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trans-Bis(dimethylglyoximato-κ^2N,N')-(1-hexenyl)(pyridine-κN)cobalt(III): a cobaloxime-substituted terminal alkene that rapidly isomerizes to a cobaloxime-substituted internal alkenyl complex

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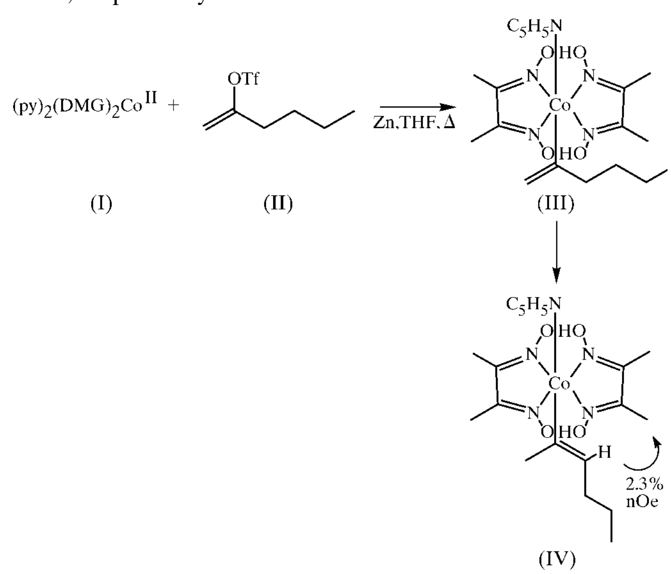
An unusual cobaloxime-substituted terminal alkene, [Co-(C_6H_{11})($C_4H_7N_2O_2$)$_2$(C_5H_5N)], has been isolated and characterized by X-ray crystallography. The double bond in the alkene readily isomerizes, but the title compound could be isolated and structurally characterized at low temperature.

Comment

We have been interested in the preparation of cobaloxime complexes [cobaloxime is bis(dimethylglyoximato)(pyridine)-cobalt] that contain Co—Csp^2 bonds and the use of these complexes in cycloaddition chemistry (Welker, 2001). In 2000, we reported a new method for the preparation of Co—Csp^2 bonds, which involved a zinc-mediated coupling of alkenyl halides and trifluoromethane sulfonates, (II), to (py)$_2$(dmg)$_2$-Co (py is pyridine and dmg is dimethylglyoximate; Pickin & Welker, 2000). One of the coupling products prepared, a 2-cobaloxime-substituted 1-hexene complex, (III), isomerized readily to (*E*)-2-cobaloxime-2-hexene, (IV). Complex (III) has now been crystallized at low temperature and its structure is reported here.

The molecular structure of (III) is depicted in Fig. 1, and selected geometric parameters are given in Table 1. The Co atom is coordinated in a slightly distorted octahedral geometry. The Co—N bond distances in the equatorial plane (Co—N1, Co—N2, Co—N3 and Co—N4) are 1.871 (5), 1.877 (5), 1.881 (5) and 1.903 (5) Å, respectively. The Co—N5$_{py}$ bond length is 2.089 (4) Å and the Co—C10 distance is 1.994 (5) Å. The Co and N1–N4 atoms are coplanar within 0.016 Å. The nearly coplanar Co1/C9/C10/C11/C12 (to within 0.05 Å) and Co1/N5/C15/C16/C17/C18/C19 (to within 0.03 Å) groups are almost parallel (5.2°) and are oriented so that they bisect the N4—Co—N1 and N2—Co—N3 angles. This arrangement minimizes the inter-ligand steric interaction of the axial ligands with the dimethylglyoxime ligands. The Co—C10 bond [1.994 (5) Å] falls in the range of other Co—Csp^2 bond lengths that we have reported for cobaloxime–dienyl complexes [1.954 (15)–2.019 (6) Å; Stokes *et al.*, 1995; Wright *et al.*, 1994]. This bond length is significantly longer than those reported previously for cobaloxime–ethenyl complexes [1.945 (5)–1.953 (3) Å; McCauley *et al.*, 2002] but comparable to Co—Csp^2 bond lengths in cobaloxime complexes containing longer C-atom chains in the alkenyl fragment [1.971 (13), 1.972 (7) and 1.976 (4) Å; Stolter *et al.*, 1975; Adams *et al.*, 1997, 1998]. Previously reported Co—Csp^3 bond lengths in cobaloxime complexes range from 1.998 (5) Å for the cobaloxime–methyl complex to 2.085 (3) Å for the isopropyl complex (Bresciani-Pahor *et al.*, 1985). The C9═C10 double bond in the hexenyl ligand [1.324 (7) Å] is largely unaffected by the presence of the cobaloxime, and this observation has also been made for the other cobaloxime-substituted alkenyl complexes referenced above. The Co—C10—C9 and Co—C10—C11 bond angles are 119.3 (4) and 117.5 (4)°, respectively. Most Co—C$^{\alpha}sp^2$—C$^{\beta}sp^2$ bond angles reported previously have been larger than 120°, but we have reported two other examples of cobaloxime–alkenyl and cobaloxime–dienyl complexes in which these angles were 118.3 (3) and 116.7 (5)° (Adams *et al.*, 1997; Stokes *et al.*, 1995). Intramolecular hydrogen-bonding interactions involving equatorial dimethylglyoximate ligands are described in Table 2. The values reported here agree with corresponding values reported for 200 compounds with 269 relevant bonds in the Cambridge Structural Database (Allen, 2002), with average O···O contacts and O—H···O angles of 2.488 Å and 168.2°, respectively.



