Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	*y*	*z*	U_{eq}
Co	0.20374 (4)	1/4	0.53256 (4)	0.0268 (1)
O	0.2989 (2)	0.29958 (6)	0.4620 (2)	0.0340 (5)
N	0.1073 (2)	0.29949 (8)	0.6027 (2)	0.0346 (6)
C1	0.2893 (2)	0.35096 (9)	0.4597 (2)	0.0287 (7)
C2	0.3688 (2)	0.38138 (9)	0.3910 (2)	0.0300 (7)
C3	0.3497 (2)	0.43479 (10)	0.3857 (2)	0.0343 (7)
C4	0.2594 (2)	0.46228 (10)	0.4444 (2)	0.0330 (7)
C5	0.1881 (2)	0.43327 (10)	0.5134 (2)	0.0359 (8)
C6	0.1997 (2)	0.37770 (10)	0.5224 (2)	0.0316 (7)
C7	0.4689 (3)	0.35529 (10)	0.3222 (2)	0.0373 (8)
C8	0.5486 (3)	0.3951 (1)	0.2610 (3)	0.0545 (10)
C9	0.4117 (3)	0.3200 (1)	0.2309 (3)	0.062 (1)
C10	0.5500 (3)	0.3227 (1)	0.4000 (3)	0.057 (1)
C11	0.2418 (3)	0.52137 (10)	0.4236 (3)	0.0402 (8)
C12	0.1762 (3)	0.5479 (1)	0.5206 (3)	0.058 (1)
C13	0.3610 (4)	0.5493 (1)	0.4067 (4)	0.088 (1)
C14	0.1654 (4)	0.5282 (1)	0.3164 (3)	0.079 (1)
C15	0.1157 (3)	0.35043 (10)	0.5911 (3)	0.0402 (8)
C16*A*†	−0.0103 (6)	0.2751 (3)	0.6493 (5)	0.033 (2)
C16*B*†	0.0317 (6)	0.2787 (3)	0.6999 (6)	0.034 (2)
C17	−0.0698 (3)	0.3128 (1)	0.7349 (3)	0.0464 (9)
C18*A*†	−0.1003 (5)	0.2666 (2)	0.5519 (4)	0.045 (2)
C18*B*†	0.1077 (5)	0.2693 (2)	0.8056 (4)	0.043 (2)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Co—O	1.846 (2)	C5—C6	1.423 (4)
Co—N	1.850 (2)	C6—C15	1.419 (4)
O—C1	1.312 (3)	C7—C8	1.528 (4)
N—C15	1.306 (3)	C7—C9	1.538 (4)
N—C16*A*	1.552 (7)	C7—C10	1.530 (4)
N—C16*B*	1.517 (7)	C11—C12	1.515 (4)
C1—C2	1.428 (3)	C11—C13	1.521 (4)
C1—C6	1.416 (4)	C11—C14	1.532 (5)
C2—C3	1.377 (3)	C16*A*—C16*B*ⁱ	1.563 (7)
C2—C7	1.530 (4)	C16*A*—C17	1.541 (7)
C3—C4	1.408 (4)	C16*A*—C18*A*	1.539 (8)
C4—C5	1.355 (4)	C16*B*—C17	1.485 (7)
C4—C11	1.536 (4)	C16*B*—C18*B*	1.524 (8)
O—Co—Oⁱ	86.2 (1)	O—Co—Nⁱ	179.55 (9)
O—Co—N	94.02 (8)	N—Co—Nⁱ	85.8 (1)

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

There was a centrosymmetric distribution of intensities. The structure was solved by heavy-atom methods in *Pnma*. Disorder in the central –CMe_2—CMe_2– section of the ligand, due to incompatibility of the ring puckering with the crystallographic mirror symmetry, gave alternative half-occupied positions for C16 and C18; alternative sites for C17 could not be distinguished. Structure solution in space-group $Pn2_1a$ showed the same disorder, with large correlation coefficients for refined corresponding parameters of pairs of atoms in the rest of the molecule. H atoms were included at updated riding positions [C—H 0.95 Å and $B(H) = 1.2B_{eq}(C)$].

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976) in *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Bis[2,3-butanedione dioximato(1−)-*N*,*N*′](pyridine){[(*R*)-5,6,7,8-tetrahydro-8-indolizinyl]methyl}cobalt(III)

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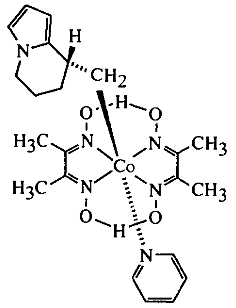
Abstract

The title compound, $[Co(C_9H_{12}N)(C_4H_7N_2O_2)_2(C_5H_5N)]$, has the expected structure with the C-bonded heterocyclic ligand *trans* to pyridine. The Co—C bond

lengths in the two independent molecules [2.032 (5) and 2.009 (6) Å] are near the lower end of the range found for related compounds and do not account for the observed thermal instability.

