

C126	0.5049 (5)	0.2056 (3)	0.1468 (4)	0.0244 (12)
C131	0.3134 (5)	0.2209 (3)	0.2958 (4)	0.0183 (11)
C132	0.2435 (5)	0.2653 (3)	0.2177 (4)	0.0208 (11)
C133	0.1802 (5)	0.3284 (3)	0.2339 (4)	0.0287 (13)
C134	0.1904 (5)	0.3485 (3)	0.3306 (5)	0.0310 (13)
C135	0.2592 (5)	0.3052 (3)	0.4092 (4)	0.0246 (12)
C136	0.3195 (5)	0.2413 (3)	0.3923 (4)	0.0216 (11)

Table 2. Selected geometric parameters (Å, °)

W1—C1	1.974 (6)	W1—Se1	2.6581 (6)
W1—C3	2.003 (6)	Se1—P	2.1944 (14)
W1—C2	2.026 (6)	P—C131	1.789 (5)
W1—C15	2.284 (5)	P—C111	1.796 (5)
W1—C14	2.293 (5)	P—C121	1.821 (5)
W1—C11	2.338 (5)	C1—O1	1.150 (7)
W1—C13	2.361 (5)	C2—O2	1.124 (6)
W1—C12	2.395 (5)	C3—O3	1.143 (6)
C1—W1—C3	74.2 (2)	C111—P—C121	106.9 (2)
C1—W1—C2	76.2 (2)	C131—P—Se1	113.8 (2)
C3—W1—C2	110.2 (2)	C111—P—Se1	108.0 (2)
C1—W1—Se1	134.2 (2)	C121—P—Se1	112.9 (2)
C3—W1—Se1	81.7 (2)	O1—C1—W1	179.3 (5)
C2—W1—Se1	76.6 (2)	O2—C2—W1	173.2 (5)
C15—W1—Se1	133.72 (14)	O3—C3—W1	175.6 (5)
C14—W1—Se1	139.06 (13)	C112—C111—P	121.6 (4)
C11—W1—Se1	97.86 (13)	C116—C111—P	118.8 (4)
C13—W1—Se1	104.48 (13)	C122—C121—P	119.9 (4)
C12—W1—Se1	83.50 (13)	C126—C121—P	119.7 (4)
P—Se1—W1	111.43 (4)	C132—C131—P	121.7 (4)
C131—P—C111	107.0 (2)	C136—C131—P	119.2 (4)
C131—P—C121	107.9 (2)		

Data collection: XSCANS (Siemens, 1994a). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994b). 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: NA1204). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

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[(R)-1,2-Bis(allyloxycarbonyl)ethyl]bis(dimethylglyoximato-N,N')[(R)-1-phenylethylamine]cobalt(III)

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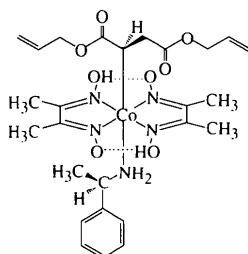
Abstract

A new bis(dimethylglyoximato)cobalt(III) complex with a bulky chiral alkyl group bonded to the Co atom has been prepared, [Co(C₄H₇N₂O₂)₂(C₁₀H₁₃O₄)(C₈H₁₁N)]. The crystal was irradiated with a xenon lamp. Racemization of the crystalline state was not observed for the crystal since the reaction cavity for the chiral alkyl group appears to be too small.

Comment

In a series of studies of crystalline-state racemization in bis(dimethylglyoximato)cobalt(III) (cobaloxime) complexes by X-ray or visible-light exposure, three chiral reactive groups, namely, 1-cyanoethyl [ce; –CH(CH₃)CN] (Ohashi, 1988), 1-methoxycarbonyl-ethyl [mce; –CH(CH₃)COOCH₃] (Kurihara, Ohashi, Sasada & Ohgo, 1983; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984) and 1,2-dimethoxycarbonyl-ethyl [dmce; –CH(COOCH₃)CH₂COOCH₃] (Sakai *et al.*, 1993; Ohashi *et al.*, 1995), have been found to be racemized with retention of the single-crystal form. The 1,2-diethoxycarbonyl-ethyl group [dece; –CH(COOC₂H₅)CH₂COOC₂H₅] (Yamada *et al.*, 1995), however, did not exhibit crystalline-state racemization. Recently, several cobaloxime complexes having a bulkier chiral group, *i.e.* 1,2-diallyloxycarbonyl-ethyl [dace; –CH(COOCH₂CH=CH₂)CH₂COOCH₂-CH=CH₂], have been prepared. Since well formed

crystals of the title complex, (I), were obtained from an aqueous methanol solution, the crystal structure was analyzed and the reactivity on exposure to a xenon lamp was examined.



