

Related literature. The structural features of the title compound are consistent with those of other dimeric tin(IV) chloride and mono-organotin trichloride derivatives such as $\text{SnCl}_3(\text{OR})\cdot\text{ROH}$ [$R = \text{Me}$ (Sterr & Mattes, 1963), $R = \text{Et}$ (Webster & Collins, 1974)]; $\text{SnCl}_3(\text{OH})\cdot\text{H}_2\text{O}\cdot L$ (Barnes, Sampson & Weakly, 1980); $\text{Sn}(\text{O}^i\text{Pr})_4\cdot i\text{PrOH}$ (Hampden-Smith, Wark, Rheingold & Huffman, 1991; Reuter & Kremser, 1991); and $R\text{Sn}(\text{OH})\text{Cl}_2\cdot\text{H}_2\text{O}$ [$R = \text{Et}$ (Lecomte, Protas & Devaud, 1976), $R = ^n\text{Bu}$ (Holmes, Shafieezad, Chandrasekhar, Holmes & Day, 1988), $R = ^i\text{Pr}$, ^tBu (Puff & Reuter, 1989)]. In all these cases the two octahedrally coordinated Sn atoms are bridged by two $\mu_2\text{-OH}$ or $\mu_2\text{-OR}$ groups. Differences only exist with respect to crystal packing and the formation of additional hydrogen bridges to further solvent molecules. In the present case a second methanol molecule is bonded *via* a short hydrogen bond to the methanol molecule which coordinates directly with the Sn atom and forms a weak hydrogen bond to the adjacent Cl atom.

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Structure of Aqua{[3,3'-(1,3-propanedioldinitrilo)bis(2-butanone oximato)]-N,N',N'',N'''}(2,2,2-trifluoroethyl)cobalt(III) Hexafluorophosphate

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Abstract. $[\text{Co}(\text{C}_{11}\text{H}_{19}\text{N}_4\text{O}_2)(\text{C}_2\text{H}_2\text{F}_3)(\text{H}_2\text{O})]\text{PF}_6$, $M_r = 544.2$, monoclinic, $P2_1/c$, $a = 6.906$ (3), $b = 14.545$ (3), $c = 21.236$ (9) Å, $\beta = 99.05$ (2)°, $V = 2106$ (1) Å³, $Z = 4$, $D_x = 1.72$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 9.8$ cm⁻¹, $F(000) = 1104$, $T = 293$ K, $R = 0.046$ for 3583 unique reflections with $I > 3\sigma(I)$. The axial fragment of the distorted octahedral polyhedron of Co is characterized by Co—C and Co—O distances of 2.007 (4) and 2.066 (3) Å, respectively. The geometry of the CH_2CF_3 group departs significantly from that expected for sp^3 hybridization at the C atom bearing the F substituents (*cis* steric influence).

Experimental. The complex was prepared as previously reported (Parker, Bresciani-Pahor,

Zangrando, Randaccio & Marzilli, 1985). Red-brown crystal with approximate dimensions 0.20 × 0.20 × 0.60 mm, Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, lattice constants by least squares refinement of setting angles of 25 reflections with $14 \leq \theta \leq 22^\circ$. Measurements carried out at room temperature, three standard reflections measured every 4000 s showed no significant variation in intensity, ω -2 θ scan; scan angle $(0.70 + 0.35\tan\theta)^\circ$. 5403 reflections measured in the range $3 \leq \theta \leq 28^\circ$, with $-9 \leq h \leq 9$, $0 \leq k \leq 19$, $0 \leq l \leq 27$. The intensities of 3583 unique reflections with $I > 3\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption based on empirical ψ scans ($T_{\text{max,min}} = 99.7, 86.6\%$), and used for structure determination. The structure was solved by conventional Patterson and Fourier methods and refined through full-matrix least-squares calculations with $\sum w(|F_o| - |F_c|)^2$ minimized. 316 parameters refined, anisotropic temperature factors for all

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Table 1. Final fractional coordinates and equivalent isotropic thermal parameters (\AA^2)