Comment

We are exploring the synthetic utility of (β-hydroxyalkyl)cobaloximes in the formation of new C—C, C—N and C—O bonds through β-heteroatom exchange with retention of stereochemistry (Gage & Branchaud, 1996; Grubb & Branchaud, 1997). We have synthesized a pyrrole-fused heterocyclic cobaloxime derived from carbon-nucleophile cyclization onto a π-cation formed by the reaction of [(*S*)-5-*N*-pyrrolyl-2-hydroxypentyl]-cobaloxime with pyridinium *p*-toluenesulfonate (Gage & Branchaud, 1997). The product, (I), proved to be thermally unstable. We have determined its crystal structure to ascertain whether the Co—C bond is longer than in a typical primary alkylcobaloxime as a result of the bulk of the heterocyclic alkyl ligand, thus leading to ready homolysis at ambient temperatures.



(I)

The asymmetric unit contains two independent molecules. Their structures are shown in Fig. 1. Molecules 1 and 2 have the same general structure but differ in the following points of detail:

(i) the σ-bonded alkyl ligands differ in orientation, as expressed by the torsion angles about the Co—C bonds [N2—Co1—C14—C15 83.4 (5) and N9—Co2—C36—C37 56.4 (7)°] and about the adjacent C—C bonds [Co1—C14—C15—C16 154.7 (4) and Co2—C36—C37—C38 139.4 (5)°].

(ii) The atoms of the two fused rings are coplanar to within 0.1 Å, except that the atoms of the six-membered rings opposite the common bonds [C21 and C22 in molecule 1, and C43 and C44 in molecule 2] are displaced by 0.30–0.35 (1) Å from the mean planes. The resultant twists of the six-membered rings are in opposite senses in the two independent alkyl ligands, although these ligands both have the *R* configuration, as expected from the chemical synthesis.

(iii) The dihedral angle between the mean planes of the two butanedione dioximato ligands is 6.9 (1)° in molecule 1, but 11.5 (1)° in molecule 2 (observed range 1.1–11.6°; Randaccio, Bresciani-Pahor & Zangrando, 1989). Both CoN_4 groups, however, are planar to within 0.016 (6) Å.

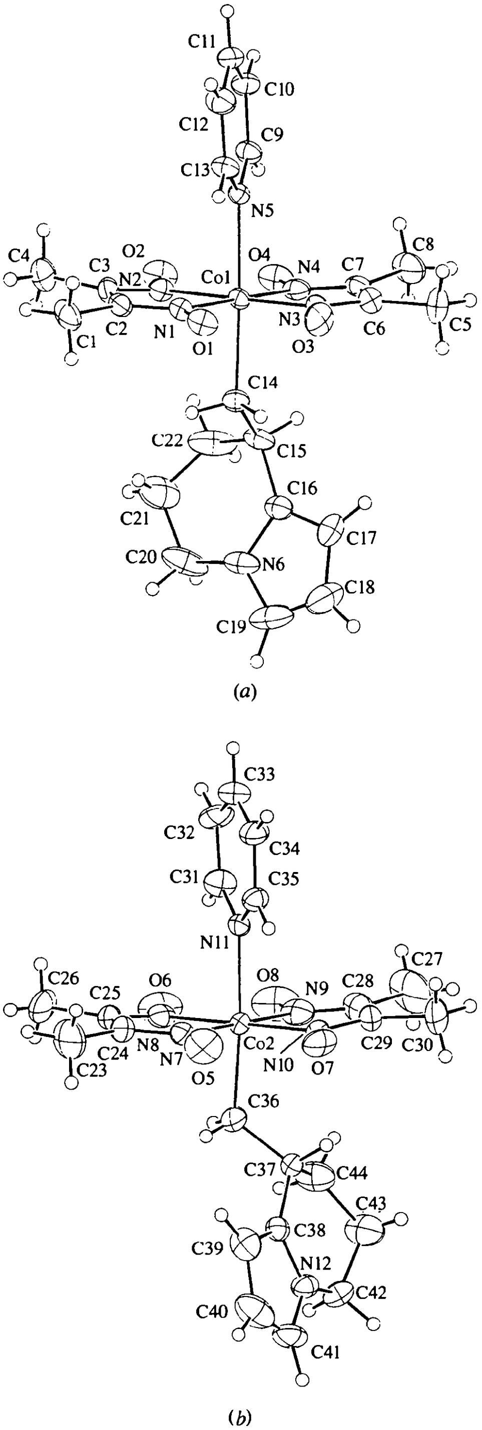


Fig. 1. View of the two independent molecules (30% probability displacement ellipsoids) of the title compound.

