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A New Type of Organocobalt Complex with a Buckled Equatorial Ligand

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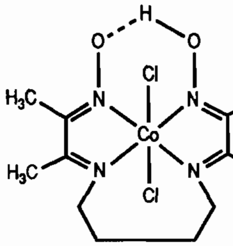
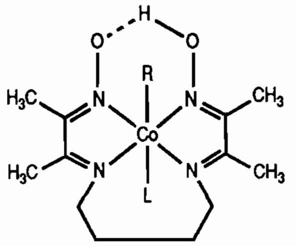
Abstract

Weakening of the Co–C bond in coenzyme B_{12} has been attributed to steric influences, especially to flexing or folding of the equatorial corrin ring. With this in mind we have synthesized four new cobalt complexes with unusual steric properties as model compounds: Co((DO)(DOH)bn)Cl_2 (I), where (DO)(DOH)bn is the equatorial ligand $N^2,N^{2'}$-butanediylbis(2,3-butanedione 2-imine 3-oxime), and organocobalt complexes $[LCo((DO)(DOH)bn)R]^+$, where R = methyl, ethyl (II), or methylpropyl and L = OH_2. The NMR spectra and crystal structures of Co((DO)(DOH)bn)Cl_2 (I) and $[OH_2Co((DO)(DOH)bn)CH_2CH_3]ClO_4$ (II) are reported.



I



II

The respective crystal systems, space groups, lattice constants and final *R* factors for these two compounds are as follows: I orthorhombic, $P2_12_12_1$, $a = 14.017(2)$, $b = 29.014(4)$, $c = 8.005(2)$ Å, $Z = 8$, $R = 0.061$, $R_w = 0.076$; II monoclinic, $C2/c$, $a = 21.820(3)$, $b = 7.386(2)$, $c = 25.652(4)$ Å, $\beta = 101.22(1)°$, $Z = 8$, $R = 0.077$, $R_w = 0.075$. These are the first cobalt complexes reported with the (DO)(DOH)bn equatorial ligand; in both I and II the equatorial nitrogen donor atoms form a planar array around the Co atom, in contrast to the non-planar coordination geometry in $[Cu((DO)(DOH)bn)](ClO_4)$. The (DO)(DOH)bn ligand folds toward the two central carbon atoms of the four-carbon bridge in both complexes. In complex II the equatorial ligand folds toward the water ligand at an angle of 6.0°; it is also folded (3.8, 12.0°) in both independent molecules of I, where the two axial Cl^- ligands are identical. The new ethylcobalt complex (II) is similar to coenzyme B_{12} in that there is an equatorial ligand with a 'built-in' fold, and in the steric adjustments produced by the folded equatorial ligand. The Co–C and C–O bonds are lengthened to 2.012(6) and 2.119(3) Å and the Co–C–C bond angle of the alkyl ligand is widened to 119.3(5)°.

Introduction

There has been continuing interest in organocobalt complexes which might serve as model compounds for coenzyme B_{12} since Schrauzer and co-workers synthesized cobaloximes in the 1960s [1–3], and Costa and Mestroni prepared organometallic derivatives of Co(III)SALEN and Co(III)BAE [4]**. The electrochemical [5] and thermodynamic [6–10] properties of these model complexes have been compared with coenzyme B_{12}. The detailed mechanism by which coenzyme B_{12} catalyzes rearrangement reactions is not known, but there is strong evidence [11–17] that an early step in the rearrangement reaction is the homolytic cleavage of the cobalt–carbon bond. In an attempt to understand how the elongation and cleavage of this bond might be promoted by various steric and electronic factors, the structures of many organocobalt complexes have been determined [18–31]. Cobalt complexes of the equatorial ligand (DO)(DOH)pn† first synthesized by Costa *et al.* [32–34] and a similar ligand (EMO)-

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**BAE = bis(acetylacetone)ethylendiiminato; SALEN = bis(salicylaldehyde)ethylendiiminato.

†2,3,9,10-Tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diolato(1−) or (1,3-propanediyldinitrilo)di-(2-butanoneoximato)(1−) or $N^2,N^{2'}$-propanediylbis(2,3-butanedione 2-imine 3-oxime).

(EMOH)pn * synthesized by Finke *et al.* [35] appear to mimic the electrochemical properties of coenzyme B_{12} better than the bis(dimethylglyoximato) ligands, perhaps because these ligands have the same charge (−1) as does the corrin ring in B_{12} [5, 17, 36].

Weakening of the Co–C bond in coenzyme B_{12} has been attributed to steric influences, especially to flexing or folding of the equatorial corrin ring [37]. The corrin ring in B_{12} is non-planar because there is one saturated carbon atom in the 15-membered macrocyclic ring. Furthermore, the steric bulk of the benzimidazole base *trans* to the cobalt–carbon bond causes additional distortion of the corrin ring, so that it is bent up at an angle of 15° [38, 39]**. This folding of the equatorial ligand may exert a 'levering' effect which results in 'mechanochemical' cleavage of the Co–C bond [10, 23, 40–42]. Similarly, it has been proposed that interactions between the enzyme and corrin side chains may further distort the ring, thus facilitating the cleavage of the Co–C bond in the catalytic step [43]. A recent comparison study [42] of 13 corrin crystal structures by techniques such as direct superposition, partitioned distance matrix analysis and factor analysis has shown that the major conformational variability in these structures is the degree of folding in the corrin ring.

We report here the synthesis, NMR spectra and X-ray crystal structure of two new cobalt complexes: $Co((DO)(DOH)bn)Cl_2$ (**I**) and $[OH_2Co((DO)(DOH)bn)CH_2CH_3]ClO_4$ (**II**), where (DO)(DOH)bn is the equatorial ligand $N^2,N^{2'}$-butanediylbis(2,3-butanedione 2-imine 3-oxime). The seven-membered chelate ring which is formed by the four-carbon bridge in this ligand is expected to cause distortions in these organocobalt complexes as does the folding of the corrin ring in B_{12}. We also report the synthesis of two other organocobalt complexes with this equatorial ligand, the methyl and methylpropyl complexes (Scheme 1).