(I)

The molecular structure of (I) with the atomic numbering scheme is shown in Fig. 1. The Co—C9 bond length of 2.070 (4) Å in (I) is similar to the corresponding bond lengths of 2.069 (7) and 2.068 (7) Å found in complexes of dmce and dece, respectively. The torsion angle C10—C9—C14—C15 of $-70.2(5)^\circ$ is similar to the corresponding torsion angles found in dmce complexes, which range from $-77(2)$ to $-58.4(8)^\circ$. Such a *gauche* conformation forces the dace group to adopt an L-type conformation, as is also observed for the dmce and dece groups. The C11—C12—C13 and C16—C17—C18 bond angles in the two allyl groups,

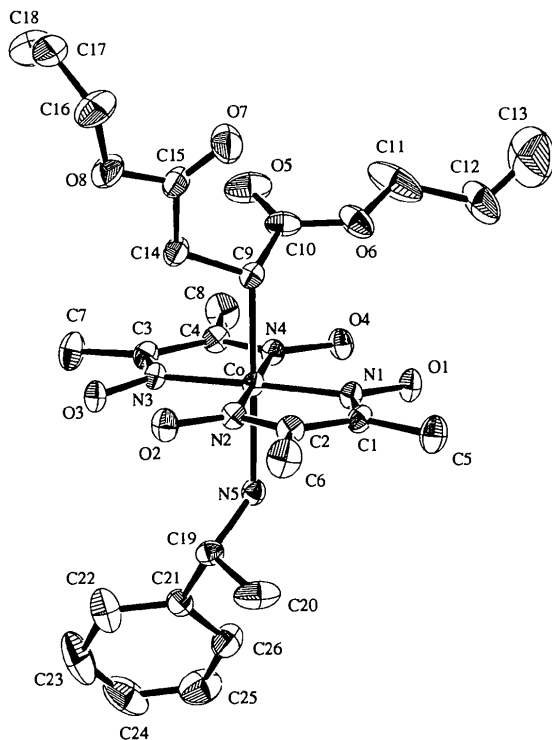


Fig. 1. ORTEPII (Johnson, 1976) drawing of the title molecule with 30% probability displacement ellipsoids.

of $125(1)$ and $125.5(7)^\circ$, respectively, are significantly larger than the usual sp^2 angle. The other bond distances and angles are not significantly different from the corresponding angles of related complexes.

Molecules are linked by an N5—H52...O2($2-x$, $\frac{1}{2}+y$, $2-z$) hydrogen bond along the *b* axis (Fig. 2). The C=C double bonds of neighboring allyl groups have contact distances of 3.63 (2) [C13...C18($1-x$, $\frac{1}{2}+y$, $1-z$)] and 4.09 (1) Å [C12...C17($1-x$, $\frac{1}{2}+y$, $1-z$)] (Fig. 2). Although the distances satisfy Schmidt's topochemical requirement for [2+2] photodimerization (Cohen & Schmidt, 1964), the two bonds are not parallel. This explains why the [2+2] photodimerization was not observed.

