

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.

Acta Cryst. (1994). **C50**, 1690–1692

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

(Received 5 December 1993; accepted 21 April 1994)

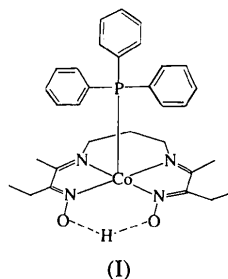
Abstract

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(C₁₃H₂₃N₄O₂)(C₁₈H₁₅P)], 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(DMG)₂' model complex (Brescian-Pahor, Forcolin, Marzilli, Randaccio, Summers & Toscano, 1985), no structure determination for a Co^I complex of the Costa ligand system, Co^IL[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.



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^{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.

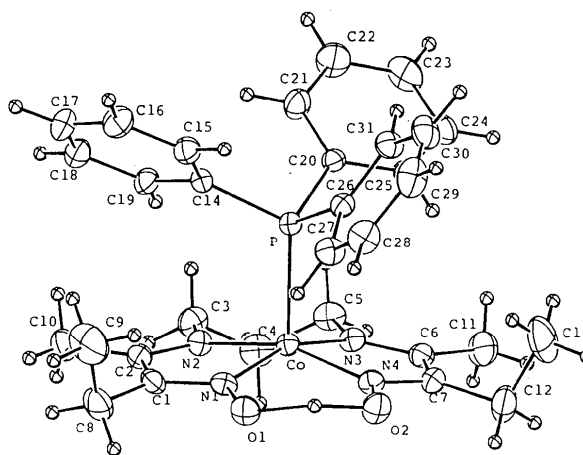


Fig. 1. The molecular structure and atomic numbering scheme of the title complex. Displacement ellipsoids are drawn at the 30% probability level.

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]₂ (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

vacuum-dried microcrystalline purple $\text{Co}^{\text{I}}(\text{PPh}_3)[\text{C}_2(\text{DOH})(\text{DO})\text{pn}]$ was 1.2 g (2.0 mmol; 79%), but it was found to be impure by ^{31}P NMR (see below). Purification of 200 mg of $\text{Co}^{\text{I}}(\text{PPh}_3)[\text{C}_2(\text{DOH})(\text{DO})\text{pn}]$ in a Vacuum Atmospheres nitrogen drybox was accomplished by washing the complex with 50 ml of hexane, dissolving the solid in benzene, filtering it, evaporating the soluble fraction to dryness in a rotary evaporator, and then by crystallization of the solid obtained under nitrogen from benzene by hexane vapor diffusion. An elemental analysis (Mikroanalytisches Labor Pascher; sample manipulated under N_2) showed the resultant $\text{Co}^{\text{I}}(\text{PPh}_3)[\text{C}_2(\text{DOH})(\text{DO})\text{pn}]$ to be analytically pure; calculated (found): C 63.3 (63.4), H 6.51 (6.49), N 9.52 (9.62), P 5.26% (5.33%). Spectroscopy in d_6 -benzene and under N_2 : ^{31}P NMR, 42.7 p.p.m. [air oxidation produces impurities at -4.6 (major, broad resonance) and 25.4 p.p.m. (minor, sharp resonance)]; visible spectrum, $\lambda_{\text{max}} = 650$ nm. The data crystal was manipulated under silicone grease and sealed in a special glass capillary.

Crystal data

$[\text{Co}(\text{C}_{13}\text{H}_{23}\text{N}_4\text{O}_2)(\text{C}_{18}\text{H}_{15}\text{P})]$ Mo $K\alpha$ radiation
 $M_r = 588.6$ $\lambda = 0.71073 \text{ \AA}$
 Monoclinic Cell parameters from 25
 $P2_1/c$ reflections
 $a = 14.727 (7) \text{ \AA}$ $\theta = 11-13^\circ$
 $b = 10.123 (5) \text{ \AA}$ $\mu = 0.670 \text{ mm}^{-1}$
 $c = 20.361 (10) \text{ \AA}$ $T = 296 \text{ K}$
 $\beta = 105.02 (3)^\circ$ Irregular prism
 $V = 2932 (5) \text{ \AA}^3$ $0.50 \times 0.30 \times 0.12 \text{ mm}$
 $Z = 4$ Red-black
 $D_x = 1.33 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4 2294 observed reflections
 diffractometer $[I \geq 3\sigma(I)]$
 $\omega-2\theta$ scans $[1.0-5.3^\circ$
 min^{-1} ; width $(1.00 +$
 $0.344\tan\theta)^\circ]$ $R_{\text{int}} = 0.042$
 Absorption correction: $\theta_{\text{max}} = 25^\circ$
 empirical (DIFABS; $h = -16 \rightarrow 16$
 Walker & Stuart, 1983) $k = -12 \rightarrow 0$
 $T_{\text{min}} = 0.66$, $T_{\text{max}} = 1.13$ $l = 0 \rightarrow 21$
 4293 measured reflections 3 standard reflections
 4133 independent reflections frequency: 60 min
 intensity variation: $\pm 1\%$

