

(2-Carbamoylethyl)bis(dimethylglyoximato-*N,N'*)[(*R*)-1-(1-naphthyl)ethylamine]cobalt(III) ethanol solvate and bis(dimethylglyoximato-*N,N'*)-[2-(*N*-methylcarbamoyl)ethyl][methyl(*S*)-phenylalaninate-*N*]cobalt(III)

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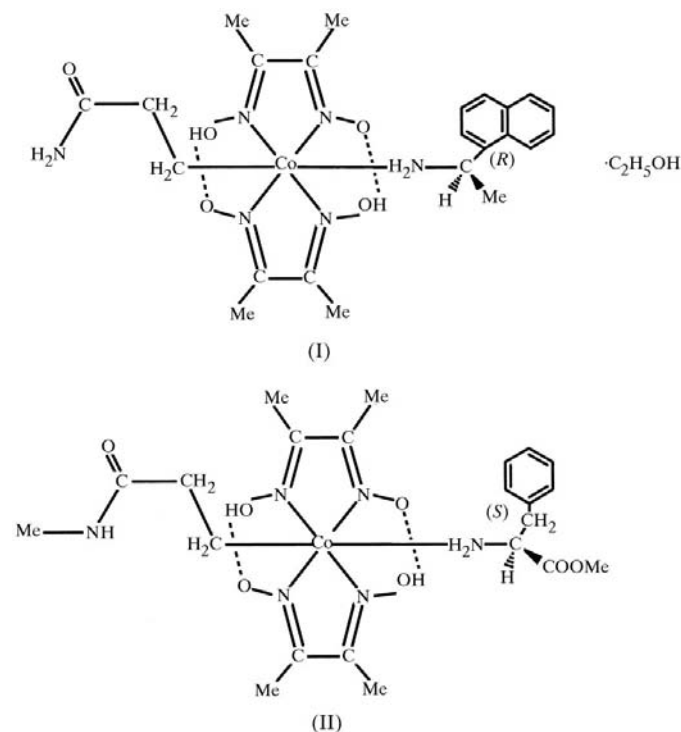
The 2-carbamoylethyl and 2-(methylcarbamoyl)ethyl groups in the title cobaloxime complexes, [Co(C₄H₇N₂O₂)₂(C₃H₆NO)(C₁₀H₁₃N)]·C₂H₆O and [Co(C₄H₇N₂O₂)₂(C₄H₈NO)(C₁₀H₁₃NO₂)], were isomerized to 1-carbamoylethyl and 1-(methylcarbamoyl)ethyl groups, respectively, on exposure to visible light in the solid state. Although both the crystal structures and the intermolecular hydrogen bonds are different in the two crystals, similar reaction rates were observed.

Comment

The photoinduced isomerization of various substituents such as 2-cyanoethyl, 2-methoxycarbonylethyl, 3-cyanopropyl, *trans*-2-butenyl and 4-cyanobutyl groups in cobaloxime complexes have been studied (Ohgo & Takeuchi, 1985; Ohgo *et al.*, 1994, 1997; Uchida *et al.*, 1987; Kurashima *et al.*, 1995; Amano, 1996; Sekine *et al.*, 1998; Yamada *et al.*, 1995; Vithana *et al.*, 2000). The mechanisms and kinetics have been elucidated in terms of reaction cavity, which is defined as a void space around the reactive group (Ohashi *et al.*, 1981). A series of cobaloxime complexes with the 2-(*N*-substituted carbamoyl)ethyl group, including the title compounds, (I) and (II), were synthesized to analyze the relationship between the void space and the intermolecular hydrogen bond (Ohgo *et al.*, 1996), since the 2-carbamoylethyl group has both hydrogen donor (NH) and acceptor (C=O) atoms.

The crystal structures of (I) viewed along the *c* axis and (II) viewed along the *b* axis are shown in Figs. 1 and 2, respectively. The molecular structures of (I) and (II) are shown in Figs. 3 and 4. There are two ethanol solvent molecules in (I). Selected

bond distances, angles and torsion angles are given in Tables 1 and 3, respectively. The 2-carbamoylethyl and 2-(methylcarbamoyl)ethyl groups take perpendicular forms to



the cobaloxime planes, since the conformations around Co—C9—C10—N5 and C10—C11—N5—C12 are *trans*. The hydrogen bonds in (I) and (II) are given in Tables 2 and 4, respectively. The hydrogen-bond network involves the crystal solvent and the reactive group, whereas there are no inter- or intramolecular hydrogen bonds in complex (II) except for intramolecular ones in the equatorial ligands. The powdered sample of each complex was irradiated with a solar simulator (flux density: 100 mW cm⁻²) and the ratios of 1-substituted ethyl to 2-substituted ethyl complex were determined by high-pressure liquid chromatography at a definite time interval. Assuming first-order kinetics, the rate constants were calcu-

