Monoclinic
$C2/c$
$a = 9.178 (1)$ Å
$b = 11.722 (2)$ Å
$c = 16.100 (5)$ Å
$\beta = 90.96 (2)°$
$V = 1731.9 (6)$ Å^3
$Z = 4$
$D_x = 1.510$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 7.42–17.5°$
$\mu = 1.45$ mm^{-1}
$T = 298 (3)$ K
Parallelepiped
$0.44 \times 0.32 \times 0.28$ mm
Deep violet

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{min} = 0.873$, $T_{max} = 0.999$
2663 measured reflections
2521 independent reflections

2071 observed reflections
$[I \geq 2.5(I)]$
$R_{int} = 0.019$
$\theta_{max} = 29.9°$
$h = 0 \rightarrow 12$
$k = -16 \rightarrow 16$
$l = -22 \rightarrow 22$
3 standard reflections frequency: 60 min intensity variation: $\pm0.5\%$

Refinement

Refinement on F
$R = 0.045$
$wR = 0.049$
$S = 1.78$
2071 reflections
118 parameters
Only H-atom U's refined
Unit weights applied
$(\Delta/\sigma)_{max} = 0.059$

$\Delta\rho_{max} = 0.53 (8)$ e Å^{-3}
$\Delta\rho_{min} = -0.40 (8)$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 0.21 (1) mm
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	Occupancy	x	y	z	B_{eq}
Co	1.00	1/2	0.45528 (5)	1/4	2.695 (23)
Cl(1)	1.00	0.42314 (14)	0.59486 (8)	0.16271 (7)	5.15 (5)
Cl(2)	1.00	1/2	0.09937 (10)	1/4	5.17 (7)
N(1)	1.00	0.6964 (3)	0.44819 (25)	0.19995 (21)	3.87 (13)
N(2)	1.00	0.4246 (3)	0.34068 (24)	0.16897 (19)	3.78 (12)
C(1)	1.00	0.7764 (4)	0.3512 (3)	0.2369 (3)	4.75 (20)
C(2)	1.00	0.2627 (5)	0.3440 (4)	0.1740 (3)	5.11 (20)
C(3)	0.35	0.4366 (19)	0.2540 (14)	0.0292 (8)	6.3 (7)
C(3')	0.65	0.8539 (9)	0.4486 (8)	0.0700 (5)	6.7 (4)
C(4)	1.00	0.4677 (6)	0.3464 (4)	0.0802 (3)	5.47 (22)
C(5)	1.00	0.6285 (7)	0.3475 (4)	0.0689 (3)	6.3 (3)
C(6)	1.00	0.7095 (6)	0.4483 (4)	0.1077 (3)	5.87 (22)

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

Co—Cl(1)	2.262 (1)	N(2)—C(4)	1.492 (6)
Co—N(1)	1.989 (3)	C(1)—C(2^i)	1.488 (7)
Co—N(2)	1.989 (3)	C(3)—C(4)	1.39 (1)
N(1)—C(1)	1.473 (5)	C(3')—C(6)	1.468 (9)
N(1)—C(6)	1.491 (6)	C(4)—C(5)	1.490 (8)
N(2)—C(2)	1.490 (5)	C(5)—C(6)	1.525 (8)
Cl(1)—Co—Cl(1^i)	87.34 (5)	Co—N(2)—C(2)	106.5 (3)
Cl(1)—Co—N(1)	93.1 (1)	Co—N(2)—C(4)	120.2 (3)
Cl(1)—Co—N(1^i)	90.4 (1)	C(2)—N(2)—C(4)	109.4 (3)
Cl(1)—Co—N(2)	88.83 (9)	N(1)—C(1)—C(2^i)	107.9 (3)
Cl(1)—Co—N(2^i)	176.05 (9)	N(2)—C(2)--C(1^i)	108.1 (3)
N(1)—Co—N(1^i)	175.2 (1)	N(2)—C(4)—C(3)	118.5 (7)
N(1)—Co—N(2)	90.8 (1)	N(2)—C(4)—C(5)	113.3 (4)

N(1)—Co—N(2^i)	86.0 (1)	C(3)—C(4)—C(5)	97.4 (9)
N(2)—Co—N(2^i)	95.0 (1)	C(4)—C(5)—C(6)	115.7 (4)
Co—N(1)—C(1)	108.5 (2)	N(1)—C(6)—C(5)	111.1 (4)
Co—N(1)—C(6)	119.5 (3)	N(1)—C(6)—C(3')	120.0 (6)
C(1)—N(1)—C(6)	110.8 (3)	C(3')—C(6)—C(5)	105.6 (5)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

The structure was solved by direct and Fourier methods, and refined using least-squares techniques. H atoms were located by difference Fourier synthesis and theoretical calculations. All computation was performed using the *NRCVAX* system of programs (Gabe, Le Page, White & Lee, 1987).