Experimental

Reagents

All chemicals were reagent grade: 1,4-diaminobutane and 2,3-butanedione monoxime, Aldrich; $CoCl_2 \cdot 6H_2O$, $CoBr_2 \cdot 6H_2O$, methyl iodide, ethyl iodide, Fisher; $NaBH_4$, Mallinckrodt. All solvents were reagent grade.

Preparation of Equatorial Ligand and Complexes

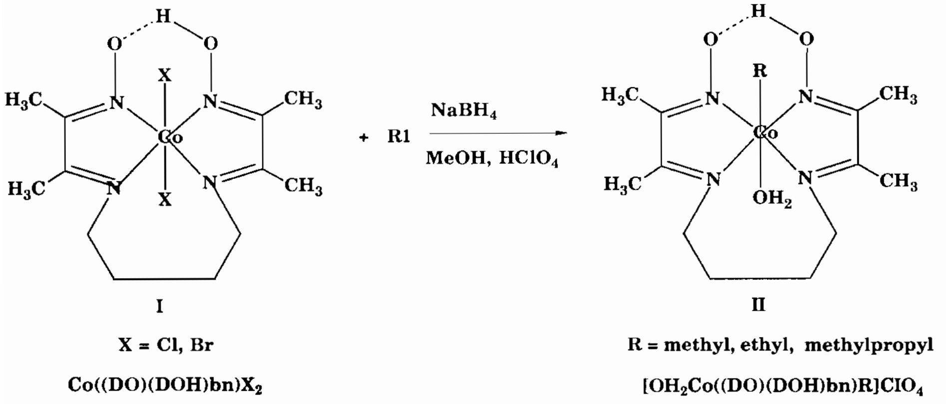
Caution: perchlorate salts may be explosive if heated or subjected to mechanical shock. Organocobalt complexes were kept in the dark to avoid light-induced cleavage of the Co–C bond.

$N^2,N^{2'}$-Butanediylbis(2,3-butanedione 2-imine 3-oxime) ((DO)(DOH)bn) (Scheme 2)

The synthetic procedure was adapted from those of Costa *et al.* [32–34] and Martin *et al.* [44]. The ligand is formed by a Schiff base condensation between 2,3-butanedione monoxime (40 g, 400 mmol) and 1,4-diaminobutane (17.6 g, 20.1 ml, 200 mmol) in 140 ml absolute ethanol. The mixture was refluxed in a three-neck flask for 1.5 h, cooled, stoppered and refrigerated for 48 h. The white precipitate was filtered from the orange–yellow supernatant liquid, washed copiously with diethyl ether, and used without further purification (33.4 g, 67.5%, melting point (m.p.) 149–151 ℃).

$Co^{III}((DO)(DOH)bn)Cl_2$ (I)

The procedure was adapted from the preparation of $Co((DO)(DOH)pn)X_2$ [32–34]. (DO)(DOH)bn (7.6 g, 30 mmol) was partially dissolved with gentle heating and stirring in 200 ml acetone in a 500 ml



Scheme 1.

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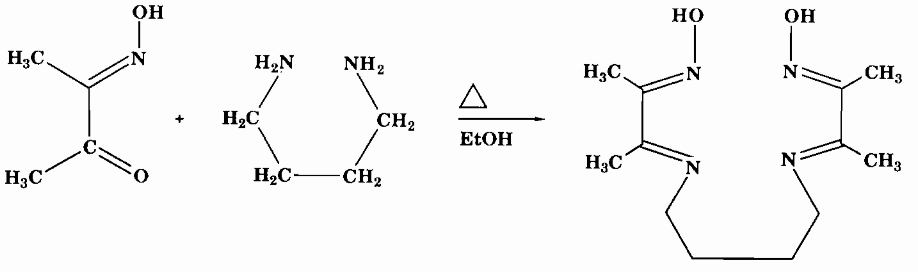
*2,10-Diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,11-diolato(1−).

**Angle between planes 1 and 2: plane 1, N(21), C(4), C(5), C(6), N(22), C(9), C(10); plane 2, N(24), C(16), C(15), C(14), N(23), C(11), C(10).



(DO)(DOH)bn

Scheme 2.

pear flask. Ar was bubbled through the suspension. Simultaneously, $CoCl_2 \cdot 6H_2O$ (7.1 g, 30 mmol) was dissolved in a minimum of distilled H_2O and Ar was bubbled through the solution. After 30 min the Co^{II} solution was transferred to the pear flask with a syringe that had been purged with Ar. After 1 h of stirring under Ar, the mixture was poured into a 1000 ml beaker and stirred in air until dry. The resultant sticky, black solid was washed with H_2O, revealing the green solid Co^{III} complex (**I**). After air drying, the solid was dissolved in 20 ml of 2:1 acetone:H_2O; slow evaporation yielded dark green needles of **I** (0.7 g, 6%, decomposition 260–262 °C). A number of different procedures were used in an attempt to improve the yield; none succeeded.