Refinement

Refinement on F $(\Delta/\sigma)_{\text{max}} = 0.01$
 $R = 0.037$ $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
 $wR = 0.038$ $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
 $S = 1.40$ Atomic scattering factors
 2294 reflections from *International Tables*
 352 parameters for *X-ray Crystallography*
 $w = 4F_o^2/[\sigma^2(I) + (0.02I)^2]$ (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
Co	0.35351 (5)	0.12865 (7)	0.17068 (3)	2.81 (3)
P	0.21076 (9)	0.07396 (13)	0.10298 (7)	2.86 (6)
O1	0.2909 (2)	0.2370 (4)	0.2806 (2)	4.3 (2)

O2	0.3151 (2)	0.3975 (3)	0.1979 (2)	4.7 (2)
N1	0.3244 (3)	0.1304 (5)	0.2544 (2)	3.4 (2)
N2	0.3960 (3)	-0.0419 (4)	0.2020 (2)	3.1 (2)
N3	0.4234 (3)	0.1442 (4)	0.1057 (2)	3.2 (2)
N4	0.3530 (3)	0.3102 (4)	0.1618 (2)	3.3 (2)
C1	0.3315 (4)	0.0182 (6)	0.2880 (3)	3.8 (3)
C2	0.3720 (4)	-0.0821 (5)	0.2564 (3)	3.8 (3)
C3	0.4451 (4)	-0.1341 (6)	0.1675 (3)	4.7 (3)
C4	0.5128 (4)	-0.0624 (6)	0.1359 (3)	4.9 (3)
C5	0.4658 (4)	0.0316 (6)	0.0798 (3)	4.6 (3)
C6	0.4287 (4)	0.2637 (6)	0.0811 (3)	3.7 (3)
C7	0.3883 (4)	0.3615 (5)	0.1136 (3)	3.7 (2)
C8	0.2994 (4)	0.0081 (6)	0.3516 (3)	5.8 (3)
C9	0.1931 (5)	0.0011 (9)	0.3369 (3)	9.1 (5)
C10	0.3838 (4)	-0.2204 (6)	0.2828 (3)	5.5 (3)
C11	0.4741 (4)	0.2964 (6)	0.0248 (3)	6.0 (3)
C12	0.3838 (5)	0.5061 (6)	0.0993 (3)	5.9 (3)
C13	0.2939 (6)	0.5443 (7)	0.0479 (4)	8.5 (4)
C14	0.1482 (3)	-0.0621 (5)	0.1321 (2)	2.9 (2)
C15	0.0592 (4)	-0.0455 (5)	0.1428 (3)	4.1 (3)
C16	0.0168 (4)	-0.1492 (7)	0.1683 (3)	5.2 (3)
C17	0.0620 (5)	-0.2677 (6)	0.1847 (3)	5.3 (3)
C18	0.1489 (4)	-0.2856 (6)	0.1732 (3)	5.0 (3)
C19	0.1916 (3)	-0.1823 (5)	0.1475 (3)	3.8 (3)
C20	0.2140 (3)	0.0283 (5)	0.0166 (2)	3.0 (2)
C21	0.1934 (4)	-0.0962 (5)	-0.0108 (3)	4.6 (3)
C22	0.2023 (5)	-0.1241 (6)	-0.0755 (3)	6.1 (3)
C23	0.2324 (4)	-0.0284 (8)	-0.1128 (3)	5.7 (4)
C24	0.2514 (4)	0.0966 (6)	-0.0871 (3)	4.6 (3)
C25	0.2429 (3)	0.1239 (5)	-0.0223 (3)	3.8 (2)
C26	0.1229 (3)	0.2046 (5)	0.0885 (3)	3.1 (2)
C27	0.1120 (4)	0.2733 (6)	0.1444 (3)	4.3 (3)
C28	0.0419 (4)	0.3673 (6)	0.1372 (3)	5.1 (3)
C29	-0.0157 (4)	0.3947 (6)	0.0734 (4)	5.8 (3)
C30	-0.0046 (4)	0.3283 (6)	0.0181 (3)	5.3 (3)
C31	0.0630 (4)	0.2306 (5)	0.0255 (3)	4.0 (3)