$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i a_j$. Atoms F6–F9 and F6*–F9* have half occupancy (see text).

	x	y	z	B_{eq}
Co	0.18196 (7)	0.76086 (3)	0.40027 (2)	2.350 (8)
F1	0.4486 (5)	0.5260 (2)	0.3345 (2)	6.15 (7)
F2	0.4393 (6)	0.5593 (2)	0.4313 (2)	8.00 (9)
F3	0.1762 (5)	0.5313 (2)	0.3682 (2)	7.95 (9)
O1	-0.1868 (4)	0.7061 (2)	0.3328 (2)	4.56 (7)
O2	-0.0950 (4)	0.6357 (2)	0.4380 (2)	4.38 (7)
O3	0.0283 (4)	0.8588 (2)	0.4427 (1)	3.36 (6)
N1	-0.0302 (4)	0.7586 (2)	0.3321 (2)	3.18 (6)
N2	0.0817 (5)	0.6742 (2)	0.4528 (2)	3.06 (6)
N3	0.3912 (4)	0.7635 (2)	0.4712 (2)	3.05 (6)
N4	0.2738 (5)	0.8530 (2)	0.3476 (2)	3.10 (6)
C1	-0.1824 (8)	0.8251 (4)	0.2302 (2)	5.5 (1)
C2	-0.0219 (6)	0.8152 (3)	0.2855 (2)	3.67 (9)
C3	0.1607 (6)	0.8688 (3)	0.2949 (2)	3.52 (8)
C4	0.2027 (9)	0.9351 (4)	0.2451 (2)	5.9 (1)
C5	0.4652 (6)	0.8994 (3)	0.3649 (2)	4.4 (1)
C6	0.5185 (6)	0.9095 (3)	0.4365 (2)	4.12 (9)
C7	0.5653 (6)	0.8211 (3)	0.4723 (2)	4.3 (1)
C8	0.5130 (8)	0.6962 (4)	0.5769 (3)	5.8 (1)
C9	0.3670 (6)	0.7094 (3)	0.5174 (2)	3.49 (8)
C10	0.1830 (6)	0.6583 (3)	0.5083 (2)	3.50 (8)
C11	0.1146 (9)	0.5972 (3)	0.5566 (2)	5.4 (1)
C12	0.3301 (6)	0.6710 (3)	0.3541 (2)	3.43 (8)
C13	0.3460 (7)	0.5746 (3)	0.3724 (2)	4.3 (1)
P	0.9262 (2)	0.10923 (9)	0.37065 (6)	4.54 (3)
F4	0.8640 (6)	0.0128 (3)	0.3416 (2)	9.7 (1)
F5	1.0015 (7)	0.1980 (3)	0.4092 (2)	9.6 (1)
F6	0.715 (1)	0.1121 (6)	0.3872 (5)	10.4 (2)
F7	1.138 (1)	0.1023 (6)	0.3580 (4)	8.9 (2)
F8	0.985 (2)	0.0533 (6)	0.4365 (4)	12.1 (3)
F9	0.855 (1)	0.1668 (7)	0.3141 (3)	11.4 (2)
F6*	0.790 (1)	0.1044 (5)	0.4217 (3)	7.6 (2)
F7*	1.042 (1)	0.1208 (6)	0.3147 (4)	12.6 (2)
F8*	1.084 (1)	0.0509 (6)	0.4138 (6)	12.5 (3)
F9*	0.768 (2)	0.165 (1)	0.3317 (5)	17.8 (4)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

