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An ethyl–cobalt complex with a buckled equatorial ligand

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Abstract

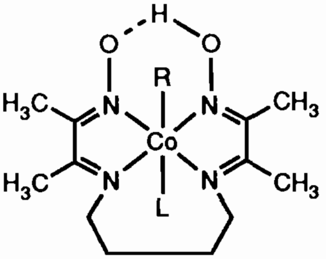
The synthesis and structure are reported for [(imidazole)Co{(DO)(DOH)bn}(ethyl)]ClO_4 (I), where R = ethyl, L = imidazole and (DO)(DOH)bn is the equatorial ligand $N^2,N^{2'}$-butanediylbis(2,3-butanedione 2-imine 3-oxime). The molecule contains a Co–C bond *trans* to an imidazole N donor atom, and a macrocyclic tetraimine equatorial ligand with a 'built-in' fold, features which are similar to those of coenzyme B_{12}. The crystal structure belongs to the monoclinic system, space group *Pc*, with $a = 11.839(2)$, $b = 13.151(3)$, $c = 15.048(3)$ Å, $\beta = 101.13(2)°$, $Z = 4$, $R_w = 0.078$. There are two molecules in the asymmetric unit, which show some interesting variations in structure. In both molecules the four-carbon bridge in the equatorial (DO)(DOH)bn ligand bends toward the imidazole ligand. The equatorial ligand is folded or buckled toward the ethyl ligand in both molecules, but the fold angles are different: 4(1) and 9(1)°. The four-carbon bridge in the equatorial ligand forms part of an unusual seven-membered chelate ring, which is flattened in one molecule and twisted in the other.

Key words: Crystal structures; Cobalt complexes; Alkyl complexes; Multidentate ligand complexes; Chelate complexes

Introduction

The B_{12} coenzyme (adenosylcobalamin) is a naturally occurring organometallic compound, containing a cobalt–carbon bond [1]. Homolytic cleavage [2] of the relatively weak Co–C bond initiates the free radical rearrangement of substrate. Steric factors in the coenzyme itself, such as the folding of the corrin ring [3] and the bulk of the axial dimethylbenzimidazole and adenosyl ligands [4], weaken [2b] the Co–C bond and thus may produce a more reactive cofactor.

In order to clarify the mechanism of B_{12} catalysis, the structural, thermodynamic and kinetic properties of model compounds have been studied. Steric crowding does lengthen and weaken the Co–C bond in cobaloximes [5]. Spectral measurements [6] combined with bond dissociation energies [7] suggest that transition state electronic effects as well as ground state steric effects are important. Complexes of the equatorial ligand (DO)(DOH)pn [8] and similar ligands (EMO)(EMOH)pn [9] and (DO)(DOH)Me_2pn [10], which have a propyl bridge between two dimethylglyoximato groups, appear to provide good models for the electrochemical properties of coenzyme B_{12} since these ligands have the same −1 formal charge as the corrin ring [11].



I

The equatorial ligand (DO)(DOH)bn with a butyl bridge between two dimethylglyoximato groups, also has a −1 formal charge. Moreover, the seven-membered chelate ring formed by the tetramethylene bridge causes a natural buckling or folding of this equatorial ligand, an appropriate feature for modeling the butterfly conformation of the corrin ring in B_{12} coenzyme [3]. The crystal structure of I where R = ethyl and L = OH_2 has been previously reported [12]; in this paper we describe the crystal structure of I with R = ethyl and L = imidazole.

Experimental

Reagents

All chemicals were reagent grade: 1,4-diaminobutane and 2,3-butanedione monoxime, Aldrich; $CoCl_2 \cdot 6H_2O$,

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ethyl iodide, Fisher; $NaBH_4$, Mallinckrodt. All solvents were reagent grade.

Synthesis of [(imidazole)Co{(DO)(DOH)bn}(ethyl)]-ClO_4

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.

The equatorial ligand, $N^2,N^{2'}$-butanediylbis(2,3-butanedione 2-imine 3-oxime), ($(DOH)_2bn$), and the corresponding Co(III) complex, $Co^{III}((DO)(DOH)bn)Cl_2$, were prepared as previously described [12]. $Co^{III}((DO)(DOH)bn)Cl_2$ (0.47 g, 1 mmol) was stirred in a deaerated mixture of 45 ml methanol and 0.34 g (5 mmol) imidazole in a 200 ml pear flask. (If present in large quantities, OH_2 will substitute instead of the imidazole ligand.) Ar was bubbled through the mixture for 15 min while the complex dissolved, then CH_3CH_2I (0.25 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_3CH_2I 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 MeOH 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. Reddish orange X-ray quality crystals were obtained from 2:1 acetone/pentane. *Anal.* Calc. for $C_{17}H_{30}N_6ClCoO_6$: C, 40.21; H, 5.76; N, 16.55; Cl, 6.98; Co, 11.60; O, 18.90. Found (analyzed for all elements): C, 38.91; H, 5.68; N, 16.18; Cl, 6.91; Co, 10.75; O, 20.85%. (The results suggest slight contamination from perchlorate, a common problem.)