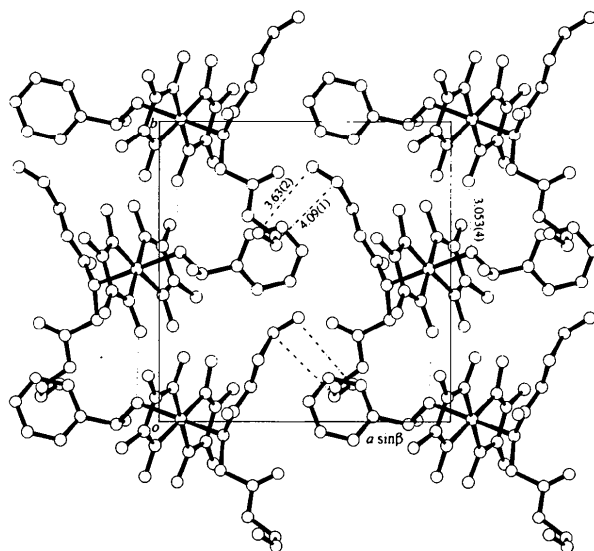


Fig. 2. The crystal structure of the title complex, with hydrogen bonds shown by dotted lines and short contacts between the C=C double bonds indicated by dot-dashed lines.

To examine why the crystal did not reveal crystalline-state racemization, the reaction cavity for the dace group was drawn and its volume calculated in the same way as reported previously (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981). Although the cavity size (68.0 \AA^3) is larger than that of the reactive dmce group observed in the methyl-diphenylphosphine complex (55.0 \AA^3 ; Ohashi *et al.*, 1995), it is not large enough for the inversion of the bulkier dace group if the difference in volume between the methyl and allyl groups is taken into account. Furthermore, there is only one molecule in an asymmetric unit and the chiral dace group is isolated from the other dace groups. In the case of bulky reactive groups, *e.g.* mce and dmce, the cooperative motion of two reactive groups, facing each other around a pseudo-inversion center, seems to be essential for the reaction in the crystals. These two conditions may cause the non-reactivity of the present crystal.

Experimental

Crystal data

[Co(C₄H₇N₂O₂)₂(C₁₀H₁₃O₄)-
(C₈H₁₁N)] $M_r = 607.54$

Monoclinic

 $P2_1$ $a = 12.083 (3) \text{ \AA}$ $b = 12.267 (3) \text{ \AA}$ $c = 9.967 (1) \text{ \AA}$ $\beta = 89.98 (2)^\circ$ $V = 1477.5 \text{ \AA}^3$ $Z = 2$ $D_x = 1.366 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ Cell parameters from 25
reflections $\theta = 14.0\text{--}15.0^\circ$ $\mu = 0.635 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Plate

 $0.60 \times 0.40 \times 0.10 \text{ mm}$

Reddish orange

C8	1.0371 (4)	0.6527 (5)	0.4979 (4)	0.059
C9	0.7813 (3)	0.4542 (3)	0.7600 (4)	0.035
C10	0.7462 (3)	0.5324 (4)	0.6547 (4)	0.050
C11	0.6624 (6)	0.7066 (6)	0.6204 (10)	0.112
C12	0.6093 (5)	0.7961 (5)	0.7231 (10)	0.097
C13	0.5244 (10)	0.8470 (8)	0.7027 (14)	0.163
C14	0.7904 (4)	0.3395 (4)	0.7056 (5)	0.049
C15	0.6812 (4)	0.2878 (4)	0.6719 (5)	0.050
C16	0.6031 (5)	0.1153 (6)	0.6100 (7)	0.083
C17	0.6007 (6)	0.0850 (6)	0.4676 (7)	0.082
C18	0.6620 (7)	0.1246 (9)	0.3771 (8)	0.118
C19	1.1451 (3)	0.4908 (3)	1.0201 (3)	0.039
C20	1.1146 (4)	0.5039 (8)	1.1663 (4)	0.073
C21	1.2662 (3)	0.5164 (4)	0.9948 (3)	0.043
C22	1.3350 (5)	0.4401 (5)	0.9427 (7)	0.078
C23	1.4480 (6)	0.4660 (8)	0.9202 (10)	0.105
C24	1.4886 (5)	0.5667 (8)	0.9476 (7)	0.090
C25	1.4192 (5)	0.6445 (7)	0.9975 (6)	0.080
C26	1.3090 (4)	0.6201 (5)	1.0209 (5)	0.061

