C2—C3	1.400 (6)	O2—C17	1.312 (6)
C3—C4	1.418 (7)	C17—C18	1.398 (7)
C3—C8	1.435 (7)	C17—C22	1.399 (7)
C4—C5	1.354 (7)	C18—C19	1.371 (8)
C5—C6	1.400 (8)	C19—C20	1.381 (8)
C6—C7	1.348 (8)	C20—C21	1.359 (7)
C7—C8	1.405 (8)	C21—C22	1.400 (7)
C8—C9	1.409 (7)	C22—C23	1.426 (7)
C9—C10	1.351 (7)		
O2—Ni—O1	172.0 (2)	O1—C11—C10	119.8 (5)
O2—Ni—N1	95.2 (2)	C11—O1—Ni	116.9 (3)
O1—Ni—N1	92.8 (2)	C12—N2—C16	120.2 (5)
O2—Ni—N2	87.3 (2)	C12—N2—Ni	118.1 (4)
O1—Ni—N2	84.8 (2)	C16—N2—Ni	118.1 (4)
N1—Ni—N2	177.5 (2)	N2—C12—C13	120.4 (5)
C23—N1—C1	117.0 (4)	N2—C16—C15	118.3 (5)
C23—N1—Ni	125.1 (4)	C17—O2—Ni	127.4 (3)
C1—N1—Ni	117.9 (3)	O2—C17—C18	119.0 (5)
N1—C1—C2	111.1 (4)	O2—C17—C22	124.2 (5)
O1—C11—C2	120.7 (5)	N1—C23—C22	126.5 (5)

The structure was solved by direct phase determination. The parameters of the complete structure could be refined by full-matrix least squares. All phenyl rings were refined without any constraints. Values of distances and angles in the rings show no significant differences from those of an ideal benzene ring. The H atom on the piperidine N atom was not located; other H atoms were treated using a riding model with fixed isotropic U's.

Data collection: SDP (Frenz, 1985). Cell refinement: SDP. Data reduction: REDU4 (Stoe & Cie, 1988). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: PLUTON93 (Spek, 1993); Xtal (Hall, Flack & Stewart, 1992). Software used to prepare material for publication: SHELXL93.

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The Helical Packing of a Chiral Alkyl Cobaloxime in the Solid State

BERND GIESE, JENS HARTUNG AND HANS-JÖRG LINDNER

Institut für Organische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 22, D-64287 Darmstadt, Germany

INGRID SVOBODA AND HELMUT PAULUS

Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstrasse 20, 64287 Darmstadt, Germany
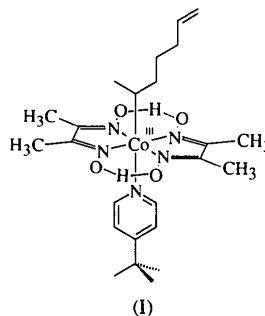
Abstract

Three units of the chiral title complex, (4-tert-butyl-pyridine-N)bis(dimethylglyoximato-N,N')[(R)-6-hepten-2-yl]cobalt(III), [Co(C$_7$H$_{13}$)(C$_4$H$_7$N$_2$O$_2$)$_2$(C$_9$H$_{13}$N)], form one complete turn of a right-handed screw along the crystallographic c axis. The molecule shows a long C—Co bond [2.086 (7) Å] and a significant distortion in the hybridization of the Co-bound C atom from sp^3 towards sp^2 [C28—C27—C29 = 120.9 (6), Co—C27—C29—C30 = −172 (1) and C28—C27—C29—C30 = 41 (2)°].

Comment

In the course of several mechanistic studies with alkyl-bis(dimethylglyoximato)(pyridine)cobalt(III) complexes [i.e. alkyl(pyridine)cobaloximes] (Branchaud, Meier & Malekzadeh, 1987; Giese & Hartung, 1992; Hartung, Hertel & Trach, 1993), primary alkylcobaloximes proved to be less prone to photolytic cleavage of the Co—C bond upon irradiation with incandescent light than the secondary derivatives. These findings were attributed to larger steric interactions between secondary alkyl and the two dimethylglyoxime ligands compared to the strain between a primary alkyl residue and the equatorial macrocycle (Halpern, 1985). In order to ob-

(I)

tain an insight into the ground-state properties of (I), the most photolabile cobalt compound of our photochemical studies, its solid-state structure was determined.

Fig. 1 shows the geometry of the (R)-6-heptenyl-cobaloxime (I). The absolute stereochemistry of (I) was determined using the Flack (1983) parameter [0.01 (5)]. The four oxime N atoms form an equatorial plane around the central Co ion. The alkyl ligand is bound via a long C—Co bond of 2.086(7) Å, which is comparable to the values found for 2-propylcobaloximes of 2.085(3) and 2.099(2) Å (Marzilli, Toscano, Randaccio, Bresciani-Pahor & Calligaris, 1979). The C28—C27—C29 bond angle of 120.9(6)° and the Co—C27—C29—C30 and C28—C27—C29—C30 torsion angles of −172(1) and 41(2)°, respectively, suggest a re-hybridization of C27 from sp^3 to sp^2.

