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(cis-1,2-Dichlorovinyl)bis(dimethylglyoximato-N,N')(pyridine-N)cobalt(III) Chloroform Solvate, [Co(dmgH)2(py)-(CCl=CHCl)].CHCl3

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Abstract

In the title complex, [Co(C2HCl2)(C4H7N2O2)2(C5H5-N)].CHCl3, the Co atom exhibits a distorted octahedral coordination with the two dimethylglyoximate (dmgH)

ligands in equatorial positions [Co—N 1.891 (2)–1.897 (3) Å]. The axial positions are occupied by the pyridine (py) and cis-1,2-dichlorovinyl ligands [N—Co—C 179.0 (1)°], which are nearly coplanar. The Co—Cl distance is 1.958 (3) Å. The Co—N_{py} bond length of 2.028 (2) Å indicates a lower *trans* influence for the dichlorovinyl ligand compared with alkyl ligands.

Comment

Organocobaloximes, [Co(dmgH)2(L)R] (dmgH2 is dimethylglyoxime, L is an axial base and R is a σ-organo ligand), are not only model complexes for vitamin B$_{12}$ coenzymes (Schrauzer, 1976, 1977; Randaccio, Bresciani-Pahor, Zangrando & Marzilli, 1989), but have also been widely used for investigations of the reactivity of σ-Co—C bonds and the *trans* influence of σ-organo ligands (Pattenden, 1988; Sweany, 1995). We report here the molecular structure of the cis-1,2-dichlorovinyl (R = CCl=CHCl) complex, (1), with pyridine as the axial base L.

(1)
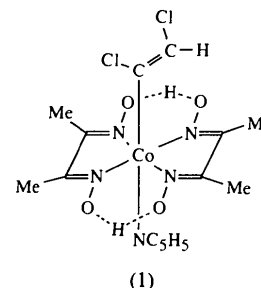
The crystal structure of (1) consists of discrete molecules of the complex [Co(dmgH)2(py)(CCl=CHCl)] and chloroform solvate molecules. The Co atom exhibits distorted octahedral coordination, with four oxime N-atom donors in equatorial positions. The two dimethylglyoximato ligands are connected by two strong intramolecular hydrogen bonds [O2···O3 2.501 (4) and O1···O4 2.490 (3) Å]. The four Co—N bond distances range from 1.891 (2) to 1.897 (3) Å. These values do not differ significantly from those of other organocobaloximes (Bresciani-Pahor *et al.*, 1985).

The four oxime N atoms are coplanar to within 0.007 Å. The Co atom is displaced by 0.010 (1) Å (*d*) from the mean plane towards the pyridine ligand. The two nearly planar dmgH ligands (r.m.s. deviations of 0.023 and 0.024 Å for the C7–C10, N3, N4, O3, O4 and C3–C6, N1, N2, O1, O2 planes, respectively) subtend an interplanar angle, α, of 1.3 (1)°. The values of *d* and α are smaller than in the vinyl complex [Co(dmgH)2(py)(CH=CH2)] [(2); *d* = 0.04 Å and α = 6.3°; Bresciani-Pahor, Calligaris & Randaccio, 1980] and in many other organocobaloximes (Bresciani-Pahor *et al.*, 1985; Randaccio *et al.*, 1989).

The N5—Co—Cl unit is linear [N5—Co—Cl 179.0 (1)°]. The dichlorovinyl and pyridine ligands are

nearly coplanar, with an interplanar angle of 2.6 (1)°. The plane of the axial ligands is essentially perpendicular to the equatorial plane, bisecting the angles N1— Co—N4 and N2—Co—N3.

The bond lengths Co—C1 1.958 (3) and Co—N5 2.028 (2) Å are slightly shorter than in complex (2) [1.966 (6) and 2.073 (3) Å; Bresciani-Pahor et al., 1985] and [Co(dmgH)₂(py){CCl=C(C₆H₄Cl)₂}] [(3); 1.97 (1) and 2.05 Å; Stotter, Sheldrick & Taylor, 1975]. The Co—N5 distance of 2.028 (2) Å implies a smaller trans influence for the σ-vinyl ligand CCl=CHCl compared with alkyl ligands [Me, CH₂CMe₃, Et, CHMe₂; Co—N 2.068 (3)–2.099 (2) Å] (Bresciani-Pahor et al., 1985).