References

Bosnich, B., Poon, C. K. & Tobe, M. L. (1965). *Inorg. Chem.* **4**, 1102–1108.
Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1987). *Acta Cryst.* **A43**, C-294.
Hay, R. W., Bembi, R. & House, D. A. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1927–1930.
Hay, R. W. & Piplani, D. P. (1977). *J. Chem. Soc. Dalton Trans.* pp. 1956–1960.
Lindoy, L. F. (1989). In *The Chemistry of Macrocyclic Ligand Complexes*. New York: Cambridge Univ. Press.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

Dipyridiniomethane Chloropentafluoro-osmate(IV), [(C$_5$H$_5$N)$_2$CH$_2$][OsF$_5$Cl]

CLEMENS BRUHN AND WILHELM PREETZ

Institut für Anorganische Chemie, Universität Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany

Abstract

The sublattice of the mixed-ligand complex anions, [OsF$_5$Cl]$^{2-}$, of the title compound [*N,N*-methylenepyridinium chloropentafluoroosmate(IV)] is completely ordered. Due to the mutual *trans* influence in the asymmetric Cl—Os—F axis, the Os—F distance of

1.959 (4) Å is slightly longer in comparison to the average value of 1.919 Å found for the symmetric F—Os—F axes. Accordingly, the Os—Cl distance of 2.329 (2) Å is shortened in relation to that of 2.364 Å in the octahedral complex anion of $K_2[OsCl_6]$.

Comment

Mixed-ligand complex ions of the type $[MX_nY_{6-n}]^{2-}$ (M = Re, Tc, Os, Ir, Pt; $X \neq Y$ = F, Cl, Br, I; n = 0–6) have been synthesized systematically by stereospecific substitution reactions (Preetz & Erlhöfer, 1989). They are excellent examples for the study of the influence of altered local symmetry on the chemical and physical properties. The vibrational and NMR spectra, especially of compounds containing F ligands, exhibit significant splittings and shifts of the bands (Preetz, Ruf & Tensfeldt, 1984; Parzich, Peters & Preetz, 1993; Alyoubi, Greenslade, Foster & Preetz, 1990). Bond interactions due to the mutual *trans* influence between different ligands have been quantified by normal coordinate analysis (Erlhöfer & Preetz, 1989; Preetz & Irmer, 1990). However, a shortcoming of previous force-field calculations is that they are based on estimated molecular parameters. Until recently, most of the structure determinations have failed because of the statistical arrangement of the mixed halogeno complex ions in lattices of high symmetry and, consequently, no detailed information about bond lengths and angles has been available (De, 1972; Keller & Homborg, 1976). This problem is overcome using the dication dipyridiniomethane, $[(C_5H_5N)_2CH_2]^{2+}$ (Brüdgam & Hartl, 1986), which forms completely ordered AB-type salts with mixed-ligand complex dianions (Bruhn & Preetz, 1994). In the course of our work on mixed F/Cl complexes of Os^{IV}, we isolated the title compound (I) by ion-exchange chromatography.

(I)
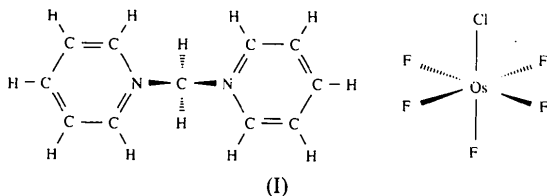
The slightly distorted octahedral complex ion with nearly $mm4$ (C_{4v}) local symmetry is characterized by one asymmetric F—Os—Cl axis and two symmetric substituted F—Os—F axes. Due to the stronger *trans* influence of Cl compared with F, the Os—F bond is weakened and the Os—Cl bond is strengthened. As a result, the Os—F distance of 1.959 (4) Å is slightly lengthened in comparison to those of the F—Os—F axes [1.915 (4), 1.916 (4) and 1.926 (4) Å]. The Os—Cl bond length of 2.329 (2) Å is significantly shorter than in the homoleptic compound $K_2[OsCl_6]$ (2.364 Å; Mc-

Cullough, 1936). For intramolecular steric reasons, the angles between Cl—Os and F1, F2 and F3 are slightly widened [91.1 (2) to 91.8 (2)°]. The displacement ellipsoids are noticeably anisotropic, stretched in the Os–F1–F1–F2–F3 plane, possibly as a result of a tipping disorder around the Cl—Os—F4 axis (Fig. 1).

