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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1186). Services for accessing these data are described at the back of the journal.

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Bis(1,1,1,5,5,5-hexafluoroacetylacetonato-*O,O'*)bis(2,2,6,6-tetramethylpiperidinyl-1-oxy-*O*)cobalt(II)†

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Abstract

The structure of $[Co(C_5HF_6O_2)_2(C_9H_{18}NO)_2]$, measured at 173 K, is isostructural with the analogous manganese derivative at 295 K previously reported. The main differences are that in the title compound the nitroxyl O atom is disordered over two positions in a 9:1 ratio, and the *M*—O—N angle (where *M* is the metal) is about 20° more acute than reported for the manganese derivative.

† Alternative name: bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato-*O,O'*)bis(2,2,6,6-tetramethyl-1-piperidyl 1-oxide-*O*)cobalt(II).

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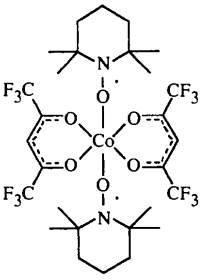
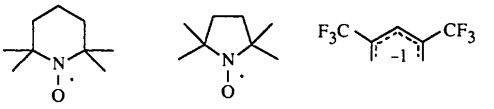
Comment

Adducts of nitroxyl free radicals (and closely related nitronyl nitroxides) with metal complexes containing the 1,1,1,5,5,5-hexafluoroacetylacetonato anion (hfac) have been of interest for their unusual magnetic and structural properties (Caneschi, Gatteschi & Rey, 1991; Porter, Dickman & Doedens, 1986). Reaction of $M(hfac)_2$ complexes with nitroxyls such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (tempo) or 2,2,5,5-tetramethylpyrrolidinyl-1-oxy (proxyl), where *M* = Mn (Dickman, Porter & Doedens, 1986), Co, Ni (Porter, Dickman, & Doedens, 1988), Cu (Dickman & Doedens, 1981) or V=O (Drago, Kuechler & Kroeger, 1979), results in mono- or bis-nitroxyl adducts which exhibit antiferromagnetic coupling between unpaired electrons on the metal and the radical. Previous structural studies of the isostructural compounds $M(hfac)_2(proxyl)_2$ (*M* = Mn, Co, Ni) and $Mn(hfac)_2(tempo)_2$, (II), revealed a large difference in the *M*—O—N angle for the tempo derivative compared with the proxyl adducts (Dickman *et al.*, 1986; Porter *et al.*, 1988). The more acute angle observed for the proxyl derivatives was attributed to the smaller steric hindrance of the nitroxyl O atom by the five-membered ring methyl groups compared with the piperidinyl methyl groups.



(I)



tempo proxyl hfac

(II)

The title compound, (I), had been prepared previously but was found to be relatively unstable at room temperature and no structural analysis was performed at the time (Dickman, 1984). The facile decomposition of the cobalt derivative was assumed to be due to the smaller ionic radius of cobalt compared with manganese, resulting in more unfavorable steric interaction between the tempo radical and $Co(hfac)_2$ moieties. The present structural analysis of (I) was performed at low temperature in order to investigate the basis of the relative instability of the cobalt derivative and the reproducibility of a larger *M*—O—N angle in six-coordinate tempo complexes.

The present low-temperature study of (I) shows it to be isostructural with (II) and the proxyl complexes described above (Figs. 1 and 2). The general features of (I) and (II) are in agreement, displaying a *trans* geometry of ligands in a centrosymmetric complex. The six-membered piperidine ring of (I) and (II) is in the chair conformation typically found for the tempo radical. In (II), the N atom was displaced 0.336 Å out of the plane formed by C1, C2, C4 and C5, while C3 was displaced in the other direction by 0.717 Å. In (I), these displacements are 0.333 (3) and 0.721 (5) Å, respectively. The piperidinyl ring conformations thus appear to be almost identical for (I) and (II).