Chirality is not only found in the alkyl cobalt complex but also in the crystal packing of (I). Fig. 2 shows a stereoview along the crystallographic c axis. Complexes are aligned along a right-handed screw with t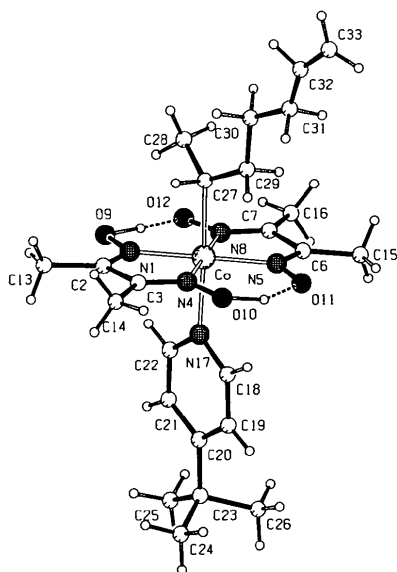hree molecules forming one complete turn. The view along the edge of the planar dimethylglyoxime ligands shows a triangle of three cobaloximes. Each of the units is twisted 120° towards the other.

The solid-state structure of (I) shows steric interactions between the alkyl ligand and the cobaloxime moiety, which could be partly responsible for the enhanced reactivity of (I) compared to that of the primary 5-hexenylcobaloxime derivative (Hartung, Hertel & Trach 1993).

Experimental

Compound (I) was prepared as previously reported (Giese & Hartung, 1992). Orange–brown rod-like crystals were grown from 2-propanol. Although the racemic 6-hepten-2-yl-cobaloxime was obtained from racemic 2-bromo-6-heptene, crystallization of (I) from 2-propanol yields an enantiomorphic conglomerate. The selected crystal, in the shape of a hexagonal rod capped with hexagonal pyramids, displayed the R configuration.

Crystal data

[Co(C_7H_{13})($C_4H_7N_2O_2$)$_2$- ($C_9H_{13}N$)]	Mo $K\alpha$ radiation
$M_r = 521.54$	$\lambda = 0.71069$ Å
Hexagonal	Cell parameters from 68
$P6_1$	reflections
$a = 12.017(1)$ Å	$\theta = 3.5–22.8°$
$c = 32.942(2)$ Å	$\mu = 0.661$ mm^{-1}
$V = 4119.5(5)$ Å^3	$T = 293(2)$ K
$Z = 6$	Prism
$D_x = 1.261$ Mg m^{-3}	$0.70 \times 0.27 \times 0.27$ mm
	Orange–brown

Data collection

Stoe Stadi-4 diffractometer	$R_{int} = 0.0311$
$\omega/2\theta$ scans	$\theta_{max} = 22.5°$
Absorption correction:	$h = -12 \rightarrow 1$
none	$k = 0 \rightarrow 12$
3976 measured reflections	$l = 0 \rightarrow 35$
1829 independent reflections	3 standard reflections
1522 observed reflections	frequency: 90 min
$[I > 2\sigma(I)]$	intensity decay: 1.0%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.171$
$R[F^2 > 2\sigma(F^2)] = 0.0471$	$\Delta\rho_{max} = 0.390$ e Å^{-3}
$wR(F^2) = 0.1665$	$\Delta\rho_{min} = -0.335$ e Å^{-3}
$S = 1.093$	Extinction correction: none
1829 reflections	Atomic scattering factors
306 parameters	from International Tables
Oxime H atoms located on	for Crystallography (1992,
a difference Fourier map	Vol. C, Tables 4.2.6.8 and
and refined isotropically	6.1.1.4)
$w = 1/[\sigma^2(F_o^2) + (0.1187P)^2$	Absolute configuration:
$+ 1.9433P]$	Flack (1983) parameter
where $P = (F_o^2 + 2F_c^2)/3$	$= 0.01(5)$

Fig. 1. The structure of the (R)-6-hepten-2-ylcobaloxime (I).

Fig. 2. Stereoview of the packing of the (R)-6-hepten-2-ylcobaloxime (I) along the c axis.

