Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

[2-(*N*,*N*-Dimethylcarbamoyl)ethyl]bis(dimethylglyoximato)[(*R*)-1-phenylethylamine]cobalt(III)

Yoshiki Ohgo,[a]* Yuji Ohashi,[b] Mitsuru Shida,[c] Mieko Hagiwara,[c] Yoshifusa Arai,[c] Seiji Takeuchi[c] and Yoshiaki Ohgo[c]

[a]Department of Chemistry, Toho University School of Medicine, 5-21-16 Omorinishi, Ota-ku, Tokyo 143-8540, Japan, [b]Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551, Japan, and [c]Niigata College of Pharmacy, Kamishin-ei cho, Niigata 950-2081, Japan

Correspondence e-mail: yohgo@med.toho-u.ac.jp

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.010 Å
R factor = 0.045
wR factor = 0.122
Data-to-parameter ratio = 9.9

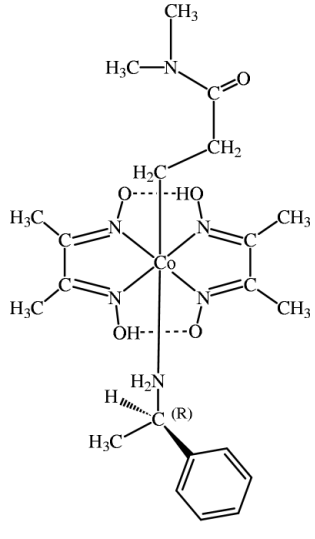
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 2 January 2001
Accepted 15 January 2001
Online 19 January 2001

The 2-(*N*,*N*-dimethylcarbamoyl)ethyl group of the title complex, $[Co(C_4H_7N_2O_2)_2(C_5H_{10}NO)(C_8H_{11}N)]$, forms a hydrogen bond with the (*R*)-1-phenylethylamine group of a neighboring molecule, which may be a reason why the group gave low reactivity in the solid-state photoisomerization to 1-(*N*,*N*-dimethylcarbamoyl)ethyl group.

Comment

A series of cobaloxime complexes containing the 2-(*N*-substituted-carbamoyl)ethyl group were synthesized to analyze the relationship between the void space and the intermolecular hydrogen bond (Ohgo *et al.*, 1996, 2001), since the 2-carbamoylethyl group has both the hydrogen-donor (NH) and acceptor (C═O) atoms. In the course of the studies on photoracemization and (*β*–*α*) photoisomerization in a series of cobaloxime complexes, the 2-substituted-carbamoylethyl groups in some cobaloxime complexes were found to be isomerized to the 1-substituted-carbamoylethyl groups. Futhermore, asymmetric induction up to 69% ee was observed in the photoreaction of the above complexes. In terms of this asymmetric induction, the hydrogen bonds of the reactive groups may play a role. The title compound, (I), was synthesized to make clear the role of hydrogen bonds in the solid-state photoreaction, systematically.



(I)

The crystal structure of (I) viewed along the *a* axis is shown in Fig. 1 and Fig. 2 shows the molecule of (I) with the numbering of the atoms. The *trans* conformations around Co—C9—C10—N5 and C10—C11—N5—C12 indicate that

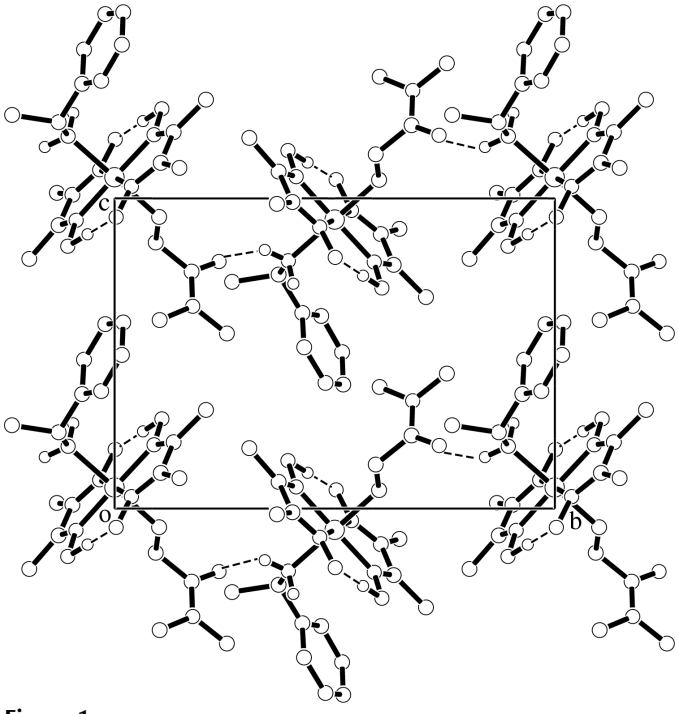


Figure 1
The crystal structure of the title compound viewed along the *a* axis. Dotted lines show the hydrogen bonds.