Data collection

Rigaku AFC-7S diffractometer

 $\omega/2\theta$ scansAbsorption correction:
none

3711 measured reflections

3546 independent reflections

3218 observed reflections

 $[I > 2\sigma(I)]$ $R_{\text{int}} = 0.023$ $\theta_{\text{max}} = 27.48^\circ$ $h = 0 \rightarrow 15$ $k = 0 \rightarrow 15$ $l = -12 \rightarrow 12$

3 standard reflections

monitored every 100

reflections

intensity decay: 1.9%

Refinement

Refinement on F^2 $R(F) = 0.037$ $wR(F^2) = 0.102$ $S = 1.043$

3546 reflections

360 parameters

Only coordinates of H atoms
refined $w = 1/[\sigma^2(F_o^2) + (0.0617P)^2$ $+ 0.2682P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.33 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992),Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Absolute configuration:

Flack (1983) parameter

 $= 0.02 (2)$ Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Co	0.92562 (3)	0.5072	0.85091 (4)	0.028
O1	0.8225 (3)	0.7020 (2)	0.9486 (3)	0.045
O2	0.9381 (2)	0.3002 (2)	0.9781 (3)	0.046
O3	1.0468 (2)	0.3184 (2)	0.7652 (3)	0.043
O4	0.9152 (2)	0.7147 (2)	0.7237 (3)	0.041
O5	0.7670 (3)	0.5257 (5)	0.5363 (3)	0.079
O6	0.6882 (3)	0.6157 (3)	0.7068 (4)	0.062
O7	0.5936 (3)	0.3288 (4)	0.6745 (6)	0.096
O8	0.6975 (3)	0.1819 (3)	0.6414 (4)	0.066
N1	0.8418 (3)	0.5944 (3)	0.9688 (3)	0.034
N2	0.8983 (3)	0.4017 (3)	0.9858 (3)	0.035
N3	1.0138 (3)	0.4213 (2)	0.7354 (3)	0.032
N4	0.9527 (3)	0.6123 (3)	0.7165 (3)	0.033
N5	1.0724 (3)	0.5617 (2)	0.9355 (3)	0.036
C1	0.8089 (3)	0.5489 (4)	1.0791 (4)	0.038
C2	0.8403 (3)	0.4340 (4)	1.0878 (4)	0.039
C3	1.0503 (3)	0.4680 (4)	0.6275 (4)	0.037
C4	1.0117 (3)	0.5804 (4)	0.6145 (4)	0.038
C5	0.7471 (4)	0.6088 (5)	1.1858 (5)	0.059
C6	0.8154 (5)	0.3617 (5)	1.2051 (5)	0.063
C7	1.1267 (4)	0.4136 (4)	0.5311 (5)	0.056

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

Co—N1	1.885 (3)	O7—C15	1.172 (6)
Co—N3	1.889 (3)	O8—C15	1.348 (6)
Co—N4	1.888 (3)	O8—C16	1.437 (6)
Co—N2	1.895 (3)	C9—C10	1.484 (6)
Co—C9	2.070 (4)	C9—C14	1.513 (5)
Co—N5	2.075 (3)	C11—C12	1.63 (1)
O5—C10	1.209 (5)	C12—C13	1.22 (1)
O6—C10	1.344 (6)	C14—C15	1.503 (6)
O6—C11	1.443 (7)	C16—C17	1.468 (9)
C9—Co—N5	178.0 (1)	O6—C11—C12	103.3 (6)
C10—O6—C11	118.0 (5)	C13—C12—C11	125 (1)
C19—N5—Co	123.0 (2)	C15—C14—C9	114.1 (4)
C10—C9—C14	111.6 (3)	O8—C15—C14	109.2 (4)
C10—C9—Co	110.4 (2)	O8—C16—C17	111.8 (5)
C14—C9—Co	112.8 (3)	C18—C17—C16	125.5 (7)
O6—C10—C9	111.5 (3)		
C11—O6—C10—C9	170.9 (4)	C16—O8—C15—C14	178.0 (4)
C14—C9—C10—O6	150.1 (3)	C9—C14—C15—O8	-172.0 (4)
C10—O6—C11—C12	-172.0 (4)	C15—O8—C16—C17	110.2 (6)
C10—C9—C14—C15	-70.2 (5)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1195). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Di- μ -isocyanato-bis[isocyanato(1,10-phenanthroline)copper(II)]