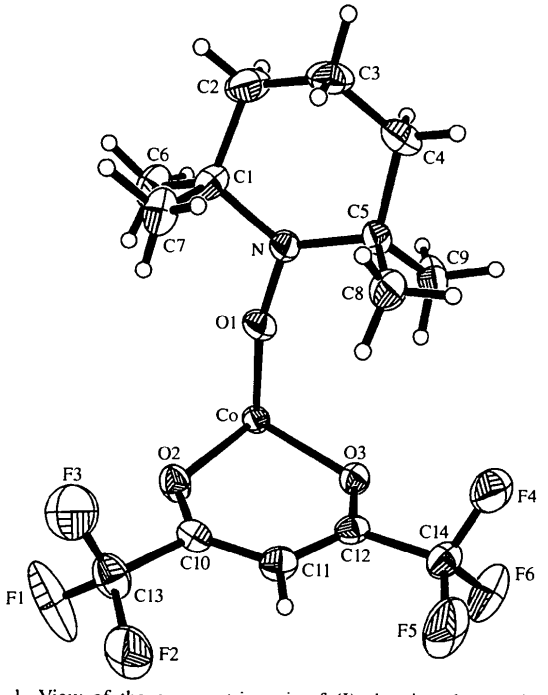


Fig. 1. View of the asymmetric unit of (I) showing the numbering scheme. Displacement ellipsoids are drawn at 50% probability. H atoms are drawn as circles of arbitrary radii. The disordered O atom O1*A* (directly behind O1) has been omitted.

An unexpected finding is the Co—O—N angle of 145.1 (2)° compared with the analogous angle reported for the manganese complex of 167.2 (5)°. The more acute angle for the present complex agrees more closely with those observed for the room-temperature structures of the Mn, Co and Ni(hfac)$_2$(proxyl)$_2$ complexes in which the *M*—O—N angles were 145.3 (4), 139.4 (4) and 137.1 (4)°, respectively (Dickman *et al.*, 1986; Porter *et al.*, 1988). In (I), the nitroxyl O atom is disordered over two positions, shown in Fig. 2. The major peak for the nitroxyl O atom is displaced 0.563 (7) Å from the C1—N—C5 plane. The minor peak is displaced 0.20 (2) Å from the same plane but in the opposite direction. These correspond to angular displacements of the N—O bond out of the C1—N—C5 plane by 25.6 (1) and 8.8 (2)°, respectively, compared with 19.4° for free tempo (Lajzerowicz-Bonneteau, 1976). Although there are apparently no previous reports of this type of disorder for a nitroxyl radical, theoretical calculations on piperidinyl nitroxyls (Komaromi & Tronchet, 1995) indicate that a large (40°) motion of the N—O bond out of the C—N—C plane has a relatively small activation energy of about 1.5 kcal mol^{-1}.

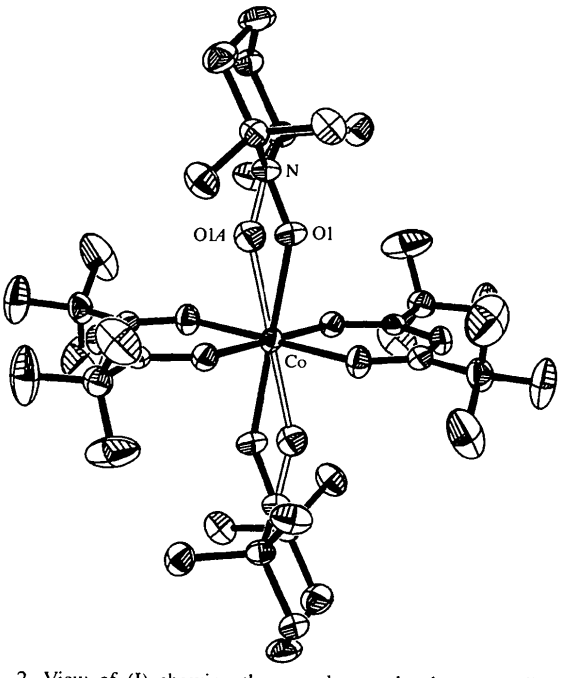


Fig. 2. View of (I) showing the complete molecule, perpendicular to the O1—N—O1*A* plane, with displacement ellipsoids at 50% probability. H atoms have been omitted for clarity. Bonds involving O1*A* are shown in outline.