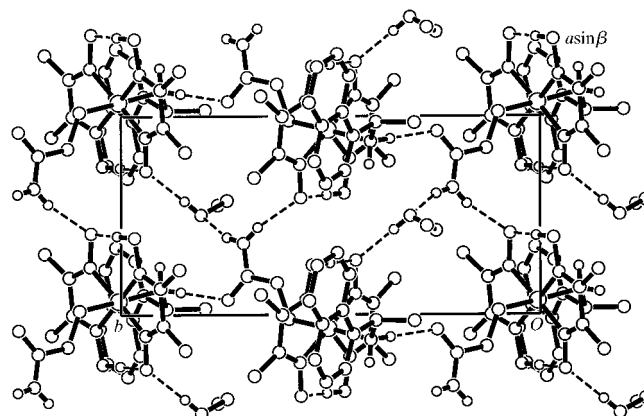


Figure 1
The crystal structure of (I) viewed along the *b* axis. Dotted lines show the hydrogen bonds.

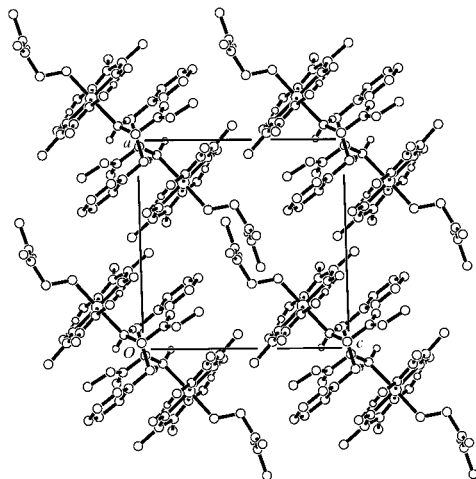


Figure 2
The crystal structure of (II) viewed along the *b* axis.

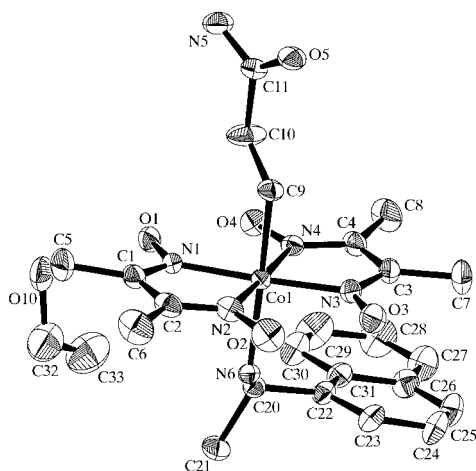


Figure 3
The molecular structure (ORTEP; Johnson, 1965) of (I) with the atomic numbering. Displacement ellipsoids are shown at the 50% probability level.

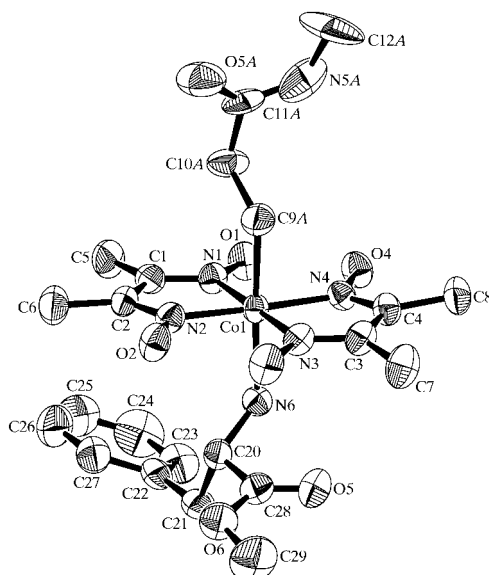


Figure 4
The molecular structure of (II) with the atomic numbering. Displacement ellipsoids are shown at the 50% probability level.

lated from the time courses of the ratios to be $3.68 \times 10^{-5} \text{ s}^{-1}$, (I), and $4.34 \times 10^{-5} \text{ s}^{-1}$, (II). Although the intermolecular hydrogen bonds are different between the two crystals, similar reaction rates were observed. Systematic research on the relationship between the structure and the reaction rate is in progress.

Experimental

The preparation of (2-carbamoyl ethyl)bis(dimethylglyoximate)[(*R*)-1-(1-naphthyl)ethylamine]cobalt(III) and bis(dimethylglyoximate)-[2-(methylcarbamoyl)ethyl][methyl (*S*)-phenylalaninate]cobalt(III) were carried out according to literature methods with minor changes (Ohgo *et al.*, 1996). Crystals of both (I) and (II) were obtained by recrystallization from ethanol/hexane.