The Cl ligand of the complex ion is symmetrically located with respect to the pyridine rings of the cation with distances to N of 3.525 (4) Å. The normals to the pyridine rings form an angle of 58.55 (15)°. The cation is linked to the complex ion by weak hydrogen bridges, the shortest distance being 2.107 (5) Å for F2—HM2 (Fig. 1). The packing in the orthorhombic unit cell is shown in Fig. 2.
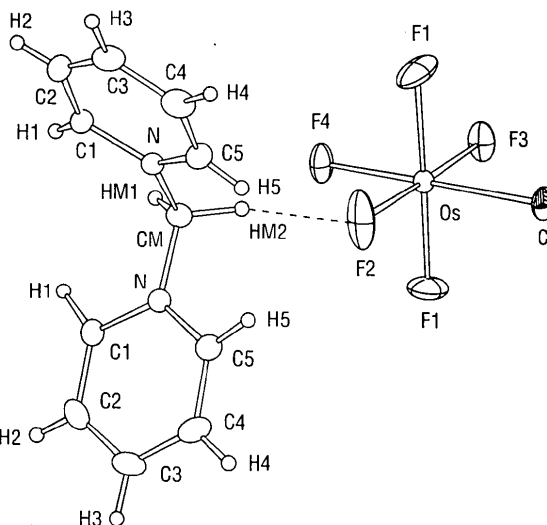

Fig. 1. View of the $[OsF_5Cl]^{2-}$ anion and the $[(C_5H_5N)_2CH_2]^{2+}$ cation. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms are drawn as spheres of arbitrary size.
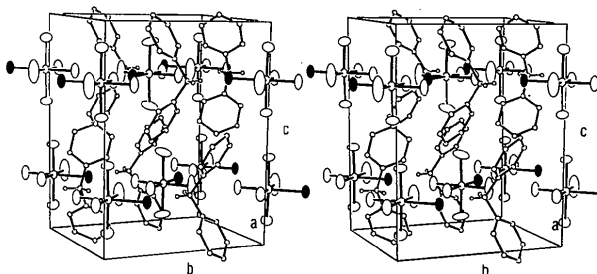

Fig. 2. Stereoview of the crystal packing. Aromatic H atoms are omitted for clarity.

Experimental

By reaction of $K_2[OsCl_6]$ with BrF_3 at room temperature, a mixture containing several compounds of the series $[OsF_nCl_{6-n}]^{2-}$, n = 0–6, is formed, from which

$[OsF_5Cl]^{2-}$ has been separated by ion-exchange chromatography on diethylaminoethylcellulose (Preetz, Ruf & Tensfeldt, 1984). $[(C_5H_5N)_2CH_2][OsF_5Cl]$ was precipitated from an N,N-dimethylformamide solution of the tetra-n-butylammonium complex salt with dipyridiniomethane dibromide and recrystallized from water/acetone, forming suitable single crystals.

Crystal data

$(C_{11}H_{12}N_2)[OsClF_5]$
$M_r = 492.88$
Orthorhombic
$Pnma$
$a = 10.515$ (10) Å
$b = 13.295$ (10) Å
$c = 9.349$ (10) Å
$V = 1306.8$ (21) Å^3
$Z = 4$
$D_x = 2.505$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 6.62–11.98°$
$\mu = 10.011$ mm^{-1}
$T = 293$ (2) K
Prismatic
$0.3 \times 0.2 \times 0.2$ mm
Orange

Data collection

Enraf–Nonius CAD-4-Turbo four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scans)
$T_{min} = 0.35$, $T_{max} = 0.99$
2290 measured reflections
1201 independent reflections
1118 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0224$
$\theta_{max} = 24.97°$
$h = 0 \to 12$
$k = -15 \to 15$
$l = -11 \to 0$
3 standard reflections frequency: 240 min intensity variation: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0196$
$wR(F^2) = 0.0489$
$S = 1.178$
1200 reflections
122 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 1.6802P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 1.031$ e Å^{-3}
$\Delta\rho_{min} = -0.816$ e Å^{-3}
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0039 (2)
Atomic scattering factors from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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}
Os	0.96329 (2)	1/4	0.03528 (2)	0.02123 (12)
Cl	0.79740 (13)	1/4	−0.1298 (2)	0.0376 (4)
F1	0.9683 (3)	0.3940 (3)	0.0357 (4)	0.0699 (13)
F2	0.8453 (4)	1/4	0.1913 (4)	0.087 (2)
F3	1.0889 (4)	1/4	−0.1147 (4)	0.0474 (10)
F4	1.1011 (3)	1/4	0.1763 (4)	0.0458 (10)
N	0.4221 (4)	0.3414 (3)	−0.0453 (3)	0.0249 (7)
CM	0.4781 (6)	1/4	0.0172 (7)	0.0288 (14)
C1	0.4863 (4)	0.3908 (3)	−0.1501 (4)	0.0315 (9)
C2	0.4406 (5)	0.4804 (4)	−0.2007 (5)	0.0414 (12)
C3	0.3302 (5)	0.5194 (4)	−0.1454 (5)	0.0421 (11)
C4	0.2639 (5)	0.4669 (4)	−0.0433 (5)	0.0430 (12)
C5	0.3120 (4)	0.3777 (4)	0.0058 (5)	0.0334 (9)