The cobaloxime–alkenyl complex (III), which contains a terminal alkene, underwent facile double-bond isomerization upon attempted silica chromatography or simply upon standing in $CDCl_3$. The rate constant for isomerization was determined by analysis of the appearance of the alkenyl methyl signal, as described below. The alkenyl complex to which (III) isomerized was demonstrated to contain the

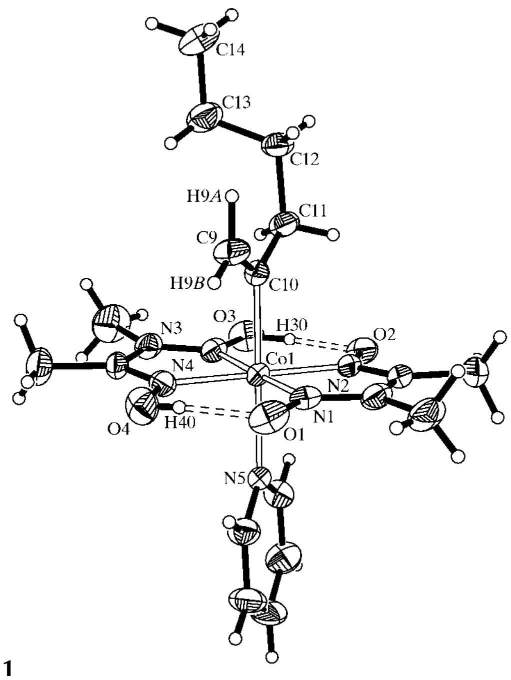


Figure 1
The molecular structure of (III). All non-H atoms are represented by displacement ellipsoids at the 50% probability level. H atoms are represented by spheres of arbitrary radii, which are in no way representative of the true thermal motion of the atoms. Hydrogen-bonding interactions are represented by double dashed lines.

(E)-alkene geometry shown in (IV), on the basis of the observation of a strong nOe (nuclear Overhauser effect) from the alkenyl H atom to the methyl groups of the dimethylglyoxime ligand, and the absence of an nOe from those same methyl groups to the methyl or methylene H atoms α to the alkene in the hexenyl ligand.

Experimental

Complex (III) was prepared as described by Pickin & Welker (2000). Crystals were grown by slow diffusion of pentane into a 1,2-dichloroethane solution of (III) at 253 K. The isomerization kinetics experiment was carried out in $CDCl_3$. The rate constant was determined by analysis of the appearance of the alkenyl methyl signal, and this analysis was carried out for several half lives. An array of ^{1}H spectra (acquisition time of 1.0 min) were acquired every 10.0 min for 170 min (nine half lives). All spectra were processed and phased with the same parameters. The appearance of the alkenyl methyl signal was integrated relative to the *ortho*-pyridine signal. *SIGMAPLOT*2000 (SPSS Science Inc., Chicago, IL) was used to determine the rate constant for an integration (I) *versus* time (t) plot. The equation for an exponentially rising peak with a maximum of $I = I_o[1 - \exp(-kt)]$ was used to fit the data. A rate constant of 3.9×10^{-2} min^{-1} ($R = 0.9707$) with a half life of 18 min was calculated.

Crystal data

$[Co(C_6H_{11})(C_4H_7N_2O_2)_2(C_5H_5N)]$	$D_x = 1.402$ Mg m^{-3}
$M_r = 451.41$	Mo $K\alpha$ radiation
Monoclinic, Pn	Cell parameters from 39 reflections
$a = 8.268$ (3) Å	$\theta = 3.0$–12.0°
$b = 11.757$ (3) Å	$\mu = 0.84$ mm^{-1}
$c = 11.0253$ (19) Å	$T = 228$ (2) K
$\beta = 93.721$ (18)°	Chunk, orange
$V = 1069.5$ (4) Å^3	$0.45 \times 0.24 \times 0.18$ mm
$Z = 2$	