Compound (I)

Crystal data

[Co(C₄H₇N₂O₂)₂(C₃H₆NO)-
(C₁₂H₁₃N)]·C₂H₆O
M_r = 578.55
Monoclinic, *P*2₁
a = 7.852 (3) Å
b = 15.962 (5) Å
c = 11.951 (4) Å
 β = 105.48 (3)°
V = 1443.6 (9) Å³
Z = 2

D_x = 1.331 Mg m⁻³
Mo *K*α radiation
Cell parameters from 25
reflections
 θ = 12.50–15.00°
 μ = 0.642 mm⁻¹
T = 298 K
Prismatic, red
0.50 × 0.50 × 0.10 mm

Data collection

Rigaku AFC-5 diffractometer
 $\omega/2\theta$ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
*T*_{min} = 0.740, *T*_{max} = 0.939
3442 measured reflections
3442 independent reflections
3097 reflections with *I* > 2σ(*I*)
Refinement

θ_{max} = 27.50°
h = 0 → 10
k = 0 → 20
l = -15 → 14
3 standard reflections
every 100 reflections
frequency: 50 min
intensity decay: none

Table 1

Selected geometric parameters (Å, °) for (I).

Co1–N4	1.883 (3)	Co1–N1	1.890 (3)
Co1–N2	1.887 (4)	Co1–C9	2.013 (4)
Co1–N3	1.889 (3)	Co1–N6	2.092 (3)
Co1–C9–C10–C11	−179.6 (4)	C10–C11–N5–H05A	−179.8
C9–C10–C11–N5	−163.4 (6)		

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O2–H02···O3	1.008 (5)	1.482 (4)	2.491 (6)	179.7 (3)
O4–H04···O1	1.006 (3)	1.489 (3)	2.495 (5)	179.9 (3)
N6–H06A···O10 ⁱ	0.90	2.56	3.288 (6)	139
N6–H06B···O5 ⁱⁱ	0.90	2.09	2.993 (5)	177
N5–H05A···O10 ⁱⁱⁱ	0.86	2.12	2.946 (5)	160
N5–H05B···O3 ^{iv}	0.86	2.14	2.980 (6)	167
O10–H010···O1	0.82	1.88	2.703 (5)	179

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) −*x*, *y* − ½, −*z*; (iii) −1 − *x*, ½ + *y*, −*z*; (iv) *x* − 1, *y*, *z*.

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.124$
 $S = 1.120$
 3442 reflections
 356 parameters

H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0887P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.05 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e } \text{Å}^{-3}$

Compound (II)

Crystal data

$[\text{Co}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_4\text{H}_8\text{NO})\text{-}(\text{C}_{10}\text{H}_{13}\text{NO}_2)]$
 $M_r = 554.49$
 Monoclinic, $P2_1$
 $a = 11.097 (4) \text{ Å}$
 $b = 10.914 (3) \text{ Å}$
 $c = 11.178 (4) \text{ Å}$
 $\beta = 91.50 (3)^\circ$
 $V = 1353.3 (7) \text{ Å}^3$
 $Z = 2$

$D_x = 1.361 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.50\text{--}15.00^\circ$
 $\mu = 0.684 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Prismatic, red
 $0.50 \times 0.50 \times 0.50 \text{ mm}$

Data collection

Rigaku AFC-5 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.726$, $T_{\max} = 0.726$
 3291 measured reflections
 3291 independent reflections
 2981 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 27.55^\circ$
 $h = 0 \rightarrow 14$
 $k = 0 \rightarrow 14$
 $l = -14 \rightarrow 14$
 3 standard reflections
 every 100 reflections
 frequency: 50 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.136$
 $S = 1.073$
 3291 reflections
 382 parameters

H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.1018P)^2 + 0.0925P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.40 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{Å}^{-3}$

H atoms were refined using a riding model. The positional parameters of the H atoms were constrained to have C—H distances of 0.96 Å for primary, 0.97 Å for secondary, and 0.93 Å for aromatic H atoms. H-atom U values were constrained to $1.2U_{\text{eq}}$ of the atoms to which they are attached (1.5 for methyl groups). The absolute configurations of (I) and (II) were set by reference to the known absolute configurations of the chiral amino ligands.

For both compounds, 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: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL97*.

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Table 3

Selected geometric parameters (Å, °) for (II).

Co1—N1	1.875 (3)	Co1—N4	1.890 (4)
Co1—N2	1.878 (4)	Co1—C9A	2.011 (5)
Co1—N3	1.885 (3)	Co1—N6	2.096 (4)
Co1—C9A—C10A—C11A	−173.8 (8)		
C9A—C10A—C11A—N5A	75.0 (17)		
Co1—C9B—C10B—C11B	174.9 (10)		
C9B—C10B—C11B—N5B	109 (2)		
C10B—C11B—N5B—C12B	−172.7 (15)		
C10A—C11A—N5A—C12A	−167.1 (17)		

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O2—H02 \cdots O3	1.004 (4)	1.471 (4)	2.474 (6)	179.6 (3)
O4—H04 \cdots O1	1.000 (3)	1.486 (4)	2.486 (5)	179.7 (3)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1103). Services for accessing these data are described at the back of the journal.

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