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A BF₂-Bridged Cobalt Dimethylglyoxime Complex

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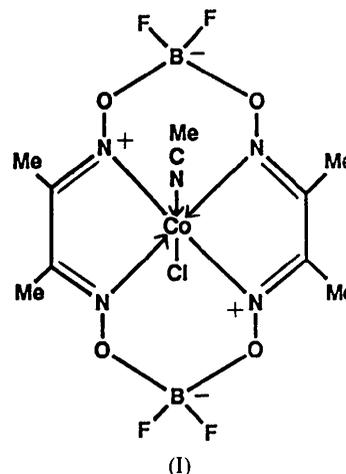
Abstract. (Acetonitrile)chloro(2,2,9,9-tetrafluoro-5,6,12,13-tetramethyl-1,3,8,10-tetraoxa-4,7,11,14-tetraaza-1,8-diboracyclotetradeca-4,6,11,13-tetraene- κ^4N)cobalt(III), [CoCl(C₂H₃N)(C₈H₁₂B₂F₄N₄O₄)], $M_r = 461.3$, orthorhombic, $P2_12_12_1$, $a = 9.912$ (1), $b = 13.485$ (1), $c = 13.534$ (1) Å, $V = 1809$ Å³, $Z = 4$, $D_x = 1.69$, D_m (floatation) = 1.67 g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, μ (Mo $K\alpha$) = 11.5 cm⁻¹, $F = 928$, $T = 292$ K, $R = 0.031$ for 2062 unique observed [$I/\sigma(I) \geq 3.0$] reflections. The molecule contains octahedrally coordinated Co^{III} with axial Cl and MeCN; Co—N(dimethylglyoxime) 1.885 (3), Co—N(MeCN) 1.898 (3), Co—Cl 2.202 (1) Å. The BF₂ groups are displaced from the equatorial coordination plane, alternately up and down.

Introduction. The use of substituted cobalt glyoxime complexes as dioxygen carriers is handicapped by their rapid autoxidation. It has been shown (Lance, Goldsby & Busch, 1991) that the replacement of the bridging H⁺ atoms in the O···H···O units by BF₂⁺ groups leads to a dramatic reduction in the decomposition rate. We now report the X-ray structure of the parent dimethylglyoxime complex containing BF₂⁺ groups (I).

Experimental. The complex was prepared as described in Lance *et al.* (1991). Red platy crystals were obtained from acetonitrile/ether. Data were

collected with a Nicolet P2₁ four-circle diffractometer in the ω - 2θ mode. Maximum 2θ was 55° with scan range $\pm 1.0^\circ$ (2θ) around the $K\alpha_1$ - $K\alpha_2$ angles, scan speed 2–24° min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.5 of the scan time. hkl ranges were: 0/12, 0/17, 0/17.

Six standard reflections were monitored every 100 reflections, and showed only random fluctuations during data collection. Unit-cell dimensions and standard deviations were obtained by a least-squares fit of 15 reflections ($15 < 2\theta < 25^\circ$). Reflections were processed to give 2321 unique reflections, of which 2062 were considered observed [$I/\sigma(I) \geq 3.0$]. These