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

Os—F1^i	1.915 (4)	N—CM	1.471 (5)
Os—F1	1.915 (4)	CM—N^i	1.472 (5)
Os—F2	1.916 (4)	CM—HM1	0.91 (8)
Os—F3	1.926 (4)	CM—HM2	1.05 (8)
Os—F4	1.959 (4)	C1—C2	1.368 (7)
Os—Cl	2.329 (2)	C2—C3	1.373 (8)
N—C5	1.341 (6)	C3—C4	1.373 (8)
N—C1	1.360 (5)	C4—C5	1.368 (7)
F1^i—Os—F1	176.8 (2)	C5—N—C1	120.8 (4)
F1^i—Os—F2	90.94 (12)	C5—N—CM	120.1 (4)
F1—Os—F2	90.94 (12)	C1—N—CM	119.1 (4)
F1^i—Os—F3	88.99 (12)	N—CM—N^i	111.4 (5)
F1—Os—F3	88.99 (12)	N—CM—HM1	109.6 (23)
F2—Os—F3	177.1 (2)	N^i—CM—HM1	109.6 (23)
F1^i—Os—F4	88.76 (10)	N—CM—HM2	110.1 (17)
F1—Os—F4	88.76 (10)	N^i—CM—HM2	110.1 (17)
F2—Os—F4	88.1 (2)	HM1—CM—HM2	105.8 (57)
F3—Os—F4	89.0 (2)	N—C1—C2	119.7 (4)
F1^i—Os—Cl	91.25 (10)	C1—C2—C3	119.7 (5)
F1—Os—Cl	91.25 (10)	C2—C3—C4	120.0 (5)
F2—Os—Cl	91.1 (2)	C5—C4—C3	119.1 (5)
F3—Os—Cl	91.79 (15)	N—C5—C4	120.8 (5)
F4—Os—Cl	179.19 (11)		

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure and prepare material for publication: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Alyoubi, O. A., Greenslade, D. J., Foster, M. J. & Preetz, W. (1990). *J. Chem. Soc.* pp. 381–383.
Brüdgam, I. & Hartl, H. (1986). *Acta Cryst.* C42, 866–868.
Bruhn, C. & Preetz, W. (1994). *Acta Cryst.* C50, 1555–1557.
De, A. K. (1972). Dissertation, Karlsruhe.
Enraf–Nonius (1993). *CAD*-4 *Software*. Version 1.2. Enraf–Nonius, Delft, The Netherlands.
Erlhöfer, P. & Preetz, W. (1989). *Z. Naturforsch. Teil B*, 44, 1214–1220.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Keller, H.-L. & Homborg, H. (1976). *Z. Anorg. Allg. Chem.* 422, 261–265.
McCullough, J. D. (1936). *Z. Kristallogr.* 94, 143–149.
Parzich, E., Peters, G. & Preetz, W. (1993). *Z. Naturforsch. Teil B*, 48, 1169–1174.
Preetz, W. & Erlhöfer, P. (1989). *Z. Naturforsch. Teil B*, 44, 412–418.
Preetz, W. & Irmer, K. (1990). *Z. Naturforsch. Teil B*, 45, 283–289.
Preetz, W., Ruf, D. & Tensfeldt, D. (1984). *Z. Naturforsch. Teil B*, 39, 1100–1109.