Co—O3	2.066 (3)	Co—N4	1.916 (3)
Co—N1	1.891 (3)	Co—C12	2.007 (4)
Co—N2	1.886 (3)	C12—C13	1.453 (6)
Co—N3	1.916 (3)		
O3—Co—N1	87.5 (1)	N1—Co—C12	90.5 (2)
O3—Co—N2	86.7 (1)	N2—Co—N3	81.4 (1)
O3—Co—N3	91.1 (1)	N2—Co—N4	177.2 (1)
O3—Co—N4	90.7 (1)	N2—Co—C12	96.7 (2)
O3—Co—C12	176.3 (1)	N3—Co—N4	99.6 (1)
N1—Co—N2	97.4 (1)	N3—Co—C12	91.0 (1)
N1—Co—N3	178.2 (1)	N4—Co—C12	86.0 (2)
N1—Co—N4	81.6 (1)	Co—C12—C13	121.4 (3)

non-H atoms, H atoms placed in calculated positions (C—H 0.95 \AA) with isotropic B values of 1.3 times the value of B_{eq} of the atoms to which they are attached, except the oxime proton which was located by means of a ΔF map. $R = 0.046$, $wR = 0.050$, $w = 1/[\sigma(F_o)^2 + (0.01F_o)^2 + 4.0]$; maximum $\Delta/\sigma = 0.58$. The final difference map had a maximum at $0.51 \text{ e } \text{\AA}^{-3}$. The PF_6^- counter ion was found to be disordered with splitting of F6–F9 atoms in two parts with an occupancy factor of 0.5 for each, and rotated by $\sim 40^\circ$ about the F4—P—F5 direction. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). No correction for secondary extinction was applied. Calculations were carried out on a MicroVAX 2000

computer using the Enraf–Nonius CAD-4 system of programs (Frenz, 1981).

Final fractional coordinates and equivalent isotropic thermal parameters of non-H atoms are reported in Table 1* and relevant bond lengths and angles in Table 2. Fig. 1 shows a drawing of the cation with the atom-numbering scheme (*ORTEP*; Johnson, 1965).

Related literature. Organocobalt complexes having the tetradentate equatorial ligand [3,3'-(1,3-propanediyl)dinitrilo]bis(2-butanone oximate), (DO)-(DOH)pn, were prepared some years ago (Costa, Mestroni & de Savognani, 1969) as a new model for coenzyme B_{12} . Several $[L\{\text{Co}(\text{DO})(\text{DOH})\text{pn}\}R]\text{PF}_6$ complexes (where L is a neutral ligand and R a mononegative alkyl group) have been characterized by X-ray analyses (Randaccio, Bresciani-Pahor Zangrando & Marzilli, 1989).

The axial Co—O bond length of 2.066 (3) \AA , in the present compound, is in agreement with the suggestion that, in $[L\{\text{Co}(\text{DO})(\text{DOH})\text{pn}\}R]^+$ and in the analogous $L\text{Co}(\text{DH})_2R$ (where DH is a dimethylglyoximate anion), the Co—L bond length increases with the increasing σ -donating ability (electronic *trans* influence) of the alkyl group (Randaccio *et al.*, 1989). In fact this distance is the shortest found in the series of aqua derivatives $\text{H}_2\text{O}[\text{Co}(\text{DO})(\text{DOH})\text{pn}]R^+$, with $R = \text{Me}$ (Marzilli, Bresciani-Pahor, Randaccio, Zangrando, Finke & Myers, 1985), Et, CH_2Ph and $i\text{Pr}$ (Zangrando, Parker, Bresciani-Pahor, Thomas, Marzilli & Randaccio,

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional parameters for H atoms, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54860 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0283]

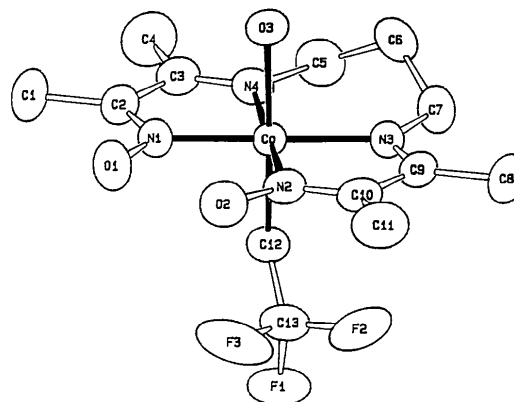


Fig. 1. *ORTEP* (Johnson, 1965) drawing and atom-numbering scheme of the cation $[\text{H}_2\text{O}\{\text{Co}(\text{DO})(\text{DOH})\text{pn}\}\text{CH}_2\text{CF}_3]^+$ (displacement ellipsoids drawn at the 50% probability level).