The C=C distance [1.324 (7) Å] does not differ significantly from the corresponding value in complex (3) [1.37 (2) Å; Stotter et al., 1975]. The angle Co— C1—C2 [123.3 (3)°] is not far from the ideal value of 120°. In contrast, this angle is 133.0 (1)° in complex (3) (Stotter et al., 1975). Furthermore, Co—CH₂—C angles of up to 130° were found in alkylcobaloximes, far from the ideal value of 109°; this was attributed to steric the interaction of bulky organo groups with the equatorial (dmgH)₂ moiety (Bresciani-Pahor et al., 1985; Randaccio et al., 1989).
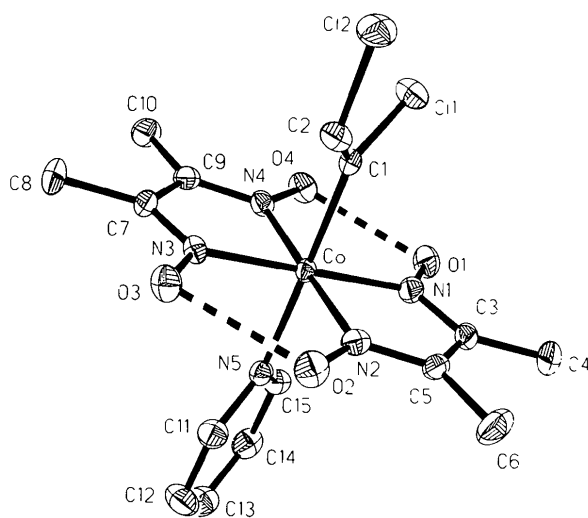

Fig. 1. Perspective drawing of (1). Ellipsoids represent 50% probability levels. H atoms and the solvent have been omitted for clarity. Intramolecular hydrogen bonds are indicated as dashed bonds. The minor orientation of the dichlorovinyl ligand is not shown.

Experimental

The method used for the preparation of (1) is analogous to that used for the preparation of other organocobaloximes (Bulkowski, Cutler, Dolphin & Silverman, 1980; Kemmitt & Russell, 1982; Sweany, 1995). [Co(dmgH)₂(py)]₂ (0.98 g, 1.33 mmol) reacts with Cl₂C=CHCl (0.73 g, 5.56 mmol) in methanol in the presence of NaOH (0.13 g, 3.25 mmol) to give crystals of [Co(dmgH)₂(py)(CCl=CHCl)], which were filtered off, washed with methanol and heptane and

dried in vacuo (yield 0.44 g, 70%). Recrystallization from chloroform/heptane afforded crystals of [Co(dmgH)₂(py)-(CCl=CHCl)].CHCl₃, (1), suitable for X-ray analysis.

Crystal data

[Co(C₂HCl₂)(C₄H₇N₂O₂)₂-(C₅H₅N)].CHCl₃	Mo Kα radiation
M_r = 583.56	λ = 0.71073 Å
Triclinic	Cell parameters from 53
P1	reflections
a = 8.1522 (12) Å	θ = 4.6–12.4°
b = 8.8910 (8) Å	μ = 1.361 mm⁻¹
c = 8.9605 (8) Å	T = 173 (2) K
α = 82.552 (8)°	Tablet
β = 89.561 (4)°	0.70 × 0.40 × 0.20 mm
γ = 63.421 (4)°	Brown
V = 575.00 (11) Å³	
Z = 1	
D_x = 1.685 Mg m⁻³	
D_m not measured	

Data collection

Siemens P4 diffractometer	R_int = 0.014
ω scans	θ_max = 27.5°
Absorption correction:	h = −9 → 9
ψ scans (XEMP; Nicolet, 1987)	k = −10 → 11
	l = −11 → 11
T_min = 0.765, T_max = 0.966	3 standard reflections
	monitored every 247
7363 measured reflections	reflections
4752 independent reflections	intensity decay: none
4604 observed reflections [I > 2σ(I)]	

Refinement

Refinement on F²	Δρ_max = 0.578 e Å⁻³
R(F) = 0.0291	Δρ_min = −0.707 e Å⁻³
wR(F²) = 0.0752	Extinction correction: none
S = 1.053	Atomic scattering factors
4752 reflections	from International Tables
301 parameters	for Crystallography (1992,
w = 1/[σ²(F_o²) + (0.0417P)² + 0.3884P]	Vol. C, Tables 4.2.6.8 and 6.1.1.4)
where P = (F_o² + 2F_c²)/3	Absolute configuration:
(Δ/σ)_max = 0.018	Flack (1983)
	Flack parameter = 0.031 (11)

