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[*N*,*N*′-Bis(2-methoxycarbonyl-3-oxobutylidene)-ethylenediaminato-κ^4*O*,*N*,*N*′,*O*′]cobalt(**II**)

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Key indicators

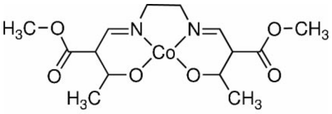
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.041
wR factor = 0.135
Data-to-parameter ratio = 11.1

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

The title compound, [Co($C_{14}H_{18}N_2O_6$)], is the first structurally characterized example of a β-ketoiminato Co^{II} complex without axial ligands. It adopts a square-planar *cis*-[CoN_2O_2] coordination geometry, and lies on a mirror plane. The planar complexes are stacked along 2_1 screw axes parallel to *b* to form columns, the Co$\cdots$Co distance in the column being 3.5213 (2) Å.

Comment

β-Ketoiminato Co^{II} complexes have been the subject of extensive study because of their powerful utility as catalysts for borohydride reduction (Ohtsuka *et al.*, 2001), regioselective conversion of α,β-unsaturated carboxyamides (Kato & Mukaiyama, 1990) and other reactions. Furthermore, optically active β-ketoiminato Co$^{II/III}$ (Yamada *et al.*, 1999, 2003) and Mn^{III} (Nagata *et al.*, 1994) complexes have long been employed as chiral catalysts in asymmetric syntheses. Hence, their crystal structures, including the determination of absolute configuration (Ohba *et al.*, 2001), have been investigated. Because of difficulty in isolation and crystallization, studies of the crystal structures of β-ketoiminato Co^{II} complexes without axial ligands have never been undertaken. However, it was recently revealed that sublimation gave rise to single crystals suitable for X-ray structure analysis. Here we report the first structural study of the Co^{II} complex of the title compound, (I).



(I)

In (I), all the non-H atoms lie on a mirror plane at $y = \frac{1}{4}$ except for the ethylenediamine moiety, where the atom C12 is disordered over two sites. Therefore, the bulk of the molecule is planar, as shown in Fig. 1. The Co^{II} complex has a four-coordinate square planar *cis*-[CoN_2O_2] coordination geometry, in which Co—N and Co—O bond distances are 1.836 (3) and 1.840 (3), and 1.864 (2) and 1.865 (2) Å, respectively (Table 1). These values are slightly shorter than those of the related Co^{III} complexes with axial ligands. The *trans*-O—Co—N bond angles are approximately 180°, and the *cis*-O—Co—N, *cis*-N—Co—N, and *cis*-O—Co—O bond angles are approximately 90°. As for the ligand of (I), the geometric parameters reported here agree with the corresponding values reported for analogous Schiff base ligands in the Cambridge Structural Database (Allen, 2002).

There is no obvious evidence of intramolecular or intermolecular hydrogen bonds. On the other hand, adjacent

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planar molecules related by the 2_1 screw axis parallel to *b* are stacked alternately with a Co···Co distance of 3.5213 (2) Å, forming one-dimensional columns.

Experimental

The title compound, (I), was synthesized and purified according to the method of Kato & Mukaiyama (1991). Red needle-like single crystals of (I) suitable for X-ray diffraction were obtained by sublimation at 473 K.

Crystal data

$C_{14}H_{18}CoN_2O_6$
$M_r = 369.23$
Orthorhombic, *Pnma*
$a = 14.791$ (2) Å
$b = 6.939$ (1) Å
$c = 15.424$ (3) Å
$V = 1583.0$ (4) Å^3
$Z = 4$
$D_x = 1.549$ Mg m^{-3}

Mo Kα radiation
Cell parameters from 25 reflections
$\theta = 10.0$–$12.1°$
$\mu = 1.12$ mm^{-1}
$T = 298.2$ K
Fragment cut from needle, red
$0.50 \times 0.23 \times 0.20$ mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.742$, $T_{max} = 0.800$
2447 measured reflections
1963 independent reflections
1817 reflections with $I > 2\sigma(I)$

$R_{int} = 0.050$
$\theta_{max} = 27.5°$
$h = -7 \rightarrow 19$
$k = -9 \rightarrow 3$
$l = -20 \rightarrow 0$
3 standard reflections every 150 reflections intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.135$
$S = 1.05$
1817 reflections
142 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.864 (2)	N1—C5	1.477 (5)
Co1—O4	1.865 (2)	N2—C12	1.502 (5)
Co1—N1	1.840 (3)	C5—C12	1.418 (6)
Co1—N2	1.836 (3)		
O1—Co1—O4	88.04 (10)	N1—Co1—N2	86.8 (1)
O1—Co1—N1	92.6 (1)	Co1—N1—C5	113.4 (2)
O1—Co1—N2	179.5 (1)	Co1—N2—C12	112.5 (2)
O4—Co1—N1	179.4 (1)	N1—C5—C12	111.4 (3)
O4—Co1—N2	92.5 (1)	N2—C12—C5	108.7 (3)
N1—C5—C12—N2	27.3 (3)		

Since the intensity of diffraction was considerably weak, we did not use all the independent reflections for the refinement. There is positional disorder of the atom C12 over two sites, which are equally occupied and are related by a mirror. It was assumed that the ethylenediamine moiety has two possible conformations, namely C5(H4A/H4*B*)–C12(H12/H13) and C5(H4*A*^{i}/H4*B*^{i})–C12^i(H12^i/H13^i) [symmetry code: (i) $x, \frac{1}{2} - y, z$]. The N1—C5—C12—N2 torsion angle of 27.3 (3)° is within the normal range for the ethylenediamine ligand. All H atoms were placed at calculated positions (C—H = 0.95–0.97 Å), and allowed for as riding, with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

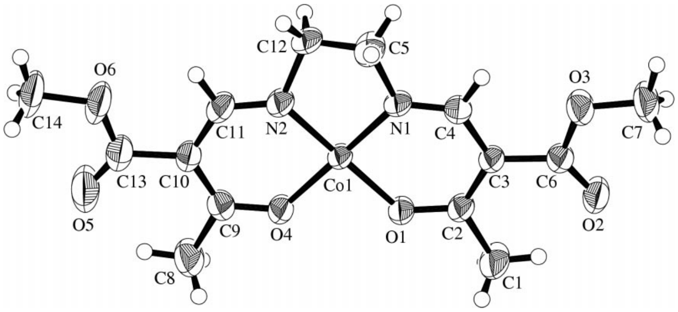

Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. One of the two possible conformations of the disordered ethylenediamine moiety has been omitted for clarity.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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