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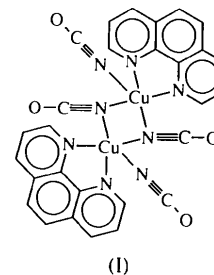
Abstract

The structure of blue $[\text{Cu}_2(\text{NCO})_4(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ consists of $[\text{Cu}(\text{NCO})_2(\text{phen})]$ subunits (phen is 1,10-phenanthroline) in a distorted planar arrangement, the subunits existing in centrosymmetrically related pairs in the crystal packing. The subunits have a distorted four-coordinate square-planar arrangement of N atoms about the central Cu atom; pairs of these $[\text{Cu}(\text{NCO})_2(\text{phen})]$ subunits form dimers by interaction of the fifth position on each Cu center with an N atom of an isocyanate ligand of the associated subunit. The coordination around each Cu atom is best described as distorted square-pyramidal.

Comment

The crystal structure of $[\text{Cu}(\text{NCS})_2(\text{phen})]$ (Parker & Breneman, 1993) has been shown to contain an infinite linear chain of NCS^- -bridged Cu atoms. It was anticipated that the isocyanate complex (I) might have a similar structure and packing arrangement, and exist as discrete pairs of $[\text{Cu}(\text{NCO})_2(\text{phen})]$ subunits. Three related structures have been determined and these exhibit

a similar bridging pattern involving the isocyanate ligands. The complexes $[\text{Cu}_2(\text{bpm})(\text{NCO})_4]_n$ (Julve, Verdager, De Munno, Real & Bruno, 1993), where bpm is bipyrimidine, $[\text{Cu}(\text{NCO})_2(\text{diMeen})]_2$ (Mauro, Klein, Saldana, de Simone, Zukerman-Schpector & Castellano, 1990), where diMeen is *N,N*-dimethylethylenediamine, and $[\text{Cu}_2(\text{apox})(\text{NCO})_2]$ (Lloret, Julve, Faus, Ruiz, Castro, Mollar & Philoche-Levisalles, 1992), where H_2apox is *N,N'*-bis(3-aminopropyl)oxamide, have structures that are bridged end-on through the nitrogen ends of the isocyanate ligands.



An ORTEP plot (Johnson, 1965) of (I) is shown in Fig. 1, with the atom-numbering system indicated. A stereoscopic plot of the unit cell is shown in Fig. 2. The title compound consists of discrete $[\text{Cu}(\text{NCO})_2(\text{phen})]_2$ pairs which are bridged through isocyanate ligands in an asymmetrical end-on fashion. The subunits have a four-coordinate distorted square-planar arrangement of N atoms about the central Cu atom; pairs of these $[\text{Cu}(\text{NCO})_2(\text{phen})]$ subunits form dimers by the interaction of the fifth position on each Cu center with an N atom of a cyanate ligand of the associated subunit. One isocyanate ligand on each Cu center thus serves as a linkage for the dimer, with the other attached through the N atom to only one Cu atom. Each Cu atom has distorted square-pyramidal coordination, with the sixth position unoccupied.

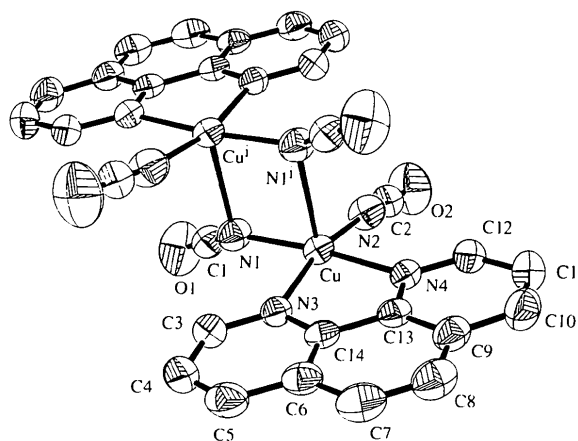


Fig. 1. A displacement ellipsoid plot (50% probability) of $[\text{Cu}(\text{NCO})_2(\text{phen})]_2$ showing the atom-numbering scheme.