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	0.33595 (4)	0.69406 (4)	0.49950 (3)	0.01353 (8)
C1	0.2917 (4)	0.5815 (3)	0.3414 (3)	0.0157 (6)
Cl1†	0.3393 (2)	0.36885 (15)	0.38221 (11)	0.0268 (2)
Cl2†	0.18816 (13)	0.57030 (12)	0.05584 (9)	0.0285 (2)
C2†	0.2306 (8)	0.6582 (8)	0.2023 (7)	0.0244 (11)
Cl1'‡	0.2069 (15)	0.6933 (12)	0.1712 (10)	0.030 (2)
Cl2'‡	0.2792 (10)	0.3093 (8)	0.2448 (8)	0.038 (2)
C2'‡	0.323 (5)	0.424 (3)	0.373 (3)	0.029 (9)
C3	0.7068 (4)	0.5019 (4)	0.4844 (3)	0.0225 (6)
C4	0.8985 (5)	0.3635 (5)	0.5154 (5)	0.0332 (8)
C5	0.6547 (4)	0.6529 (4)	0.3730 (3)	0.0216 (6)
C6	0.7911 (5)	0.6800 (5)	0.2722 (4)	0.0333 (8)

C7	−0.0335 (4)	0.8849 (4)	0.5123 (3)	0.0187 (6)
C8	−0.2258 (5)	1.0222 (4)	0.4804 (4)	0.0285 (7)
C9	0.0131 (4)	0.7332 (4)	0.6234 (3)	0.0185 (6)
C10	−0.1218 (5)	0.7060 (4)	0.7201 (4)	0.0268 (7)
C11	0.3466 (5)	0.9785 (4)	0.6345 (3)	0.0233 (6)
C12	0.3695 (5)	1.0634 (4)	0.7454 (4)	0.0328 (7)
C13	0.4261 (5)	0.9781 (4)	0.8904 (3)	0.0321 (6)
C14	0.4584 (5)	0.8120 (4)	0.9211 (4)	0.0279 (7)
C15	0.4344 (5)	0.7315 (4)	0.8051 (3)	0.0210 (6)
O1	0.5856 (3)	0.3766 (3)	0.6637 (2)	0.0249 (5)
O2	0.4175 (4)	0.9062 (3)	0.2729 (3)	0.0257 (5)
O3	0.0889 (3)	1.0142 (3)	0.3376 (2)	0.0240 (5)
O4	0.2572 (3)	0.4801 (3)	0.7231 (2)	0.0235 (5)
N1	0.5662 (4)	0.5030 (3)	0.5548 (3)	0.0192 (5)
N2	0.4838 (4)	0.7595 (3)	0.3689 (3)	0.0180 (5)
N3	0.1066 (3)	0.8851 (3)	0.4431 (3)	0.0162 (5)
N4	0.1883 (4)	0.6262 (3)	0.6273 (3)	0.0172 (5)
N5	0.3771 (4)	0.8136 (3)	0.6628 (3)	0.0183 (5)
Cl3	0.9307 (2)	0.02359 (14)	−0.0822 (2)	0.0732 (4)
Cl4	0.6449 (2)	0.2803 (2)	0.0662 (2)	0.0870 (5)
Cl5	0.9845 (2)	0.2992 (2)	0.0055 (2)	0.0747 (4)
C99§	0.8757 (10)	0.1678 (9)	0.0347 (8)	0.0371 (10)
C99'§	0.8311 (10)	0.2351 (9)	−0.0448 (9)	0.0371 (10)

† Site occupancy of 0.864 (2).   ‡ Site occupancy of 0.136 (2).   § Site occupancy of 0.50 (2).