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Table 1. Atomic coordinates for Co(Me₂GlyoxBF₂)₂(MeCN)Cl
$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co	0.33879 (5)	0.23381 (4)	0.24394 (3)	1.91 (2)
Cl	0.32499 (13)	0.09404 (8)	0.32748 (8)	3.39 (5)
N1	0.5282 (3)	0.2417 (2)	0.2569 (3)	2.42 (12)
N2	0.1498 (3)	0.2283 (2)	0.2294 (2)	2.34 (12)
N3	0.3465 (4)	0.3032 (2)	0.3646 (2)	2.33 (13)
N4	0.3328 (4)	0.1654 (3)	0.1228 (2)	2.41 (13)
N5	0.3450 (4)	0.3558 (2)	0.1741 (2)	2.41 (13)
O1	0.2345 (3)	0.3230 (3)	0.4192 (2)	3.07 (13)
O2	0.0621 (3)	0.2598 (3)	0.2999 (2)	3.06 (13)
O3	0.4427 (3)	0.1479 (3)	0.0666 (2)	3.23 (13)
O4	0.6146 (3)	0.2153 (3)	0.1841 (2)	3.40 (14)
F1	0.6666 (3)	0.1288 (3)	0.0454 (2)	5.49 (16)
F2	0.5682 (3)	0.0461 (2)	0.1717 (2)	4.94 (15)
F3	0.1269 (3)	0.4268 (2)	0.3041 (2)	4.23 (13)
F4	0.0109 (3)	0.3567 (3)	0.4317 (2)	4.84 (14)
B1	0.5743 (5)	0.1313 (5)	0.1189 (4)	3.46 (24)
B2	0.1088 (5)	0.3445 (5)	0.3609 (4)	3.31 (23)
C1	0.1887 (5)	0.0991 (4)	-0.0097 (3)	4.06 (23)
C2	0.2140 (5)	0.1483 (4)	0.0874 (3)	2.87 (18)
C3	0.1052 (4)	0.1832 (3)	0.1529 (3)	2.52 (17)
C4	-0.0408 (5)	0.1670 (4)	0.1310 (4)	3.96 (23)
C5	0.4908 (5)	0.3749 (4)	0.4945 (3)	3.53 (20)
C6	0.4632 (4)	0.3244 (3)	0.3978 (3)	2.36 (17)
C7	0.5718 (4)	0.2923 (3)	0.3309 (3)	2.59 (17)
C8	0.7164 (4)	0.3202 (4)	0.3459 (4)	4.08 (24)
C9	0.3394 (5)	0.4332 (3)	0.1429 (3)	2.69 (16)
C10	0.3292 (6)	0.5321 (3)	0.1036 (4)	4.36 (23)

Table 2. Bond lengths (Å) and angles (°) for Co(Me₂GlyoxBF₂)₂(MeCN)Cl

Cl—Co	2.202 (1)	B2—O1	1.504 (6)
N1—Co	1.889 (3)	B2—O2	1.484 (6)
N2—Co	1.885 (3)	B1—O3	1.501 (6)
N3—Co	1.884 (3)	B1—O4	1.491 (6)
N4—Co	1.882 (3)	B1—F1	1.352 (6)
N5—Co	1.898 (3)	B1—F2	1.354 (7)
O4—N1	1.353 (4)	B2—F3	1.362 (7)
C7—N1	1.286 (5)	B2—F4	1.374 (6)
O2—N2	1.358 (4)	C2—C1	1.494 (6)
C3—N2	1.279 (5)	C3—C2	1.473 (6)
O1—N3	1.359 (4)	C4—C3	1.494 (6)
C6—N3	1.274 (5)	C6—C5	1.501 (5)
O3—N4	1.349 (4)	C7—C6	1.471 (6)
C2—N4	1.293 (6)	C8—C7	1.496 (6)
C9—N5	1.127 (5)	C10—C9	1.439 (6)
N1—Co—Cl	93.6 (1)	B2—O1—N3	115.4 (3)
N2—Co—Cl	87.6 (1)	B2—O2—N2	115.6 (3)
N2—Co—N1	178.8 (1)	B1—O3—N4	117.5 (3)
N3—Co—Cl	89.0 (1)	B1—O4—N1	117.5 (3)
N3—Co—N1	81.4 (1)	O4—B1—O3	113.5 (4)
N3—Co—N2	98.6 (1)	F1—B1—O3	104.2 (4)
N4—Co—Cl	91.5 (1)	F1—B1—O4	105.9 (4)
N4—Co—N1	98.0 (1)	F2—B1—O3	109.6 (6)
N4—Co—N2	81.9 (1)	F2—B1—O4	110.2 (4)
N4—Co—N3	179.3 (2)	F2—B1—F1	113.4 (4)
N5—Co—Cl	178.0 (1)	O2—B2—O1	113.7 (7)
N5—Co—N1	88.0 (2)	F3—B2—O1	110.1 (4)
N5—Co—N2	90.8 (1)	F3—B2—O2	110.8 (4)
N5—Co—N3	90.0 (1)	F4—B2—O1	104.0 (4)
N5—Co—N4	89.5 (1)	F4—B2—O2	105.1 (4)
O4—N1—Co	123.1 (2)	F4—B2—F3	112.9 (4)
C7—N1—Co	115.9 (3)	C1—C2—N4	123.9 (4)
C7—N1—O4	119.6 (3)	C3—C2—N4	112.8 (4)
O2—N2—Co	123.4 (2)	C3—C2—C1	123.3 (4)
C3—N2—Co	116.5 (3)	C2—C3—N2	112.7 (4)
C3—N2—O2	119.7 (3)	C4—C3—N2	124.4 (4)
O1—N3—Co	122.4 (2)	C4—C3—C2	122.9 (4)
C6—N3—Co	117.0 (3)	C5—C6—N3	125.1 (4)
C6—N3—O1	120.4 (3)	C7—C6—N3	112.5 (3)
O3—N4—Co	123.5 (3)	C7—C6—C5	122.4 (4)
C2—N4—Co	116.0 (3)	C6—C7—N1	112.9 (3)
C2—N4—O3	119.7 (3)	C8—C7—N1	124.1 (4)
C9—N5—Co	170.9 (3)	C8—C7—C6	122.9 (4)
C10—C9—N5	178.8 (5)		