[Co(C7H13)(C4H7N2O2)2(C9H13N)]

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0.9268 (1)	0.4736 (1)	0.1441 (1)	0.0519 (4)
N1	0.9270 (7)	0.6305 (7)	0.1446 (3)	0.058 (2)
C2	0.9241 (9)	0.678 (1)	0.1781 (4)	0.070 (3)
C3	0.9277 (9)	0.598 (1)	0.2129 (4)	0.076 (3)
N4	0.9265 (7)	0.496 (1)	0.2010 (4)	0.065 (3)
N5	0.9261 (7)	0.3171 (7)	0.1445 (3)	0.062 (2)
C6	0.9235 (9)	0.268 (1)	0.1099 (5)	0.075 (4)
C7	0.927 (1)	0.349 (1)	0.0742 (4)	0.079 (4)
N8	0.9268 (8)	0.450 (1)	0.0876 (4)	0.068 (3)
O9	0.9226 (7)	0.6886 (8)	0.1091 (3)	0.081 (2)
O10	0.9230 (7)	0.4128 (9)	0.2277 (3)	0.081 (2)
O11	0.9196 (7)	0.2529 (7)	0.1786 (3)	0.086 (3)
O12	0.9254 (7)	0.5331 (9)	0.0608 (3)	0.082 (2)
C13	0.921 (1)	0.801 (1)	0.1841 (6)	0.107 (5)
C14	0.924 (1)	0.634 (2)	0.2549 (5)	0.107 (5)
C15	0.917 (2)	0.143 (2)	0.1028 (7)	0.133 (7)
C16	0.927 (1)	0.312 (2)	0.0325 (5)	0.110 (5)
N17	0.7262 (6)	0.3726 (6)	0.1443 (3)	0.048 (2)
C18	0.6583 (9)	0.270 (1)	0.1683 (4)	0.066 (3)
C19	0.5262 (9)	0.196 (1)	0.1671 (4)	0.068 (3)
C20	0.4547 (8)	0.2243 (8)	0.1420 (3)	0.048 (2)
C21	0.5240 (8)	0.3332 (9)	0.1183 (3)	0.055 (2)
C22	0.6536 (9)	0.4009 (9)	0.1205 (3)	0.052 (2)
C23	0.3101 (8)	0.1421 (9)	0.1411 (4)	0.062 (2)
C24	0.2555 (6)	0.1437 (8)	0.1815 (3)	0.106 (5)
C25	0.2513 (6)	0.1804 (8)	0.1060 (3)	0.104 (5)
C26	0.2747 (6)	0.0009 (8)	0.1305 (3)	0.097 (4)
C27	1.1270 (7)	0.5797 (9)	0.1464 (4)	0.077 (3)
C28	1.1876 (7)	0.6655 (9)	0.1121 (4)	0.124 (7)
C29	1.189 (1)	0.520 (1)	0.1664 (5)	0.091 (4)
C30	1.330 (1)	0.588 (1)	0.1751 (5)	0.097 (4)
C31	1.388 (2)	0.532 (2)	0.1979 (7)	0.148 (8)
C32	1.503 (2)	0.569 (2)	0.209 (1)	0.19 (1)
C33	1.578 (2)	0.546 (2)	0.225 (1)	0.26 (2)

Table 2. Selected geometric parameters ($\mathring{A}$, °)

Co—N5	1.877 (8)	C7—C16	1.44 (2)
Co—N8	1.88 (1)	N8—O12	1.34 (2)
Co—N1	1.885 (7)	N17—C22	1.34 (1)
Co—N4	1.89 (1)	N17—C18	1.34 (1)
Co—C27	2.086 (7)	C18—C19	1.38 (1)
Co—N17	2.088 (6)	C19—C20	1.35 (1)
N1—C2	1.25 (2)	C20—C21	1.39 (1)
N1—O9	1.37 (1)	C20—C23	1.51 (1)
C2—C13	1.51 (2)	C21—C22	1.35 (1)
C2—C3	1.51 (2)	C23—C24	1.49 (2)
C3—N4	1.28 (2)	C23—C25	1.54 (1)
C3—C14	1.46 (2)	C23—C26	1.57 (1)
N4—O10	1.32 (2)	C27—C29	1.43 (1)
N5—C6	1.28 (2)	C29—C30	1.49 (2)
N5—O11	1.34 (1)	C30—C31	1.41 (2)
C6—C15	1.47 (2)	C31—C32	1.27 (2)
C6—C7	1.51 (2)	C32—C33	1.20 (3)
C7—N8	1.30 (2)		
N5—Co—C27	92.2 (4)	C27—Co—N17	177.2 (4)
N8—Co—C27	92.3 (4)	C29—C27—C28	120.9 (6)
N1—Co—C27	88.0 (3)	C29—C27—Co	116.1 (7)
N4—Co—C27	87.8 (4)	C28—C27—Co	114.9 (3)

Data reduction: REDU4 (Stoe & Cie, 1992). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: PLUTON93 (Spek, 1993). Software used to prepare material for publication: SHELXL93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraethylammonium (2-Thioxo-1,3-dithiole-4,5-dithiolato-S^4, S^5)triphenylphosphinecopper(I)

Tianlu Sheng

State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

Hongjun Li

Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, People's Republic of China

Qun Huang and Xintao Wu*

State Key Laboratory of Structure Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China

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Abstract

The structure of the title compound, $(C_8H_{20}N)[Cu(C_3S_5)(C_{18}H_{15}P)]$, has been determined. There are two independent formula units. The Cu atom is tricoordi-

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