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

Co—N4	1.891 (2)	C7—C9	1.468 (4)
Co—N3	1.894 (2)	C7—C8	1.494 (4)
Co—N2	1.895 (2)	C9—N4	1.312 (4)
Co—N1	1.897 (3)	C9—C10	1.479 (4)
Co—C1	1.958 (3)	C11—N5	1.362 (4)
Co—N5	2.028 (2)	C11—C12	1.384 (4)
C1—C2	1.324 (7)	C12—C13	1.385 (5)
C1—C11	1.740 (3)	C13—C14	1.369 (5)
C12—C2	1.723 (5)	C14—C15	1.397 (4)
C3—N1	1.301 (4)	C15—N5	1.356 (4)
C3—C5	1.459 (5)	O1—N1	1.341 (3)
C3—C4	1.493 (5)	O2—N2	1.349 (3)
C5—N2	1.285 (4)	O3—N3	1.343 (3)
C5—C6	1.509 (4)	O4—N4	1.343 (3)
C7—N3	1.296 (4)		
N4—Co—N3	81.70 (11)	N3—C7—C8	123.9 (3)
N4—Co—N2	178.93 (12)	C9—C7—C8	122.5 (3)
N3—Co—N2	98.47 (11)	N4—C9—C7	111.9 (3)
N4—Co—N1	98.61 (11)	N4—C9—C10	124.4 (3)
N3—Co—N1	179.65 (13)	C7—C9—C10	123.7 (3)
N2—Co—N1	81.21 (11)	N5—C11—C12	122.4 (3)
N4—Co—C1	89.63 (11)	C11—C12—C13	119.1 (3)
N3—Co—C1	89.55 (11)	C14—C13—C12	119.5 (3)
N2—Co—C1	89.32 (11)	C13—C14—C15	119.3 (3)
N1—Co—C1	90.29 (11)	N5—C15—C14	122.1 (3)
N4—Co—N5	90.00 (10)	C3—N1—O1	121.1 (3)
N3—Co—N5	89.49 (10)	C3—N1—Co	116.7 (2)
N2—Co—N5	91.06 (10)	O1—N1—Co	122.2 (2)
N1—Co—N5	90.66 (10)	C5—N2—O2	120.3 (3)
C1—Co—N5	179.01 (14)	C5—N2—Co	116.1 (2)
C2—C1—C11	117.6 (3)	O2—N2—Co	123.5 (2)
C2—C1—Co	123.3 (3)	C7—N3—O3	121.5 (3)
C11—C1—Co	119.2 (2)	C7—N3—Co	116.2 (2)
C1—C2—C12	126.7 (4)	O3—N3—Co	122.3 (2)
N1—C3—C5	111.8 (3)	C9—N4—O4	120.6 (2)
N1—C3—C4	124.0 (3)	C9—N4—Co	116.6 (2)
C5—C3—C4	124.2 (3)	O4—N4—Co	122.8 (2)
N2—C5—C3	114.1 (3)	C15—N5—C11	117.7 (3)
N2—C5—C6	123.5 (3)	C15—N5—Co	120.7 (2)
C3—C5—C6	122.4 (3)	C11—N5—Co	121.6 (2)
N3—C7—C9	113.5 (3)		

The title structure represents one of the extremely rare cases where a synthetic racemate crystallizes in space group $P1$. Nevertheless, we believe the space group assignment to be correct. The C atom of the solvent is disordered over two equally occupied sites on either side of the Cl_3 plane.

The alternative chloroform C-atom positions are involved in C—H···O hydrogen bonding, with C99···O3($1 + x$, $-1 + y$, z) 3.039 (8) and C99'···O1(x, y, $-1 + z$) 3.062 (8) Å. The organochlorine ligand is disordered over two sites (related by a *ca.* 180° rotation about the Co—C1 bond), with occupancies of 0.864 (2) and 0.136 (2); there are no significant geometric differences between the two forms. Analogous disorder was found in complex (2) (Bresciani-Pahor *et al.*, 1980). A system of restraints (244 in all) to bond lengths and angles of the disordered components (command *SAME*) and to light-atom displacement-parameter components (commands *DELU* and *SIMU*) was used to stabilize the refinement. The H atoms on O1 and O3 were refined freely, methyl groups were refined as rigid groups and all other H atoms were refined using a riding model. The positions of the oxime H atoms were taken from a difference Fourier peak search, but their refinement was unsatisfactory (poor convergence). It is possible that they may be disordered. A referee suggested that split positions be refined, but in view of the noncentrosymmetry and chloroform disorder, we do not believe such an approach would be any more successful.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Chlorobis(η⁵-methylcyclopentadienyl)-(2,3,4,5,6-pentafluorophenyl)titanium(IV)

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Abstract

The title compound, [TiCl(C₆F₅)(C₆H₇)₂], displays distorted tetrahedral geometry at the Ti atom, as is also observed in other bis(cyclopentadienyl) complexes of titanium(IV). The Cl and the Ti atoms lie in the pentafluorophenyl plane, which bisects the interplanar angle between the methylcyclopentadienyl rings.