$[OH_2Co^{III}((DO)(DOH)bn)CH_3]ClO_4$

I (0.47 g, 1 mmol) was stirred in a deaerated mixture of 45 ml methanol and 5 ml water in a 200 ml pear flask. Ar was bubbled through the mixture for 15 min while the complex dissolved, then CH_3I (0.35 ml, 3 mmol) was added by syringe through the sidearm of the flask. Care was taken to exclude oxygen during the addition of $NaBH_4$ (0.13 g, 3 mmol) from a purged storage tube through the sidearm. The reduction of Co^{III} to Co^{I} and alkylation by CH_3I were complete after 5 min; the reaction mixture was transferred via cannula to a Schlenk filter funnel. $NaClO_4 \cdot 4H_2O$ (0.41 g, 2 mmol) in 15 ml of H_2O was added to the filtered solution. **Caution**: the mixture was rotary evaporated behind a safety shield, but not to dryness, due to the explosion hazard of the perchlorate salt. The remaining solid/oily liquid mixture was allowed to dry in a recrystallization dish, redissolved in acetone:pentane (2:1) and slowly recrystallized. Reddish-orange X-ray quality crystals were obtained from 1 M $HClO_4$. *Anal.* Calc. for $C_{13}H_{28}ClCoN_4O_8$ (1 H_2O of hydration): C, 33.74; H, 6.10; Cl, 7.66; Co, 12.73; N, 12.11; O, 27.66. Found (analyzed for all elements): C, 33.49; H, 5.71; Cl, 7.96; Co, 13.25; N, 12.18; O, 27.45%. The ^{13}C-enriched complex was prepared as above, except that the CH_3I was 90% ^{13}C.

$[OH_2Co^{III}((DO)(DOH)bn)CH_2CH_3]ClO_4$ (II)

This complex was synthesized from **I** as above except that 3 mmol (0.25 ml) CH_3CH_2I was used as the alkylation reagent. Reddish-orange X-ray quality crystals were obtained from 0.5 M $HClO_4$ or acetone. *Anal.* Calc. for $C_{14}H_{28}ClCoN_4O_7$: C, 36.65; H, 6.15; Cl, 7.73; Co, 12.85; N, 12.21; O, 24.41. Found (analyzed for all elements): C, 36.37; H, 6.00; Cl, 7.80; Co, 12.60; N, 12.09; O, 24.28%.

$[OH_2(Co^{III}((DO)(DOH)bn)CH_2CH(CH_3)_2]ClO_4$

This complex was synthesized from **I** as above except that 3 mmol (0.6 ml) 1-iodo-2-methylpropane was used as the alkylation reagent. Reddish-orange X-ray quality crystals were obtained from 1:1 ethanol:H_2O or 1 M $HClO_4$. *Anal.* Calc. for $C_{16}H_{32}ClCoN_4O_7$: C, 39.48; H, 6.62; Cl, 7.28; Co, 12.10; N, 11.51; O, 23.01. Found (analyzed for all elements): C, 38.62; H, 6.75; Cl, 6.95; Co, 11.03; N, 11.07; O, 23.75%.

Characterization

All NMR spectra were obtained on a JEOL FX-90Q spectrometer.

X-ray Methods

Crystals were mounted on a glass fiber. Preliminary space group and lattice constants were obtained from Weissenberg photographs. Final cell parameters (Table 1) were obtained by a least-squares analysis of 15 centered reflections obtained from diffractometer measurements.

Data were collected on a Syntex $P2_1$ four-circle diffractometer by means of a $2\theta:\theta$ scan (bisecting mode) at a variable speed (2.0–58.3° min^{-1}) depending upon intensity; scan:background time ratio was 0.5. Values of $\sigma(I)$ were calculated from analysis of background and peak intensities. Four check reflections measured every 100 reflections showed no decay in intensity. Values of $\sigma(F)$ were calculated as $\sigma(F) = (F/2)[\sigma^2(I)/(I)^2 + \delta^2]^{1/2}$, where δ (0.02) is an instrumental uncertainty determined from the variation in the intensity of the check reflections.

TABLE 1. Crystal data

	I	II
Molecular formula	$C_{12}H_{21}N_4CoCl_2O_2$	$C_{14}H_{28}N_4CoClO_7$
Formula weight	383.16	458.79
$F(000)$	1584	1920
Space group	$P2_12_12_1$	$C2/c$
Z	8	8
a (Å)	14.017(2)	21.820(3)
b (Å)	29.014(4)	7.386(2)
c (Å)	8.005(2)	25.652(4)
β (°)		101.22(1)
V (Å^3)	3256(1)	4055(1)
D_x (g ml^{-1})	1.56	1.50
D_{meas} (flotation) (g ml^{-1})		1.49
Radiation λ (Å)	Cu Kα (1.54178)	Mo Kα (0.71069)
μ (cm^{-1})	118.6	10.16
Crystal size (mm)	0.11 × 0.05 × 0.22	0.28 × 0.28 × 0.10
Temperature (K)	293	293
Max 2θ (°) ($\sin\theta/\lambda$ Å^{-1})	139.0(0.61)	52.0(0.62)
Collection range	0–7, 0–35, 0–9	±26, 0–8, 0–31
No. unique data measured	3481	4108
No. observed data, n	2915 $[I > 2.5\sigma(I)]$	2370 $[I > 2.0\sigma(I)]$
No. variables refined, p	379	244
Highest peak $F_o - F_c$ map (e Å^{-3})	0.62	0.66
Final $R = \Sigma \lVert F_o - F_c \rVert / \Sigma \lvert F_o \rvert$	0.061	0.077
Final $R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / w\lvert F_o\rvert^2]^{1/2}$	0.076	0.075
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-p)]^{1/2}$	0.98	4.7

The data were corrected for Lorentz and polarization factors and scaled with a Wilson plot [45a]. An empirical absorption correction as a function of ϕ was applied using intensity data from a 72-step Ψ-scan.