1987) where the corresponding Co—O bond distances, of 2.103 (3), 2.109 (2), 2.099 (1) and 2.133 (3) Å, respectively, follow the trend of increasing wavelengths of the absorption bands in the visible spectra (Zangrando *et al.*, 1987).

The observed geometrical distortions of CH₂CF₃ [F—C—F angles in the range 104.5 (4)–106.0 (6)°] and the opening of the Co—C12—C13 bond angle [121.4 (3)°] may be rationalized, as for cobaloxime derivatives (Bresciani-Pahor, Calligaris, Randaccio, Marzilli, Summers, Toscano, Grossman & Liotta, 1985), in terms of changes of *s* and *p* character in the hybrid orbitals of C12 and C13.

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Structure of 2,2-Bis(chloromercurio)propionic Acid Dimethyl Sulfoxide Solvate

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Abstract. μ -[(1-Carboxy)-1,1-ethanediy]-bis(chloromercury)-dimethyl sulfoxide (1/1), [Hg₂(C₃H₄O₂-Cl₂)₂.C₂H₆OS], $M_r = 622.3$, monoclinic, $P2_1/c$, $a = 10.249$ (9), $b = 11.184$ (2), $c = 11.377$ (7) Å, $\beta = 110.68$ (2)°, $V = 1220$ (1) Å³, $Z = 4$, $D_x = 3.388$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 257.2$ cm⁻¹, $F(000) = 1096$, room temperature, $R = 0.037$ for 1394 unique reflections [$I > 5\sigma(I)$]. The molecules of 2,2-bis(chloromercurio)propionic acid are connected to dimethyl sulfoxide molecules by O—H...O hydrogen bonds of 2.66 (2) Å. One Hg atom is approached by two O atoms [Hg...O, 2.92 (2) and 2.90 (1) Å] and the other by a Cl atom [Hg...Cl, 3.133 (6) Å] at distances shorter than the sum of the van der Waals radii.

Experimental. Dimercurated propionic acid is obtained as a minor product (up to 20%) of direct mercuration of propionic acid with mercuric propionate. Colourless crystals of its chloromercurio derivative, CH₃C(HgCl)₂COOH, crystallize from the dimethyl sulfoxide solution as a 1/1 solvate (Popović, 1988). Data were collected on a Philips PW1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Intensities were measured using

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the θ - 2θ scan mode, scan width of 1.8° and scan speed of 0.06° s⁻¹. Unit-cell parameters were determined by the least-squares procedure from 16 reflections, 11.7 < θ < 12.7°. Three standard reflections (32 $\bar{3}$, 263, 540) measured every 2 h showed a continuous drop in intensity amounting to 30% at the end of data collection. The crystal darkened under the influence of X-rays but after exposure it slowly (about one month) regained transparency. 2080 reflections were measured within the range $2 \leq \theta \leq 30^\circ$ ($0 \leq h \leq 13$, $0 \leq k \leq 15$, $-15 \leq l \leq 14$), 1908 unique ($R_{\text{int}} = 0.036$), 1394 with $I > 5\sigma(I)$. Intensities were corrected for decay, Lorentz, polarization and absorption effects (maximum, minimum transmission coefficients 0.551, 0.242) (Harkema, 1979). Crystal dimensions (mm from centroid): (100, $\bar{1}00$) 0.025, (010, $0\bar{1}0$) 0.061, (001) 0.140, ($00\bar{1}$) 0.152, ($\bar{1}51$, $\bar{1}5\bar{1}$) 0.070. Positions of the two Hg atoms were located by the Patterson method, other non-H-atom positions from a difference Fourier map. The structure was refined by the full-matrix least-squares procedure based on F with anisotropic temperature factors for all non-H atoms except the methyl carbon C5 of the DMSO solvate molecule. All atoms of the solvate molecule except O3, which is involved in