The disorder found in the present structure raises the possibility that the larger *M*—O—N angle seen in the isostructural manganese complex was a consequence of the same type of disorder which was undetected at the time. These results have stimulated a re-examination of the manganese structure, currently in progress; a preliminary account has been given (Dickman, 1996).

Experimental

The preparation of (I) has been described before (Dickman, 1984) but is given here in more detail. Co(hfac)$_2$ was prepared from the metal acetate by a standard procedure (Cotton & Holm, 1960). The tempo ligand (98% purity) was purchased from Aldrich Chemicals and used without further purification. A mixture of tempo (0.5 g, 3 mmol) and Co(hfac)$_2$ (0.5 g, 1 mmol) in 20 ml of *n*-heptane was heated with stirring in a 50 ml round-bottomed flask fitted with a reflux condenser. The mixture was refluxed for 10 min. The resulting deep-red solution was filtered with suction and allowed to stand at

room temperature in a covered beaker. Crystallization usually started quickly but sometimes had to be initiated by adding seed crystals made by allowing heptane to partly evaporate from a small portion of the solution. When the dark-red prismatic crystals reached the appropriate size the solid was gently scraped from the beaker, filtered, carefully rinsed with a small amount of *n*-heptane, briefly dried and quickly placed in a vial. Extended exposure to air was avoided due to the possibility of decomposition; samples in contact with excess radical appeared to be more stable. Typical yields were 0.5 g (70%), but more solid could be obtained by further evaporation of the heptane solution.

Crystal data

$[Co(C_5HF_6O_2)_2(C_9H_{18}NO)_2]$
M_r = 785.53
Monoclinic
$P2_1/c$
a = 10.3960 (10) Å
b = 14.468 (2) Å
c = 12.155 (2) Å
β = 112.53 (1)°
V = 1688.7 (4) Å^3
Z = 2
D_x = 1.545 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 40 reflections
θ = 4.83–12.49°
μ = 0.617 mm^{-1}
T = 173 (2) K
Block
0.4 × 0.2 × 0.2 mm
Red

Data collection

Siemens *P4/RA* diffractometer
$2\theta/\omega$ scans
Absorption correction: none
9488 measured reflections
3886 independent reflections
2821 reflections with $I > 2\sigma(I)$

R_{int} = 0.049
θ_{max} = 28.51°
$h = -1 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -15 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: 5.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.112
S = 1.03
3886 reflections
303 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.585P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	U_{eq}
Co	0	0	0	0.02149 (13)
N	0.1751 (2)	0.08668 (13)	−0.1517 (2)	0.0251 (4)
O1†	0.1533 (2)	0.05383 (14)	−0.0607 (2)	0.0293 (4)
O1*A*‡	0.084 (2)	0.0768 (14)	−0.1034 (19)	0.036 (5)
O2	0.1543 (2)	0.01076 (12)	0.16462 (14)	0.0305 (4)
O3	0.0730 (2)	−0.12909 (11)	−0.01484 (14)	0.0259 (4)
C1	0.2281 (3)	0.1845 (2)	−0.1349 (2)	0.0284 (5)
C2	0.2425 (4)	0.2182 (2)	−0.2494 (3)	0.0418 (7)
C3	0.3131 (4)	0.1484 (2)	−0.3005 (3)	0.0422 (7)
C4	0.2235 (3)	0.0623 (2)	−0.3345 (2)	0.0344 (6)
C5	0.2042 (3)	0.0156 (2)	−0.2291 (2)	0.0269 (5)
C6	0.1227 (3)	0.2435 (2)	−0.1087 (3)	0.0389 (6)
C7	0.3681 (3)	0.1865 (2)	−0.0300 (3)	0.0382 (6)
C8	0.3364 (3)	−0.0370 (2)	−0.1523 (3)	0.0372 (6)
C9	0.0809 (3)	−0.0498 (2)	−0.2746 (3)	0.0405 (7)
C10	0.2473 (2)	−0.0472 (2)	0.2128 (2)	0.0258 (5)
C11	0.2683 (3)	−0.1329 (2)	0.1695 (2)	0.0281 (5)
C12	0.1805 (2)	−0.1657 (2)	0.0586 (2)	0.0239 (5)
C13	0.3530 (3)	−0.0160 (2)	0.3352 (2)	0.0359 (6)
C14	0.2175 (3)	−0.2582 (2)	0.0161 (2)	0.0307 (5)
F1	0.2909 (2)	0.0181 (2)	0.4010 (2)	0.0816 (8)
F2	0.4368 (2)	−0.08258 (13)	0.39626 (15)	0.0592 (5)
F3	0.4343 (2)	0.0499 (2)	0.3220 (2)	0.0734 (7)
F4	0.2489 (3)	−0.24676 (12)	−0.0782 (2)	0.0673 (6)
F5	0.3239 (2)	−0.30157 (13)	0.0971 (2)	0.0691 (6)
F6	0.1119 (2)	−0.31680 (11)	−0.0146 (2)	0.0561 (5)