The structures were solved by direct methods; the atomic positions and anisotropic thermal parameters of all non-hydrogen atoms were refined on F by a full matrix least-squares procedure*. The quantity minimized was $\Sigma w[|F_o| - |F_c|]^2$ where the weights, w, were $1/\sigma^2(F)$. Correction for anomalous scattering (**I**: Co, Cl, O, N, C; **II**: Co, Cl) was applied. Positions of 22 H atoms were located in the difference electron density map for the two independent molecules of **I**; 19 H atom positions were calculated (C–H distance 1.0 Å). Electron density maps calculated from low angle reflections for **II** revealed 18 H atom positions; the positions of 10 were calculated. Isotropic H atom positions were not refined, but were included in the structure factor calculation. In the last stages of refinement of **I**, F_o was reset to the value of F_c for 6 intense reflections at $\sin\theta/\lambda < 0.099$ (correction for secondary extinction), and $\sigma(F)$ was calculated by a least-squares polynomial fit of the function $||F_o| - |F_c|| = a + bF_o + cF_o^2$, so that $\sigma(F) = 2.678 - 0.03371F_o + 0.0007926F_o^2$.

Final positions and isotropic thermal parameters of the non-hydrogen atoms are tabulated in Tables 2 and 3. The high thermal factors of C5, C6, C7, C8 especially in **II** indicate positional disorder in this part of the molecule (probably exacerbated by the high thermal motion of the perchlorate anion) and has affected the precision of the structure determination. See also 'Supplementary Material'.

Results

The ^{13}C NMR chemical shift data for complexes **I** and **II** are presented in Table 4. Methyl and methylene peak assignments were made from the splitting of the ^{1}H-coupled ^{13}C spectrum of **I** and by comparison to the ^{13}C spectrum of the corresponding methylcobalt complex. The signal for the carbon bonded to cobalt in the ethylcobalt complex (**II**) was not observed, due to broadening and rapid relaxation caused by the ^{59}Co nucleus ($I = 7/2$). The values are similar to those reported for [LCo((DO)(DOH)-pn)R]X complexes [46].

The equatorial ligand in these new organocobalt complexes, (DO)(DOH)bn, is a macrocyclic ligand closed by a hydrogen bond between two oxygen

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*The programs used for data reduction and refinement are part of ref. 45a; direct methods: 45b and c. All calculations were performed on a DEC VAX 11/750 computer. Scattering factors and corrections for anomalous dispersion were taken from refs. 45d and e.

TABLE 2. Atomic coordinates and average isotropic B (Å^2) for Co((DO)(DOH)bn)Cl$_2$ (I)[a]

Atom	x	y	z	B[b]
Co1	0.49252(7)	0.23448(3)	0.3517(1)	1.71(4)
Co2	0.51340(6)	0.46978(3)	0.7656(1)	1.68(4)
Cl2	0.3543(1)	0.21647(6)	0.2264(3)	3.11(8)
Cl1	0.6321(1)	0.25033(8)	0.4750(3)	3.32(8)
Cl1′	0.4197(1)	0.41162(6)	0.8472(3)	3.02(8)
Cl2′	0.6053(1)	0.52801(6)	0.6776(3)	3.41(9)
N1	0.5568(5)	0.1970(2)	0.1928(9)	2.8(3)
N2	0.5204(4)	0.2810(2)	0.1797(8)	2.2(2)
N3	0.4279(4)	0.2701(2)	0.5216(9)	2.2(2)
N4	0.4651(5)	0.1869(2)	0.5073(9)	2.9(3)
O1	0.5703(6)	0.1521(2)	0.214(1)	5.0(3)
O2	0.4932(6)	0.1435(2)	0.483(1)	5.4(4)
C1	0.6390(8)	0.1900(4)	−0.073(1)	5.1(5)
C2	0.5873(6)	0.2161(3)	0.058(1)	3.0(3)
C3	0.5659(4)	0.2654(3)	0.052(1)	2.4(3)
C5	0.4946(7)	0.3301(3)	0.190(1)	3.9(4)
C6	0.3882(7)	0.3365(3)	0.229(2)	4.9(5)
C7	0.3634(8)	0.3428(4)	0.409(2)	5.6(6)
C8	0.4293(7)	0.3211(3)	0.534(1)	4.0(4)
C10	0.3950(5)	0.2465(3)	0.646(1)	2.5(3)
C11	0.4168(6)	0.1970(3)	0.639(1)	3.1(3)
C12	0.3850(9)	0.1627(4)	0.768(1)	5.6(5)
C13	0.5989(7)	0.2920(4)	−0.096(1)	4.2(4)
C14	0.3388(6)	0.2644(4)	0.791(1)	4.2(4)
N1′	0.5742(4)	0.4311(2)	0.6096(8)	2.1(2)
N2′	0.6173(4)	0.4457(2)	0.9061(8)	2.1(2)
N3′	0.4452(4)	0.5108(2)	0.9194(9)	2.7(3)
N4′	0.4178(4)	0.4922(2)	0.6168(9)	2.9(3)
O1′	0.5422(4)	0.4255(2)	0.4516(7)	3.6(3)
O2′	0.4099(5)	0.4774(2)	0.4622(9)	4.4(3)
C1′	0.7101(6)	0.3813(3)	0.537(1)	3.9(4)
C2′	0.6520(5)	0.4105(2)	0.655(1)	2.3(3)
C3′	0.6754(5)	0.4191(2)	0.830(1)	2.1(3)
C5′	0.6334(7)	0.4569(3)	1.083(1)	4.2(4)
C6′	0.6390(7)	0.5074(4)	1.120(1)	4.5(4)
C7′	0.5498(8)	0.5314(3)	1.161(2)	6.2(6)
C8′	0.4580(7)	0.5102(4)	1.100(1)	4.7(5)
C10′	0.3810(5)	0.5351(3)	0.847(1)	3.4(4)
C11′	0.3653(6)	0.5252(3)	0.672(1)	3.8(4)
C12′	0.2937(7)	0.5496(4)	0.560(2)	5.9(6)
C13′	0.7614(6)	0.3965(3)	0.902(1)	3.7(4)
C14′	0.3205(7)	0.5713(3)	0.934(2)	5.8(6)

[a] e.s.d.s of the least significant digits are given in parentheses. [b] $B_{iso} = \frac{1}{3}$[trace of orthogonalized B_{ij} matrix].