Table 2. Bond lengths (\AA) and angles ($^\circ$) (excluding phenyl rings)

Co—P	2.264 (2)	N3—C5	1.462 (6)
Co—N1	1.863 (4)	N3—C6	1.319 (6)
Co—N2	1.890 (4)	N4—C7	1.329 (6)
Co—N3	1.882 (4)	C1—C2	1.414 (7)
Co—N4	1.846 (4)	C1—C8	1.494 (7)
P—C14	1.839 (5)	C2—C10	1.494 (7)
P—C20	1.830 (5)	C3—C4	1.505 (7)
P—C26	1.820 (5)	C4—C5	1.512 (7)
O1—N1	1.353 (5)	C6—C7	1.407 (7)
O2—N4	1.359 (5)	C6—C11	1.507 (7)
N1—C1	1.316 (6)	C7—C12	1.491 (7)
N2—C2	1.311 (6)	C8—C9	1.518 (8)
N2—C3	1.467 (6)	C12—C13	1.510 (9)
O1...O2	2.431 (5)		
P—Co—N1	99.3 (1)	C14—P—C26	101.6 (2)
P—Co—N2	99.0 (1)	C20—P—C26	102.8 (2)
P—Co—N3	100.6 (1)	Co—N1—O1	124.3 (3)
P—Co—N4	101.8 (1)	Co—N1—C1	117.4 (4)
N1—Co—N2	80.5 (2)	O1—N1—C1	118.2 (4)
N1—Co—N3	160.1 (2)	Co—N2—C2	115.5 (3)
N1—Co—N4	94.8 (2)	Co—N2—C3	125.5 (3)
N2—Co—N3	96.9 (2)	C2—N2—C3	118.7 (4)
N2—Co—N4	159.2 (2)	Co—N3—C5	123.4 (4)
Co—N3—C6	116.1 (3)	N2—C2—C10	124.3 (5)
C5—N3—C6	120.3 (4)	C1—C2—C10	122.2 (5)
Co—N4—O2	125.9 (3)	N2—C3—C4	111.1 (4)
Co—N4—C7	118.0 (4)	C3—C4—C5	113.7 (5)
O2—N4—C7	116.0 (4)	N3—C5—C4	111.9 (4)
N1—C1—C2	111.7 (5)	N3—C6—C7	113.2 (5)
N1—C1—C8	120.6 (5)	N3—C6—C11	124.9 (5)
C2—C1—C8	127.6 (6)	C7—C6—C11	121.9 (5)
N2—C2—C1	113.5 (5)	N4—C7—C6	111.5 (5)
N3—Co—N4	80.6 (2)	N4—C7—C12	121.5 (5)
C14—P—C20	105.1 (2)	C6—C7—C12	127.0 (5)

The structure was solved using the *PHASE* routine of *DIRDIF* (Beurskens *et al.*, 1984). Most H atoms were revealed by

a difference synthesis. The H atom of the O...H...O bond was included without refinement at the observed position and the others were placed at calculated updated positions with $B(H)$ set at $1.2 \times B_{eq}(C)$. The secondary-extinction parameter refined to a negative value and was fixed at zero in the last cycles. Calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1989).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, intermolecular contact distances for non-H atoms, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: HA1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Arena, F., Floriani, C. & Zanazzi, P. F. (1987). *J. Chem. Soc. Chem. Commun.* pp. 183–184.
- Beurskens, P. T., Bosman, W. P., Doesburg, H. M., Gould, R. O., van den Hark, Th. E. M., Prick, P. A., Noordik, J. H., Beurskens, G., Parthasarathi, V., Bruins Slot, H. J., Haltiwanger, R. C., Strumpel, M. & Smits, J. M. M. (1984). Technical Report 1984/1. Crystallographic Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Brescian-Pahor, N., Forcolin, M., Marzilli, L. G., Randaccio, L., Summers, M. F. & Toscano, P. J. (1985). *Coord. Chem. Rev.* **63**, 1–125.
- Costa, G., Mestroni, G. & De Savorgnani, E. (1969). *Inorg. Chim. Acta*, **3**, 323–328.
- Cotton, F. M. & Wilkinson, G. (1988). *Advanced Inorganic Chemistry*, 5th ed. New York: John Wiley.
- Elliot, C. M., Hershenhart, E., Finke, R. G. & Smith, B. L. (1981). *J. Am. Chem. Soc.* **103**, 5558–5566.
- Fachinetti, G., Floriani, C., Zanazzi, P. F. & Zanzari, A. R. (1979). *Inorg. Chem.* **18**, 3469–3475.
- Finke, R. G., Smith, B. L., McKenna, W. A. & Christian, P. A. (1981). *Inorg. Chem.* **20**, 687–693.
- Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*. Version 5.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1994). **C50**, 1692–1694