† Site occupancy = 0.90. ‡ Site occupancy = 0.10.

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

Co—O2	2.035 (2)	O2—C10	1.244 (3)
Co—O3	2.050 (2)	O3—C12	1.250 (3)
Co—O1*A*	2.10 (2)	C10—C11	1.396 (3)
Co—O1	2.143 (2)	C10—C13	1.540 (3)
N—O1	1.300 (3)	C11—C12	1.391 (3)
N—O1*A*	1.30 (2)	C11—H11*C*	0.87 (3)
N—C5	1.501 (3)	C12—C14	1.536 (3)
N—C1	1.504 (3)		
O2—Co—O3^i	91.30 (6)	O1*A*—N—C5	124.4 (9)
O2—Co—O3	88.70 (6)	O1—N—C1	113.8 (2)
O2^i—Co—O1*A*	78.7 (6)	O1*A*—N—C1	109.5 (9)
O2—Co—O1*A*	101.3 (6)	C5—N—C1	125.3 (2)
O3^i—Co—O1*A*	79.8 (6)	N—O1—Co	145.1 (2)
O3—Co—O1*A*	100.2 (6)	N—O1*A*—Co	150.4 (15)
O3—Co—O1*A*^{i}	79.8 (6)	C10—O2—Co	126.1 (2)
O2^i—Co—O1	95.70 (8)	C12—O3—Co	125.7 (2)
O2—Co—O1	84.30 (8)	O2—C10—C11	128.8 (2)
O3^i—Co—O1	92.79 (7)	O2—C10—C13	113.3 (2)
O3—Co—O1	87.21 (7)	C11—C10—C13	117.8 (2)
O1*A*—Co—O1	21.3 (6)	C12—C11—C10	121.9 (2)
O1*A*^{i}—Co—O1	158.7 (6)	O3—C12—C11	128.5 (2)
O1—N—O1*A*	35.1 (9)	O3—C12—C14	113.6 (2)
O1—N—C5	115.1 (2)	C11—C12—C14	117.9 (2)

Symmetry code: (i) $-x, -y, -z$.

Table 3. *Average interatomic distances and angles (Å, °) for ligands; e.s.d's are in parentheses and calculated s.d.'s are in square brackets*

	Mean	Range
C—C(tempo)	1.523 [9]	1.514 (4)–1.535 (4)
C—F	1.318 [8]	1.303 (3)–1.324 (3)
C—H(tempo)	0.96 [4]	0.89 (3)–1.03 (3)
N—C—C	108.6 [10]	107.5 (2)–110.2 (2)
C—C—C(tempo)	111 [2]	108.4 (3)–113.5 (2)
C—C—F	112 [2]	110.3 (2)–114.2 (2)
F—C—F	106.8 [7]	105.9 (2)–107.8 (2)

A hemisphere of data was collected for data averaging. After anisotropic refinement of all non-H atoms had converged, one peak clearly stronger than the rest remained in the Fourier difference map. The location of the peak was near O1 and had similar distances to the N and Co atoms. The equivalent isotropic displacement parameter of O1 was also noticeably larger than those of the atoms connected to it. These facts suggested disorder. The peak was therefore refined isotropically as an O atom (O1*A*) sharing an occupancy factor with O1. The resulting O1:O1*A* distribution ratio was about 9:1. The occupancies were fixed at this ratio in the final model.