TABLE 3. Atomic coordinates and average isotropic B (Å^2) for [OH$_2$Co((DO)(DOH)bn)CH$_2$CH$_3$]ClO$_4$ (II)[a]

Atom	x	y	z	B[b]
Co	0.86173(2)	0.06012(9)	0.64781(2)	4.46(3)
Cl	0.63441(6)	0.1927(2)	0.54574(5)	6.68(7)
O1	0.79635(16)	0.2849(6)	0.70855(15)	7.7(2)
O2	0.89851(17)	0.3941(5)	0.70125(15)	7.4(2)
O3	0.81481(14)	0.2166(5)	0.58295(12)	5.89(18)
N1	0.79684(17)	0.1286(6)	0.68237(15)	5.17(20)
N2	0.80651(18)	−0.1471(6)	0.62969(17)	5.7(2)
N3	0.92932(18)	0.0077(6)	0.61010(17)	6.6(2)
N4	0.91250(16)	0.2653(6)	0.66849(17)	5.6(2)
C1	0.6912(2)	0.0849(11)	0.6981(3)	9.1(4)
C2	0.7481(2)	0.0280(8)	0.67705(20)	5.8(3)
C3	0.7558(3)	−0.1369(9)	0.6486(2)	6.2(3)
C5	0.8172(4)	−0.3060(10)	0.5986(4)	12.4(6)
C6	0.8294(4)	−0.2449(15)	0.5439(4)	16.6(6)
C7	0.8882(8)	−0.2028(15)	0.5398(4)	18.5(10)
C8	0.9378(4)	−0.1601(14)	0.5827(5)	14.7(6)
C10	0.9722(2)	0.1334(9)	0.6165(2)	6.6(3)
C11	0.9625(3)	0.2836(9)	0.6507(2)	6.4(3)
C12	1.0088(3)	0.4366(11)	0.6628(3)	10.2(4)
C13	0.7052(3)	−0.2789(11)	0.6425(3)	9.8(4)
C14	1.0272(3)	0.1347(13)	0.5894(3)	11.0(5)
C15	0.9075(3)	−0.0764(9)	0.7115(2)	6.8(3)
C16	0.9036(3)	−0.0139(11)	0.7642(3)	8.5(4)
O4	0.6065(3)	0.2220(10)	0.4937(2)	13.1(4)
O5	0.5975(3)	0.0959(14)	0.5682(3)	22.8(6)
O6	0.6869(3)	0.1012(11)	0.5480(3)	17.5(5)
O7	0.6528(5)	0.3391(10)	0.5735(4)	20.8(8)

[a] e.s.d.s of the least significant digits are given in parentheses. [b] $B_{iso} = \frac{1}{3}$[trace of orthogonalized B_{ij} matrix].

TABLE 4. ^{13}C NMR chemical shifts of Co((DO)(DOH)bn) complexes

	I[a]	II[b]
$CH_2-N=\mathit{C}<$	174.41	175.07
$O-N=\mathit{C}<$	155.75	155.89
$N-\mathit{C}H_2-$	50.65	49.39
$N-CH_2-\mathit{C}H_2-$	24.10	23.98
$CH_2-N=C-\mathit{C}H_3$	17.90	16.93
$O-N=C-\mathit{C}H_3$	14.52	12.82
$Co-\mathit{C}H_2-CH_3$		[c]
$Co-CH_2-\mathit{C}H_3$		16.50

[a] Co((DO)(DOH)bn)Cl$_2$ (I) in CDCl$_3$; ^{1}H-decoupled; chemical shifts relative to Me$_4$Si at 0.0 ppm, Me$_4$Si internal reference, 500 accumulations. Confirmation of peak assignments from ^{1}H-coupled spectrum in CDCl$_3$. [b] [OH$_2$Co((DO)(DOH)bn)CH$_2$CH$_3$]ClO$_4$ (II) in acetone-d$_6$; ^{1}H-decoupled; chemical shifts relative to Me$_4$Si, acetone internal reference at 206.00 ppm, 11 000 accumulations. [c] This signal, a multiplet due to the nuclear spin (I = 7/2) of cobalt, is so broadened as to be unobservable. The broad Co–$\mathit{C}H_3$ signal of the methylcobalt complex, [OH$_2$Co((DO)(DOH)bn)CH$_3$]$^+$, was observed when the synthesis was repeated with ^{13}CH$_3$I as the alkylating agent.

atoms. An important feature of (DO)(DOH)bn is the four-carbon bridge between the imine nitrogen atoms, which forms an unusual seven-membered chelate ring with the cobalt ion. As shown in Figs. 1 and 2, five atoms (Co, N2, N3, C5, C8) in this chelate ring tend to be approximately coplanar (r.m.s. deviation from the plane 0.089 and 0.078 Å for I, 0.033 Å for II, 'Supplementary Material') because of the two sp^2 hybridized nitrogen atoms in the seven-membered chelate ring. The remaining two carbon atoms (C6,

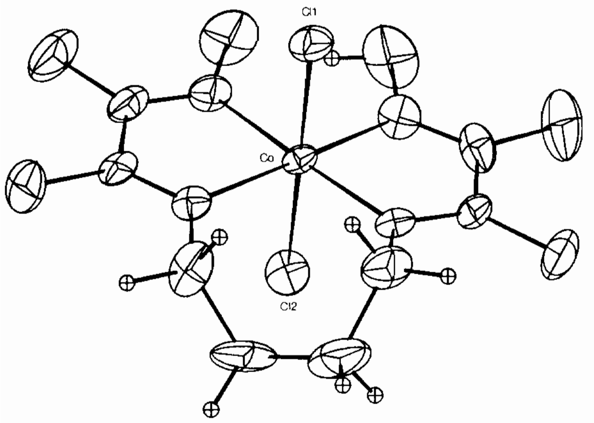


Fig. 1. Drawing of molecule 1 of Co((DO)(DOH)bn)Cl$_2$ (I) showing thermal ellipsoids at the 50% probability level. Methyl hydrogen atoms have been omitted for clarity.