Comment

The title compound, (I), displays distorted tetrahedral geometry at the metal centre, which is typical for bis-(cyclopentadienyl) complexes of titanium(IV) (if the cyclopentadienyl ligands are regarded as being attached through their ring centres *X1A* and *X1B*).

(I)
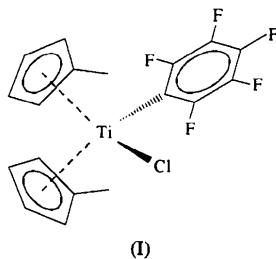
The *X1A*—Ti1—*X1B* angle of 133.5° lies in the usual range. The value of 100.41 (7)° for the Cl1—Ti1—C31 angle is much greater than the corresponding angles

of *ca* 94° found in dihalogeno complexes (Clearfield, Warner, Saldarriaga-Molina, Ropal & Bernal, 1975; Petersen & Dahl, 1975; Klouras, Nastopoulos, Demakopoulos & Leban, 1993; Jones, Kienitz & Thöne, 1994). This may be due to a repulsive interaction between the F1 and Cl1 atoms, because the Ti and Cl atoms lie in the plane of the pentafluorophenyl ring [with respective deviations of 0.016 and 0.004 (2) Å, and a mean deviation of the 11 ring atoms from the ring plane of 0.007 Å], which almost ideally bisects the interplanar angle between the methylcyclopentadienyl rings [51.08 (11)°; the interplanar angle between cyclopentadienyl (Cp) ring 1 and C₆F₅ is 25.86 (13)°, and that between Cp ring 2 and C₆F₅ is 25.23 (14)°].
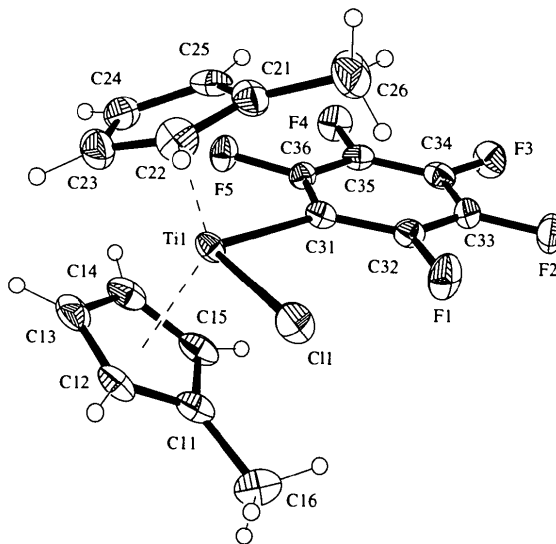

Fig. 1. The molecule of the title compound in the crystal. Ellipsoids correspond to 50% probability levels and H-atom radii are arbitrary.

The pentafluorophenyl ring shows a narrowing of the C32—C31—C36 angle to 112.3 (2)°, a well known phenomenon associated with this ligand (Jones, 1988).

The methyl groups of the Cp rings are oriented towards the space between the chlorine and pentafluorophenyl groups. The relative conformation of the methylcyclopentadienyl rings is between eclipsed and staggered (although they are not parallel), as can be seen from the C16—C11···C21—C26 torsion angle of 21.9 (3)° (ideal values: 0° for eclipsed and 36° for staggered).

The Ti—Cl bond is slightly shorter than in the dichloro complexes with cyclopentadienyl and methylcyclopentadienyl ligands [2.3340 (8) *versus* 2.359 (2)–2.367 (2), average 2.362 Å] (Clearfield *et al.*, 1975; Petersen & Dahl, 1975). Similarly, for the Ti—C31 bond, the value of 2.259 (2) Å is somewhat smaller than the Ti—Cₚₕ distance in [Cp₂TiPh₂] of 2.272 (14) Å (Kocman, Rucklidge, O'Brien & Santo, 1971), although