$(C_{11}H_{12}N_2)[OsClF_5]$

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

The Cobalt(I) Coenzyme B₁₂ Model Complex [2,10-Diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diolato(1–)](triphenylphosphine)-cobalt(I)

TIMOTHY J. R. WEAKLEY,* JEFFREY MARKS AND RICHARD G. FINKE†

Department of Chemistry, University of Oregon, Eugene, OR 97403, USA

## Abstract

The title cobalt(I) coenzyme B₁₂ model complex, {alternative IUPAC name: [4,10-dimethyl-5,9-diazatrideca-4,9-diene-3,11-dione dioximato(1–)-N,N',N'',N''']-(triphenylphosphine)cobalt(I)}, [Co($C_{13}H_{23}N_4O_2$)-($C_{18}H_{15}P$)], has square-pyramidal geometry [apical Co—P 2.264 (2), basal Co—N 1.846 (4)–1.890 (4) Å] with the Co atom displaced 0.329 (3) Å towards P from the basal mean plane. The [C₂(DOH)(DO)pn]⁻ ligand, where (DOH)₂pn is bis(diacetylmonooximeimino)propane-1,3 [notation of Costa, Mestroni & De Savorgnani (1969). *Inorg. Chim. Acta,* 3, 323–328], contains an O···O hydrogen bond [2.431 (5) Å].

Comment

Compounds containing the 'Costa' tetradentate nitrogen macrocycle ligand Co[C₂(DOH)(DO)pn] [where (DOH)₂pn is bis(diacetylmonooximeimino)propane-1,3 in the notation of Costa, Mestroni & De Savorgnani (1969)] are widely used as mimics of coenzyme B₁₂ (Elliott, Hershenhart, Finke & Smith, 1981). Despite this, and despite more than 100 crystallographic structural investigations of mostly Co^III forms of the related and commonly employed cobaloxime coenzyme B₁₂ 'Co(DMG₂)' model complex (Brescian-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985), no structure determination for a Co^I complex of the Costa ligand system, Co^I*L*[C₂(DOH)(DO)pn], nor of the cobaloxime coenzyme B₁₂ model complex, has yet been reported.

† Present address: Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA.

(I)
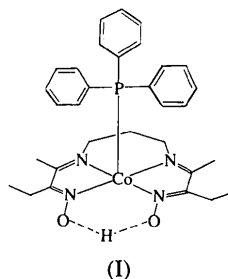
The title complex CO^I(PPh₃)[C₂(DOH)(DO)pn], (I), has the expected square-pyramidal coordination geometry with the Co atom slightly above the plane of the N atoms, which are coplanar to within 0.008 (4) Å [P—Co—N 99.0 (1)–101.8 (1)°]. The trimethylene section opposite the oximate region is inclined away from the axial PPh₃ group. For comparative purposes, the majority of cobalt(I) complexes, among which all coordination numbers from three to six are exhibited, contain several monodentate π-acceptor ligands (Cotton & Wilkinson, 1988). The nearest analogues to Co^I(PPh₃)[C₂(DOH)(DO)pn] contain Co^I bonded in a square-planar manner to a tetradentate N₂O₂ ligand; they are [Co(salen)]Na(thf) and [Co(salen)]Li(thf)₁.₅ [Co—N 1.798 (13)–1.831 (4) Å; Fachinetti, Floriani, Zanazzi & Zanzari, 1979] and the Co^I,II complex [Co(salen)]₂Na(thf)₂ [Co—N 1.845–1.857 (5) Å; Arena, Floriani & Zanazzi, 1987], where H₂salen is bis(salicylidene)ethylenediamine.
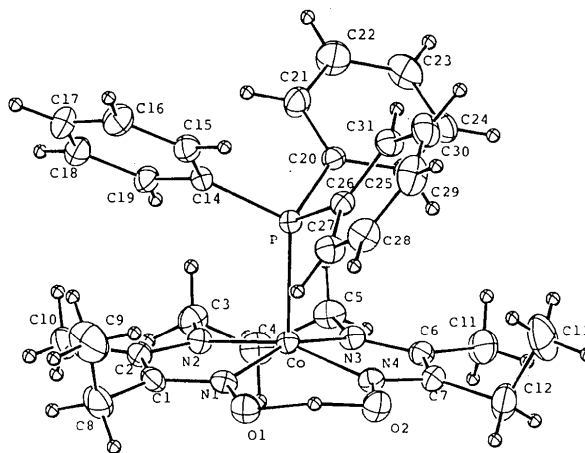

Fig. 1. The molecular structure and atomic numbering scheme of the title complex. Displacement ellipsoids are drawn at the 30% probability level.

Experimental

The air sensitive title compound was prepared under nitrogen from 0.68 g of PPh₃ (2.6 mmol), 1.51 g of Co[C₂(DOH)(DO)pn]I₂ (2.6 mmol) and 0.5 g of NaBH₄ (13.2 mmol), using degassed water/methanol/NaOH solution and a specialized Schlenk-tube apparatus detailed in a similar procedure for the preparation of Co(CO)[C₂(DOH)(DO)pn] (Finke, Smith, McKenna & Christian, 1981). The yield of