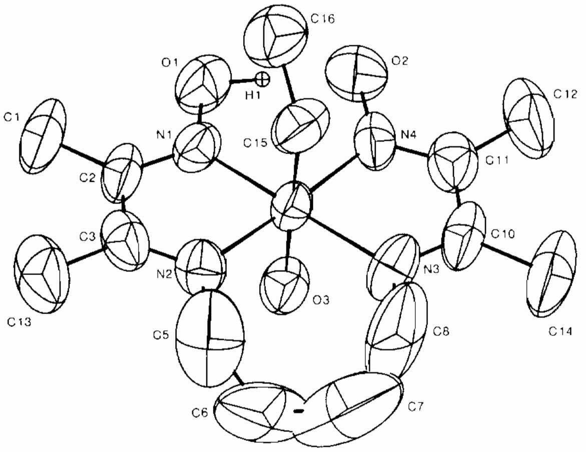


Fig. 2. Drawing of [OH$_2$Co((DO)(DOH)bn)CH$_2$CH$_3$]$^+$ (II) showing thermal ellipsoids at the 50% probability level. Methyl and methylene hydrogen atoms have been omitted for clarity.

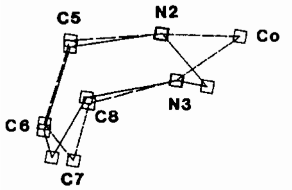


Fig. 3. Comparison of the seven-membered chelate ring of I (dashed-line bonds) to the boat conformation of cycloheptane (solid-line bonds).

C7) in complex II are bent downward toward the water ligand. A comparison between the conformation of the seven-membered chelate ring in I and the boat conformation of cycloheptane is shown in Fig. 3. The forced planarity does not allow the Co atom to undergo the symmetric flip [47] to the position it would occupy in either chair or boat form, but rather keeps the Co atom at an intermediate position between the two possible extremes. We call this the 'flip' conformation because it can be considered an intermediate in one of the possible symmetric chair/boat flips for cycloheptane.

The seven-membered rings of I are somewhat twisted (see Fig. 3), probably to relieve steric repulsion between the H atoms of C5 and C8. In cycloheptane the lowest energy forms are the twist-chair and the twist-boat for this reason [47]. C8 and C8′ are 0.36 and 0.32 Å above the plane of the four N atoms, toward Cl1 and Cl1′; and C5 and C5′ are slightly below the plane, toward C6 and C6′.

In previous studies [44] of crystal structures of Cu(II) complexes with this and a similar equatorial ligand it was concluded that the seven-membered chelate ring precludes planarity of the nitrogen atoms. The structures reported here are the first Co(III) complexes with this equatorial ligand, and in both examples the equatorial nitrogen donor atoms form a planar array around the Co atom; the r.m.s. deviation of the N atoms from the N$_4$ plane is 0.021 and 0.015 Å for I and 0.031 Å for II ('Supplementary Material'). Apparently the Co(III) ion enforces donor atom planarity much more effectively than the Cu(II) ion. The distortion in the square pyramidal Cu(II) complex could be due to a slightly larger ionic radius, to the Jahn–Teller effect, or to the unusual plasticity of the coordination sphere in Cu(II) complexes [48].

However, the N–Co–N angles and Co–N distances in both complexes are somewhat distorted from octahedral geometry because of the steric restraints on the donor atoms. The nitrogen donor atoms in the five-membered rings are restrained by the small size of these rings and by the imine double bonds, resulting in the compressed N–Co–N angles of 80 to 81°. On the other hand, the nitrogen donor atoms in the seven-membered chelate ring tend to spread apart. The N2–Co–N3 angle in the seven-membered rings is widened to 103°, and the Co–N bond lengths in this large chelate ring are lengthened. Bond lengths and bond angles for the two complexes are shown in Figs. 4–6.

The oxygen atoms of the equatorial ligand are 2.390(9) to 2.42(1) Å apart in the (DO)(DOH)bn complexes reported here. These distances are shorter than the 2.44 to 2.46 Å O···O distances found in the 'Costa' complexes, [Co((DO)(DOH)pn)R]X (Table 5) or the 2.487(2) Å mean value for cobaloximes [54] and considerably shorter than the 2.61 Å O···O distance found in the twisted [Cu(II)((DO)(DOH)bn)](ClO$_4$) complex [44].

Discussion

The bulky four-carbon bridge in the (DO)(DOH)bn equatorial ligand and the steric demands of the

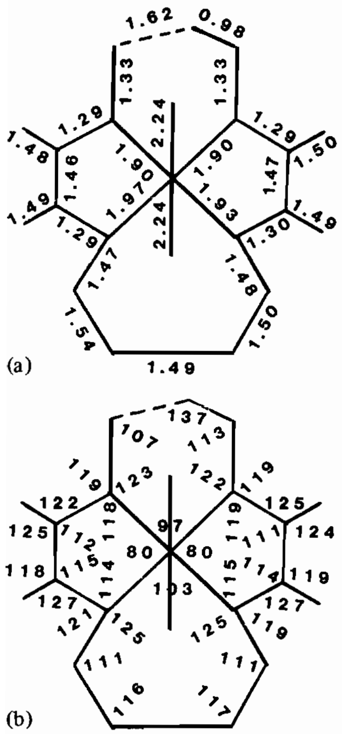


Fig. 4. Diagrams of molecule 1 of Co((DO)(DOH)bn)Cl_2 (**I**) with (a) bond lengths (Å) and (b) bond angles (°). e.s.d.s range from 0.002–0.008 Å for Co–Cl, Co–N and N–O distances, 0.01–0.02 Å for C–C distances; 0.3–0.8° for most angles, 0.7–0.9° in the four-carbon bridge.