A Salt of a Protonated (Amino)spirocyclic Cyclotriphosphazene

A. CHANDRASEKARAN†

Department of Inorganic and Physical Chemistry,
Indian Institute of Science, Bangalore 560 012, India

(Received 3 November 1993; accepted 8 April 1994)

Abstract

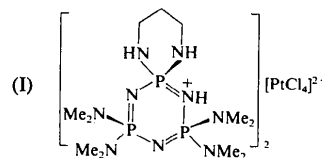
The title compound 4,4,6,6-tetrakis(dimethylamino)-2λ⁵,4λ⁵,6λ⁵-cyclotriphosphaza-1,3,5-trien-1-ium-2-spiro-2'-(2'-phospha-1',3'-diazacyclohexane) tetra-

† Current address: Department of Chemistry, University of Massachusetts, Amherst, MA 01003, USA.

chloroplatinate, [HN₃P₃(NMe₂)₄(NHCH₂CH₂CH₂NH)]₂·[PtCl₄], contains a cyclophosphazanium cation in which the hetero-substituted (amino)spirocyclic cyclotriphosphazene is protonated. The protonation has occurred on one of the P₃N₃ ring N atoms adjacent to the spiro P atom. The protonation results in lengthening of the ring P—N bonds and puckering of the phosphazene ring. In the crystal lattice, 2*n* cyclophosphazanium cations are connected by *n* [PtCl₄]²⁻ anions mediated by N—H...Cl hydrogen bonds to form a linear polymeric structure.

Comment

The transition metal chemistry of cyclophosphazenes has attracted considerable interest in recent years (Allcock, Desorcie & Riding, 1987). In this context, several cyclophosphazanium salts with metal anions such as [HN₃P₃(NMe₂)₆]₂[Mo₆O₁₉] (Allcock, Bissell & Shawl, 1973), [HN₃P₃(NMe₂)₆]₂[CoCl₄] (MacDonald & Trotter, 1974), [MeN₄P₄Me₈][Cr(CO)₅I] (Calhoun & Trotter, 1974*a*), [HN₄P₄Me₈]₂[CoCl₄] (Trotter & Whitlow, 1970), [H₂N₄P₄Me₈][PtCl₄] (O'Brien, Allen & Allcock, 1979) and [H₂N₅P₅Me₁₀][CuCl₄] (Calhoun & Trotter, 1974*b*) have been studied. The protonation and coordination are found to have similar effects in altering the phosphazene-ring bond parameters and planarity. Generally the protonation occurs on the ring N atom of the amino or alkyl cyclophosphazene. In (amino)spirocyclic phosphazenes there are two kinds of N atoms in the phosphazene ring; one set adjacent to the spiro P atom and one away from it. Since no study of hetero-substituted amino or alkyl cyclophosphazenes had been carried out, the title complex, (I), was structurally characterized. The protonation has occurred on one of the N atoms adjacent to the spiro P atom which has less steric hindrance.



The [PtCl₄]²⁻ anion is perfectly planar as the metal lies on the crystallographic centre of inversion. All the Pt—Cl bond distances are similar. The Cl—Pt—Cl angles are not exactly 90°, a fact which can be attributed to different hydrogen-bonding interactions to the Cl atoms (see Fig. 1). There are two hydrogen bonds between the [PtCl₄]²⁻ ion and the cyclophosphazanium ion [N(1)—H(1)...Cl(1) and N(11)—H(11)...Cl(2)] which result in an eight-membered ring. As the metal lies at the centre of inversion, the other two centrosymmetrically related Cl atoms are also involved in hydrogen-bonded ring formation. Hence the metal is incorporated in two eight-membered rings resulting in discrete molecules of