Despite these differences, the Co—C—C angles [122.3 (4) and 124.1 (4)°] are within the range reported for primary alkylcobaloximes [115.1 (5)–130.3 (4)°; Bresciani-Pahor *et al.*, 1985; Randaccio *et al.*, 1989]. The Co—C bond lengths [2.009 (6) and 2.032 (5) Å] are nearer the lower end of the range found for bonds *trans* to pyridine in primary alkylcobaloximes [1.995 (2)–2.083 (9) Å; Randaccio *et al.* 1989]. We conclude, therefore, that the thermal instability of this compound results from the inherent character of the fused-ring system (Angle *et al.*, 1994) rather than from the length of the Co—C bond.

Experimental

The title compound was prepared as described by Gage & Branchaud (1997). It was extracted and concentrated *in vacuo* and was twice recrystallized from deoxygenated aqueous methanol.

Crystal data

[Co($C_9H_{12}N$)($C_4H_7N_2O_2$)$_2$-(C_5H_5N)]
$M_r = 502.46$
Monoclinic
$P2_1$
$a = 9.279$ (1) Å
$b = 17.633$ (2) Å
$c = 15.505$ (1) Å
$\beta = 106.35$ (1)°
$V = 2434$ (1) Å^3
$Z = 4$
$D_x = 1.371$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14$–15°
$\mu = 0.739$ mm^{-1}
$T = 294$ K
Plate
0.31 × 0.24 × 0.04 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: azimuthal scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.87$, $T_{\max} = 1.00$
4714 measured reflections
4414 independent reflections

3610 reflections with $I > 1.5\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 20$
$l = -18 \rightarrow 17$
3 standard reflections
frequency: 60 min
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.082$
$S = 1.33$
4414 reflections
594 parameters
H atoms constrained
$w = 4F_o^2/[\sigma^2(I) + (0.02I)^2]$

$(\Delta/\sigma)_{\max} = 0.05$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Co1—N1	1.880 (4)	Co2—N7	1.881 (5)
Co1—N2	1.880 (4)	Co2—N8	1.883 (5)
Co1—N3	1.883 (4)	Co2—N9	1.880 (5)
Co1—N4	1.890 (5)	Co2—N10	1.875 (5)
Co1—N5	2.105 (4)	Co2—N11	2.062 (4)
Co1—C14	2.032 (5)	Co2—C36	2.009 (6)
N1—Co1—N2	80.9 (2)	N7—Co2—N9	179.4 (2)
N1—Co1—N3	98.5 (2)	N7—Co2—N10	97.7 (3)
N1—Co1—N4	178.8 (2)	N7—Co2—N11	89.3 (2)
N1—Co1—N5	90.5 (2)	N7—Co2—C36	89.1 (3)
N1—Co1—C14	83.7 (2)	N8—Co2—N9	98.7 (3)
N2—Co1—N3	179.0 (2)	N8—Co2—N10	179.2 (3)
N2—Co1—N4	98.3 (2)	N8—Co2—N11	89.6 (2)
N2—Co1—N5	88.7 (2)	N8—Co2—C36	86.2 (3)
N2—Co1—C14	92.6 (2)	N9—Co2—N10	82.1 (3)
N3—Co1—N4	82.3 (2)	N9—Co2—N11	90.1 (2)
N3—Co1—N5	90.5 (2)	N9—Co2—C36	91.5 (3)
N3—Co1—C14	88.1 (2)	N10—Co2—N11	90.2 (2)
N4—Co1—N5	90.5 (2)	N10—Co2—C36	94.0 (2)
N4—Co1—C14	95.4 (2)	N11—Co2—C36	175.7 (3)
N5—Co1—C14	173.7 (2)	Co1—C14—C15	122.3 (4)
N7—Co2—N8	81.6 (3)	Co2—C36—C37	124.1 (4)

H atoms on C atoms were included at riding positions, with C—H fixed at 0.95 Å and U(H) at $1.2U_{\rm eq}$(C). The four H atoms on O atoms could not be located from difference syntheses and were omitted from the refinement. The structure of opposite polarity refined to $R = 0.063$, $wR = 0.085$ and $S = 1.37$, and was rejected.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4-*PC Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1066). Services for accessing these data are described at the back of the journal.

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