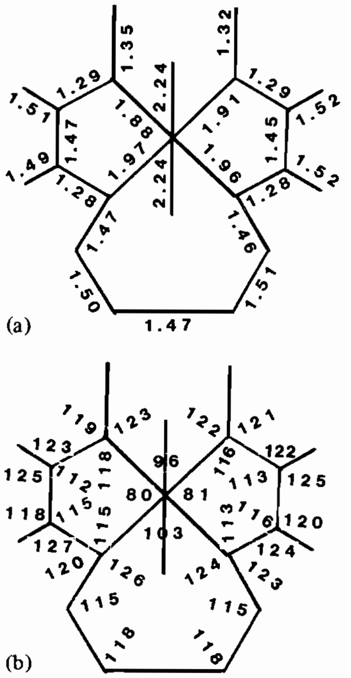


Fig. 5. Diagrams of molecule 2 of Co((DO)(DOH)bn)Cl_2 (**I**) with (a) bond lengths (Å) and (b) bond angles (°). e.s.d.s range from 0.002–0.007 Å for Co–Cl and Co–N distances, 0.009–0.02 Å for N–O and C–C distances; 0.3–0.9° for most angles, 0.8–1° in the four-carbon bridge.

axial ligands lead to several types of adjustments in the geometry of these complexes. The first steric parameter to be considered is the folding of the equatorial macrocyclic ring. Two similar planes through the diimine portions of the macrocyclic ring are chosen: plane 1 (N1, C2, C3, N2) defines the left hand side of the equatorial ligand, viewed in the orientation of Figs. 1 and 2; plane 2 (N3, C10, C11, N4) defines the right hand side of the ligand. The angle α represents the deviation from planarity of the two halves of the macrocyclic ring. The two halves of the ring may be bent upward in a V shape toward the alkyl group (positive α values), or downward, away from the alkyl ligand (negative α values). In coenzyme B_{12} the presence of the benzimidazole ligand forces the corrin ring to bend upward [38, 39]. As summarized in Table 5, the previously reported α values in model compounds have ranged from −11.3° in $[PhNH_2Co((DO)(DOH)pn)CH_3]^+$ to 14.3° in [pyCo((DO)(DOH)pn)*neo*-$C_5H_{11}]^+$. In the Co((DO)(DOH)bn)Cl_2 complex (**I**) crystal structure reported here, there are two molecules in the asymmetric unit, and thus two examples of a complex with this equatorial ligand and two identical axial ligands. In both examples the ring is buckled, at angles of 3.8° and 12.0°. Thus, the (DO)(DOH)bn equatorial ring itself seems to have a built-in tendency to fold, even without the perturbing effect of asymmetric axial ligands. This is in contrast to the (DO)(DOH)pn equatorial ligand, which is nearly flat when axial ligands are identical, in Co((DO)(DOH)pn)$(CH_3)_2$ [54]. In the $[OH_2Co((DO)(DOH)bn)CH_2CH_3]^+$ complex (**II**) reported here, the equatorial ring is bent away from the ethyl group and toward the water ligand, with an α value of −6.0°.

The complexes reported here are pictured in Figs. 1 and 2 with the four-carbon bridge 'down' as the common orientation. In this orientation methylene carbon atoms C6 and C7 extend below the plane of the four N donor atoms. In both example complexes reported here the (DO)(DOH)bn ligand bends *toward* the C6–C7 bond, even in the two independent molecules of **I**, where the axial ligands are identical. If the steric effect of the methylene groups could control ring folding, we would expect the equatorial ligand to bend away from C6 and C7 when the two axial ligands are the same.

The second type of steric adjustment in these complexes is the length of the Co–L and Co–C bonds. Steric and electronic effects from the equatorial ligand (*cis* effect) and σ-donor strength of the *trans* axial ligand both play a role [54]. The Co–C bond length in complex **II**, 2.012(6) Å, is longer than any of the Co–C distances in the methylcobalt complexes in Table 5, but slightly shorter than the Co–C dis-

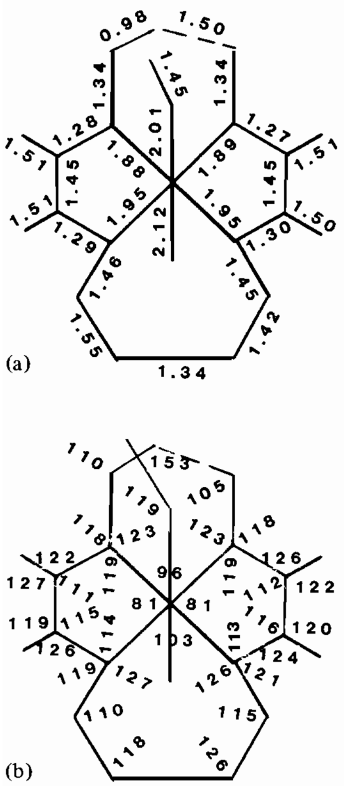


Fig. 6. Diagrams of $[OH_2Co((DO)(DOH)bn)CH_2CH_3]^+$ (II) with (a) bond lengths (Å) and (b) bond angles (°). e.s.d.s range from 0.003–0.007 Å for Co–Cl and Co–N distances, 0.006–0.009 Å for N–O and C–C distances, 0.009–0.02 Å in the four-carbon bridge; 0.2–0.6° for all angles except for 0.8–1° in the four-carbon bridge.

tances in the other ethylcobalt complexes, probably a result of water O being a weaker σ donor than the N ligands in the other ethylcobalt complexes listed. The Co–O distance in **II** is 2.119(3) Å, 0.06 and 0.02 Å longer than the Co–O distances in $OH_2Co(DH)_2CH_3$ and $[OH_2Co((EMO)(EMOH)pn)CH_3]^+$.