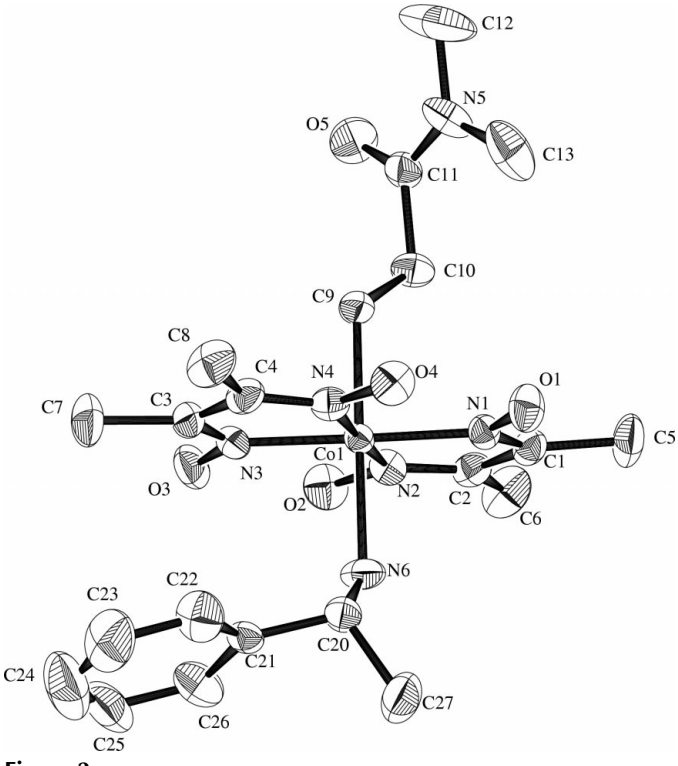


Figure 2
The molecular structure of the title compound with the atomic numbering. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted.

the 2-(*N*,*N*-dimethylcarbamoyl)ethyl group lies perpendicular to the cobaloxime plane. The torsion angle C9—C10—C11—N5, 78.8°, is almost the same angle as that in bis(dimethylglyoximato)[2-(methylcarbamoyl)ethyl][methyl (*S*)-phenylalaninate]cobalt(III), 75.0° (Ohgo *et al.*, 2000). The hydrogen bonds in (I) are given in Table 2. The N6 atom of the (*R*)-1-phenylethylamine moiety is hydrogen bonded to the O5 atom of the 2-(*N*,*N*-dimethylcarbamoyl)ethyl moiety of the neighboring molecule at $(-x, y-\frac{1}{2}, -z)$. Further investigation on the correlation between the structure and the reactivity is in progress.

Experimental

The preparation of (I) was carried out according to literature methods with minor changes (Ohgo *et al.*, 1996). Crystals were obtained by recrystallization from ethanol/hexane.

Crystal data

$[Co(C_4H_7N_2O_2)_2(C_5H_{10}NO)(C_8H_{11}N)]$
$M_r = 510.48$
Monoclinic, $P2_1$
$a = 8.8987\ (13)$ Å
$b = 14.3050\ (16)$ Å
$c = 10.1286\ (11)$ Å
$\beta = 97.096\ (9)°$
$V = 1279.5\ (3)$ Å^3
$Z = 2$
$D_x = 1.325$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.5$–$15.0°$
$\mu = 0.71$ mm^{-1}
$T = 298$ K
Prismatic, red
$0.20 \times 0.10 \times 0.05$ mm

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.871$, $T_{max} = 0.965$
3061 measured reflections
3061 independent reflections
2589 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 18$
$l = -13 \rightarrow 13$
3 standard reflections
every 100 reflections
frequency: 50 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.122$
$S = 1.02$
3061 reflections
309 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.83$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N2	1.871 (4)	Co1—N3	1.891 (5)
Co1—N1	1.876 (5)	Co1—C9	2.008 (6)
Co1—N4	1.878 (4)	Co1—N6	2.065 (5)
Co1—C9—C10—C11	−177.4 (4)	C9—C10—C11—N5	78.8 (7)
C9—C10—C11—O5	−100.0 (7)	C9—C10—C11—N5	78.8 (7)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H01···O4	1.01	1.46	2.476 (6)	180
O3—H03···O2	1.00	1.47	2.475 (7)	180
N6—H06B···O5^{i}	0.90	2.17	2.919 (7)	141

Symmetry code: (i) $-x, y-\frac{1}{2}, -z$.

The 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-atom U values were constrained to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups). The absolute configuration of (I) was set by reference to the known absolute configurations of the chiral amino ligands. There were no Friedel pairs in the measured data.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*); data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*); program(s) used to solve structure: *SAPI*91 (Fan, 1991); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL*97.

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

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