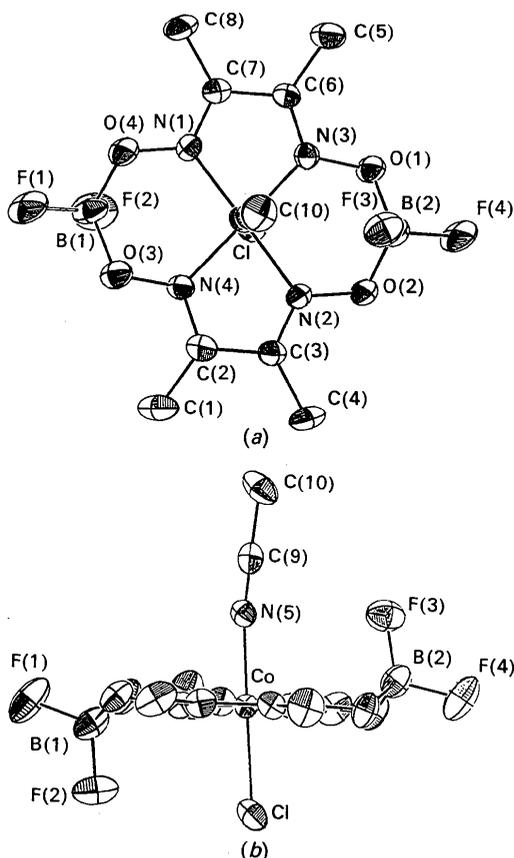


Fig. 1. (a) Face-on and (b) side-on views of the molecule, with 50% thermal ellipsoids.

were corrected for Lorentz, polarization and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.86 and 0.91. Crystal dimensions were $0.18 \times 0.31 \times 0.45$ mm. Systematic reflection conditions: $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$ indicate space group $P2_12_12_1$. The Co atom was located by Patterson methods and the light atoms were then found on successive Fourier syntheses. Anisotropic temperature factors were used for all non-H atoms. Methyl atoms were given fixed isotropic temperature factors, $U = 0.07 \text{ \AA}^2$, and were treated as rigid CH₃ units, with their initial orientation taken from the strongest H-atom peaks on a difference Fourier synthesis. The absolute structure of the individual crystal chosen was not determined. Final refinement was on F by least-squares methods refining parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height $\pm 0.4 e \text{ \AA}^{-3}$. A weighting scheme of the form $w = 1/[\sigma^2(F)]$ was used and shown to be satisfactory

by a weight analysis. Final $R = 0.031$, $wR = 0.036$. Maximum shift/e.s.d. in final cycle 0.03. Computing with *SHELX76* (Sheldrick, 1976). Scattering factors in the analytical form and anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic coordinates are given in Table 1, and bond lengths and angles in Table 2.* Views of the molecule are shown in Fig. 1.