A third form of steric adjustment involves the bonding within the axial groups and their orientation with regard to the equatorial ligand. A space-filling model of **II** is shown in Fig. 7. The terminal carbon of the ethyl group is oriented away from the four-carbon bridge of the equatorial ligand, toward the O1–H1 bond. The Co–C15–C16 angle is widened to 119.3(5)°, and the C15–C16 bond distance is shortened to 1.445(9) Å. This shortening has been noted in other alkylcobalt complexes with a widened Co–C–C angle [50]. Salient features of the geometry of complexes **I** and **II** are compared in Scheme 3.

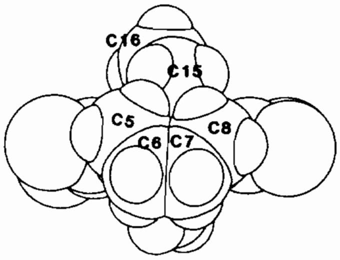
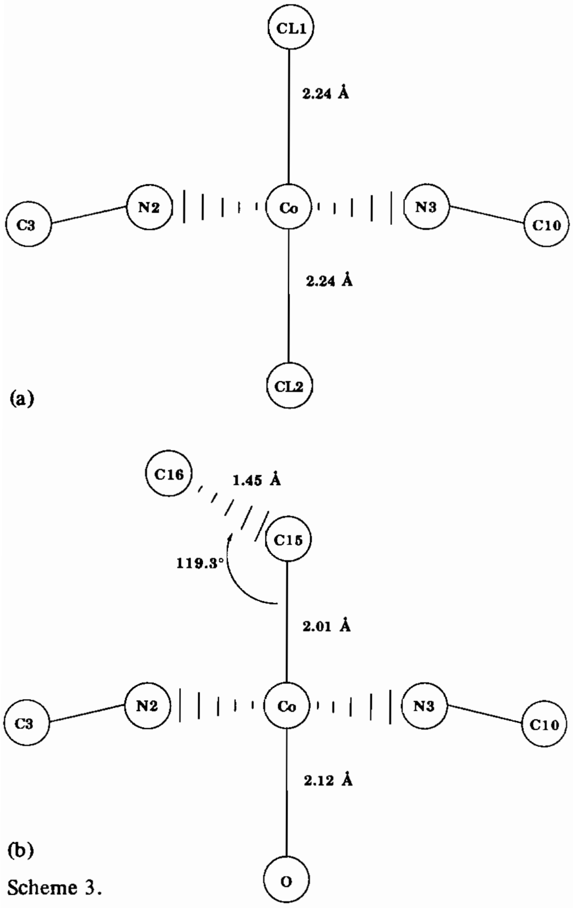


Fig. 7. Space-filling model at the van der Waals radius of **II**, showing steric interactions between H atoms on C5 and C8 of the seven-membered chelate ring, and C15 of the alkyl ligand.

TABLE 5. Comparison of structural parameters[a] of organocobalt complexes

Complex	Co–C	Co–C–C	(Co–)C–C	Co–L	O–O	α [a]	d [a]	Reference
$[OH_2Co((DO)(DOH)bn)CH_2CH_3]^+$	2.012(6)	119.3(5)	1.445(9)	2.119(3)	2.412(4)	−6.0	−0.02	this work
$Co((DO)(DOH)bn)Cl_2$				2.239(2) 2.243(2)	2.42(1)	−3.8	−0.01	this work
				2.236(2) 2.238(2)	2.390(9)	−12.0	−0.01	this work
Methylcobalamin	1.99			2.19		15.8[b]		39
Adenosylcobalamin	2.03(2)	125		2.24		14.6[b]	−0.016	38
$OH_2Co(DH)_2CH_3$	1.990(5)			2.058(3)		−4.0	0.	49
$py2NH_26NH_2Co(DH)_2CH_2CH_3$	2.025(3)	121.0(3)	1.434(6)	2.156(3)		4.0	0.01	50
$mpyimCo(DH)_2CH_2CH_3$	2.035(5)	117.8(4)	1.519(8)	2.081(3)		9.1	0.05	51
$[OH_2Co((EMO)(EMOH)pn)CH_3]^+$	1.977(4)			2.103(3)	2.445(5)	2.0	0.01	52
$[pyCo((DO)(DOH)pn)CH_3]^+$	2.003(3)			2.106(3)	2.457(4)	6.9	0.07	49
$[PhNH_2Co((DO)(DOH)pn)CH_3]^+$	1.991(4)			2.147(3)	2.441(5)	−11.3	0.	46
$[PhNH_2Co((DO)(DOH)pn)$-$CH_2CH_3]^+$	2.030(4)	118.7(3)		2.174(3)	2.453(4)	−7.1		53
$[pyCo((DO)(DOH)pn)$*neo*-$C_5H_{11}]^+$	2.083(4)	130.4(3)		2.121(3)		14.3	0.03	49

[a] Distances in Å, angles in degrees. Positive value of α indicates that the bending of the equatorial ligand is toward the alkyl group (or toward CL1/CL1′); positive value of d indicates that the displacement of Co is out of the N4 equatorial donor set toward L or toward CL2/CL2′). [b] Folding angle defined in refs. 38 and 39.



Scheme 3.

The new ethylcobalt complex (**II**) described in this report is similar to coenzyme B_{12} in that there is an equatorial ligand with a 'built-in' fold, and in the steric adjustments produced by the folded equatorial ligand. In **II** as in the coenzymes B_{12}, the axial Co–C15 and Co–O3 bonds are lengthened and the Co–C15–C16 angle is widened. These observed bond distortions support a steric mechanism [37, 42, 50, 55] for the weakening of the Co–C bond in the coenzymes prior to homolysis.

Supplementary Material

Hydrogen atom positions and thermal parameters, anisotropic thermal parameters of the non-hydrogen atoms, calculation of the least-squares planes and lists of the calculated and observed structure factors are available from the authors on request.

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