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.034$
ω scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -1 \rightarrow 10$
$T_{min} = 0.151$, $T_{max} = 0.187$	$k = -15 \rightarrow 1$
3254 measured reflections	$l = -14 \rightarrow 14$
2971 independent reflections	3 standard reflections every 197 reflections
2660 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.065P)^2 + 0.1117P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.106$	$\Delta\rho_{max} = 0.65$ e Å^{-3}
$S = 1.05$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
2971 reflections	Absolute structure: Flack (1983)
278 parameters	Flack parameter = 0.09 (2)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.871 (5)	N1—C1	1.303 (8)
Co1—N2	1.877 (5)	N2—C2	1.292 (7)
Co1—N3	1.881 (5)	N3—C3	1.297 (7)
Co1—N4	1.903 (5)	N4—C4	1.303 (8)
Co1—C10	1.994 (5)	N5—C15	1.338 (6)
Co1—N5	2.089 (4)	N5—C19	1.342 (6)
O1—N1	1.360 (6)	C1—C2	1.458 (8)
O2—N2	1.342 (6)	C3—C4	1.448 (10)
O3—N3	1.349 (6)	C9—C10	1.324 (7)
O4—N4	1.330 (6)	C10—C11	1.482 (7)
N1—Co1—N2	81.7 (2)	N4—Co1—C10	89.5 (2)
N1—Co1—N3	178.4 (2)	N1—Co1—N5	89.82 (18)
N2—Co1—N3	98.31 (19)	N2—Co1—N5	89.40 (18)
N1—Co1—N4	98.70 (19)	N3—Co1—N5	91.74 (19)
N2—Co1—N4	179.6 (2)	N4—Co1—N5	90.50 (19)
N3—Co1—N4	81.3 (2)	C10—Co1—N5	179.5 (2)
N1—Co1—C10	89.7 (2)	C9—C10—C11	123.2 (5)
N2—Co1—C10	90.6 (2)	C9—C10—Co1	119.3 (4)
N3—Co1—C10	88.8 (2)	C11—C10—Co1	117.5 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O2	0.91 (9)	1.59 (9)	2.497 (7)	170 (7)
O4—H4O···O1	0.77 (5)	1.73 (5)	2.487 (6)	172 (6)

Atoms H3O, H4O, H9A and H9B were located in a difference Fourier map and refined as independent isotropic atoms. The methyl groups (atoms C5, C6, C7, C8, C14 and their H atoms) were refined as rigid rotors, with idealized sp^3-hybridized geometry and a C—H bond length of 0.97 Å. The remaining H atoms were included in the structure-factor calculations as idealized atoms (assuming sp^2- or sp^3-hybridization of the C atoms and C—H bond lengths of 0.94–0.98 Å), riding on their respective C atoms. The isotropic displacement parameters for atoms H3O, H4O, H9A and H9B refined to final values of 0.07 (3), 0.02 (1), 0.05 (2) and 0.03 (1) Å^2, respectively. The U_{iso} parameters of the remaining H atoms were fixed at 1.2 (non-methyl) or 1.5 (methyl) times the U_{eq} values of the C atoms to which they are covalently bonded.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL-NT* (Bruker, 2001); program(s) used to solve structure: *SHELXTL-NT*; program(s) used to refine structure: *SHELXTL-NT*; molecular graphics: *SHELXTL-NT*; software used to prepare material for publication: *SHELXTL-NT*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1631). Services for accessing these data are described at the back of the journal.

References

Adams, T. A., Welker, M. E. & Day, C. S. (1998). *J. Org. Chem.* **63**, 3683–3686.

Adams, T. A., Welker, M. E., Liable-Sands, L. M. & Rheingold, A. L. (1997). *Organometallics*, **16**, 1300–1307.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bresciani-Pahor, N., Forcolin, M., Marzilli, L. G., Randaccio, L., Summers, M. F. & Toscano, P. J. (1985). *Coord. Chem. Rev.* **63**, 1–125.

Bruker (2001). *SHELXTL-NT*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

McCauley, K. M., Wilson, S. R. & van der Donk, W. A. (2002). *Inorg. Chem.* **41**, 393–404.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pickin, K. A. & Welker, M. E. (2000). *Organometallics*, **19**, 3455–3458.

Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stokes, H. L., Richardson, B. M., Wright, M. W., Vaughn, S. M., Liable-Sands, L. & Rheingold, A. L. (1995). *Organometallics*, **14**, 5520–5532.

Stolter, D. A., Sheldrick, G. M. & Taylor, R. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2124–2128.

Welker, M. E. (2001). *Curr. Org. Chem.* **5**, 785–807.

Wright, M. W., Smalley, T. L., Welker, M. E. & Rheingold, A. L. (1994). *J. Am. Chem. Soc.* **116**, 6777–6791.