Discussion. The complex is seen to contain octahedrally coordinated Co^{III} , with axial Cl^- and MeCN ligands. Apart from these ligands, the molecule is planar, with the BF_2 groups disposed above and below the plane. For application of similar molecules in oxygen binding, the planarity is advantageous in that oxidizable organic fragments are removed from the oxygen coordination site; however, it has been found that protection, both of this coordination site and of the *trans*-position occupied by the axial base, is important for stability in oxygen adducts.

A number of Co^{III} glyoxime complexes have previously been examined structurally, most of which

* Lists of anisotropic thermal parameters, H-atom coordinates and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53911 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

contain neutral axial donors (NH_3 , pyridine, pyrrolidine, etc.). For comparison with the present structure, the *trans*-azido pyridine complex is the most appropriate (Clearfield, Gopal, Kline, Sipski & Urban, 1978; Ponnuswamy & Trotter, 1983), as it contains one anionic and one neutral ligand. The two molecules have closely similar dimensions, though the Co—N distance is slightly shorter in the present example [mean 1.885 (3) Å, compared to 1.903 (4) Å]; the distance to N of the acetonitrile ligand is hardly longer [1.898 (3) Å]. The Co—N(pyridine) distance in the pyridine complex is significantly longer [1.973 (5) Å], perhaps reflecting the *trans*-influence of the N_3 ligand. The displacement of the B atoms from the coordination plane has allowed the non-bonded O...O distances [2.500 (4) Å] to remain almost identical to the O—H...O distances in the *trans*-azido pyridine complex [2.483 (6); 2.500 (6) Å].

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Di(hexahydropyridazido)thiophosphorsäure-*O*-phenylester als zweizähliger *S,N*-Ligand in einem dimeren Cadmium(II)-Komplex

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Abstract. Di- μ -chloro-bis{chloro[*O*-phenyl di(hexahydropyridazido)thiophosphate-*S,N*]cadmium(II)}, $[\text{Cd}_2\text{Cl}_4(\text{C}_{14}\text{H}_{23}\text{N}_4\text{OPS})_2]$, $M_r = 1019.42$, triclinic, $P\bar{1}$, $a = 9.150$ (3), $b = 10.356$ (4), $c = 11.506$ (6) Å, $\alpha = 87.24$ (3), $\beta = 86.12$ (4), $\gamma = 67.94$ (3) $^\circ$, $V = 1008$ (2) Å 3 , $Z = 1$, $D_x = 1.679$ Mg m $^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 15.36$ mm $^{-1}$, $F(000) = 512$, $T = 293$ K, $R = 0.037$ for 3343 unique contributing reflections. The complex has been prepared in an ethanolic solution by the reaction of bis(hexahydropyridazido)thiophosphoric acid *O*-phenyl ester and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ in a 1:1 molar ratio. The asymmetric unit is formed by one half of the centrosymmetric dimer.

The bidentate ligands coordinate through S and one of the terminal pyridazido N atoms. Cd is at the centre of a tetragonal pyramid formed by N, S, one terminal Cl and two Cl bridges to the other Cd. Bond distances: Cd—S 2.661 (1), Cd—N 2.397 (5), Cd—Cl (terminal) 2.387 (2), Cd—Cl (bridge) 2.565 (2) and 2.644 (2), P—S 1.960 (2), P—N 1.650 (5) and 1.643 (4), N—N 1.437 (6) and 1.433 (6) Å.

Einleitung. Dihydrzidothiophosphorsäure-Derivate sollten potentiell als dreizählige Chelatliganden fungieren können (Engelhardt & Scherer, 1976;