSUBOYAMA, S., MIKI, S., CHIJIMATSU, T., TSUBOYAMA, K. & SAKURAI, T. (1989). *J. Chem. Soc. Dalton Trans.* In the press.
- TSUBOYAMA, S., SAKURAI, T. & TSUBOYAMA, K. (1987). *J. Chem. Soc. Dalton Trans.* pp. 721–727.

*Acta Cryst.* (1989). **C45**, 1623–1624

## Structure of a Fischer Carbene Complex $(\text{CO})_5\text{W}=\text{C}(\text{OEt})[1-(8\text{-Iodonaphthyl})]$

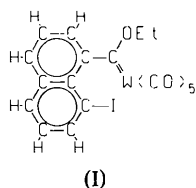
BY A. W. CORDES, J. B. GRAHAM, J. LU, R. FEREDÉ AND N. T. ALLISON

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701, USA

(Received 3 January 1989; accepted 17 February 1989)

**Abstract.** Pentacarbonyl[ethoxy(8-iodonaphthyl)methylene]tungsten,  $[\text{W}(\text{CO})_5\{\text{C}(\text{OC}_2\text{H}_5)(\text{C}_{10}\text{H}_6\text{I})\}]$ ,  $M_r = 634.0$ , monoclinic,  $P2_1/c$ ,  $a = 15.664(5)$ ,  $b = 9.373(2)$ ,  $c = 13.964(4) \text{ \AA}$ ,  $\beta = 110.79(2)^\circ$ ,  $V = 1917(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 2.20 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$ ,  $\mu = 77.8 \text{ cm}^{-1}$ ,  $F(000) = 1176$ ,  $T = 293 \text{ K}$ ,  $R = 0.031$  for 2581 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The  $\text{W}(\text{CO})_5$  group is bonded to the organic carbene with a  $\text{W}=\text{C}$  bond length of  $2.180(6) \text{ \AA}$  and the  $\text{W}-\text{C}$  bonds to the carbonyl groups average  $2.04(3) \text{ \AA}$ . In the  $\text{W}$ -carbene bonding the  $\text{W}=\text{C}-\text{O}$  bond angle is  $132.1(5)$  and the  $\text{W}=\text{C}-\text{C}$  bond angle is  $121.0(4)^\circ$ .

**Experimental.** Title compound (I) obtained by the reaction of 1-lithio-8-iodonaphthalene with tungsten hexacarbonyl followed by ethylation with triethyl-oxonium tetrafluoroborate. Orange crystals obtained



by slow evaporation of a pentane/dichloromethane solution. Data crystal  $0.14 \times 0.20 \times 0.46 \text{ mm}$  mounted with epoxy on a glass fiber. Intensities measured with an Enraf-Nonius CAD-4 diffractometer using  $\omega-2\theta$

scans of  $4-16^\circ \text{ min}^{-1}$  in  $\theta$ . Unit cell determined from least-squares analysis of angle data for 25 reflections with  $14 < 2\theta < 18^\circ$ . Analytical absorption correction based on crystal-face measurements varied from 0.51 to 1.00. Data collected to  $(\sin\theta)/\lambda$  of  $0.59 \text{ \AA}^{-1}$ ,  $-18 < h < 18$ ,  $0 < k < 11$ ,  $0 < l < 16$ . Three standard reflections (500,  $2\bar{3}1$ ,  $60\bar{2}$ ) indicated crystal decomposition of less than 0.9% over 32.9 h of data collection. 3506 reflections measured, 3351 unique ( $R_{\text{int}} = 0.02$ ), 770 reflections with  $I < 3\sigma(I)$  where  $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (0.05I)^2$ ;  $\sigma_{\text{cs}}(I)$  is standard deviation of

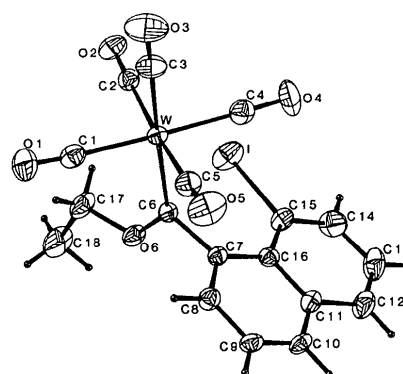


Fig. 1. ORTEP (Johnson, 1976) drawing and numbering scheme. The ellipsoids are drawn at the 30% probability surface and H atoms have been given arbitrary radii for figure clarity.