At convergence, the additional four parameters lowered the wR^2 factor (all data) compared with the non-disordered model from 12.1 to 11.2%. Anisotropic refinement of O1*A* did not result in significantly lower residuals. Additionally, the O1*A* positional and anisotropic displacement parameters exhibited very high (88–96%) correlations. Anisotropic refinement of O1*A* was abandoned for these reasons. There was no apparent disorder found for the CF_3 groups or the tempo ligand other than the nitroxyl O atom. Positional and isotropic displacement parameters of H atoms were refined without restraints, resulting in C—H distances of 1.03 (3)–0.89 (3) Å and *U* values of 0.064 (11)–0.025 (7) $Å^2$ for the tempo molecule. The corresponding values for the hfac anion C—H were 0.87 (3) Å and 0.030 (7) $Å^2$, respectively.

Data collection: *XSCANS* (Siemens, 1990). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL*.

Support from the Department of Chemistry of Georgetown University, Washington, DC, is gratefully acknowledged. The diffractometer was obtained with a grant from the National Science Foundation. The author thanks Mr Admassu Regassa for his assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1320). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1195–1197

Polysulfonylamines. LXXXVI.† Silver(I) Bis(4-fluorobenzenesulfonyl)amide Monohydrate‡

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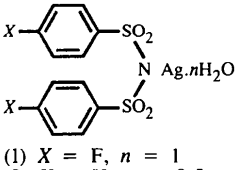
(*Received 24 March 1997; accepted 11 April 1997*)

Abstract

The title compound, $[Ag(C_{12}H_8F_2NO_4S_2)(H_2O)]_n$, consists of infinite strands $[(RSO_2)_2N–Ag(\mu\text{-}H_2O)]_\infty$ (R = 4-fluorophenyl), in which Ag extends its coordination number to five by accepting one Ag—O bond from each of the $(RSO_2)_2N^-$ ligands in the adjacent repeat units. By means of O—H···O hydrogen bonds, the strands are associated to form parallel layers. These display an inner polar region of Ag atoms, H_2O molecules and $N(SO_2)_2$ groups, outer apolar regions of stacked benzene fragments and interlayer regions consisting of F atoms.

Comment

Although silver(I) di(organosulfonyl)amides, $AgN(SO_2R)_2.nH_2O$ (n = 0 or n > 0), have not been studied extensively, even the few crystal structures currently known demonstrate for this class of compounds a rich variety of structural features, *e.g.* high coordination numbers at and aggregation of Ag centres, various bonding modes of hydrate water towards Ag and apolar–polar–apolar sandwich-type layers (DesMarteau, Zuberi, Pennington & Randolph, 1992; Näveke *et al.*, 1993; Jones, Hamann, Blaschette, Cammenga & Epple, 1993; Jones, Henschel, Weitze & Blaschette, 1994). The X-ray structure determination of the title compound, (1), is a sequel to our previous studies of silver(I) di(benzenesulfonyl)amide hemihydrate, (2), and anhydrous silver(I) di(4-toluenesulfonyl)amide, (3) (Jones, Henschel,



(1) X = F, n = 1
(2) X = H, n = 0.5
(3) X = Me, n = 0

† Part LXXXV: Moers, Blaschette & Jones (1997).
‡ Alternative name: poly{μ-aqua-O:O-μ^3-[bis(4-fluorophenylsulfonyl)-amido]-O^2:N:O^3-silver(I)}.