X-ray methods

Crystals were mounted on glass fibers. Preliminary space group and lattice constants were obtained from Weissenberg photographs. Final cell parameters (Table 1) were obtained by a least-squares analysis of 16 centered reflections $11 < 2\theta < 30°$ obtained from diffractometer measurements.

Data were collected on a Siemens-Nicolet P3m four-circle diffractometer by means of an ω-scan at a variable speed (1.0–58.6° min^{-1}) depending upon intensity; scan:background time ratio was 0.5. Four check reflections measured every 100 reflections showed no decay in intensity. The data were corrected for Lorentz and polarization factors; an empirical absorption correction (ranging from 1.0 to 0.77) as a function of ϕ was applied using intensity data from a 72-step ψ-scan.

TABLE 1. Crystal data for [(imidazole)Co{(DO)(DOH)bn}-(ethyl)]ClO_4

Molecular formula	$C_{17}H_{30}N_6ClCoO_6$
Formula weight	508.85
$F(000)$	1064
Space group	*Pc*
Z	4
a (Å)	11.839(2)
b (Å)	13.151(3)
c (Å)	15.048(3)
β (°)	101.13(2)
V (Å^3)	2298.8(8)
D_x (g ml^{-1})	1.47
D_{meas} (flotation) (g ml^{-1})	1.49
Radiation, λ (Å)	Mo Kα (0.71069)
μ (cm^{-1})	9.035
Crystal size (mm)	$0.20 \times 0.22 \times 0.45$
Temperature (K)	298
Max. 2θ (°) ($\sin \theta/\lambda$ Å^{-1})	60.0 (0.7046)
Collection range, *hkl*	± 16, $0-18$, $0-21$
No. measured data	6970
No. unique data	6733
No. observed data, n	5196 with $F > 3.0\sigma(F)$
No. variables refined, p	491
Highest peak $F_o - F_c$ map (e Å^{-3})	1.377
Final $R = \Sigma \| F_o - F_c \| / \Sigma \| F_o \|$	0.086
Final $R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma w \|F_o\|^2]^{1/2}$	0.078
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	0.91
Weighting coefficients $A_{q-l,l}$	-2.7998
	0.7012
	14.7054
	0.0010
	-1.8672
	-2.0984

Although systematic absences in Weissenberg photographs were consistent with space group $P2_1/c$, the E statistics from the diffractometer data indicated a non-centrosymmetric space group. The cobalt atom positions were located in a Patterson map and have a higher symmetry than the complete structure. The other non-hydrogen atoms were found in difference Fourier maps for space group *Pc*, with two molecules in the asymmetric unit exhibiting two quite different conformations of the equatorial ligand. The atomic positions and anisotropic thermal parameters of all non-hydrogen atoms were refined on F by a full matrix least-squares procedure [13]. The quantity minimized was $\Sigma w[|F_o| - |F_c|]^2$ where the weights, $w = 1/\sigma_F{}^2$. For most of the refinement $\sigma_F{}^2 = (F/2)[\sigma^2(I)/(I)^2 + \delta^2]^{1/2}$, where $\sigma(I)$ were calculated from analysis of background and peak intensities and δ (0.025) is an instrumental uncertainty determined from the variation in the intensity of the check reflections. For final refinement an additional term was added to $\sigma_F{}^2$:

$$\langle \sigma_m{}^2 \rangle = \sum_{q=0}^{5} \sum_{l=0}^{q} A_{q-l,l} V_\theta{}^{q-l} V_F{}^l$$

where $V_\theta = \sin\theta/\sin\theta_{max}$, $V_F = |F_o|/|F_o|_{max}$ and the A coefficients were determined by a least-squares method [14]. (Values of A are given in Table 1.) Due to disorder, perchlorate anions were treated as rigid groups with Cl–O distances of 1.40 Å and tetrahedral angles; the position and orientation of these rigid groups were refined, as well as individual isotropic thermal parameters for Cl and O atoms. In the final difference Fourier map, the two highest peaks were located less than 1 Å from the chlorine atoms. Correction for anomalous scattering was applied. The H atom which closes the macrocyclic ring by forming an H bond between the two dimethylglyoximato oxygen atoms was found in the difference Fourier map in molecule 1, but not in molecule 2. Most of the other H atom positions were calculated (C–H distance 1.0 Å). Isotropic H atom positions were not refined, but were included in the structure factor calculation. No extinction correction was applied.

Final positions and equivalent isotropic thermal parameters of the non-hydrogen atoms are tabulated in Table 2. See also 'Supplementary material'.

Results and discussion

The atom numbering scheme and anisotropic thermal parameters for molecule 1 are shown graphically in Fig. 1. The Co(III) ion in [(imidazole)Co{(DO)(DOH)bn}(ethyl)]$^+$ is octahedrally coordinated to four imine N donor atoms from the equatorial ligand, one imidazole N atom, and a carbon atom from the ethyl ligand. The macrocyclic equatorial ligand, (DO)(DOH)bn, is closed by a hydrogen bond between the two dimethylglyoximato oxygen atoms. The four-carbon bridge between the two dimethylglyoximato groups is part of a seven-membered chelate ring formed by Co1, N12, C15, C16, C17, C18 and N13. This chelate ring assumes a 'flip' [12] conformation as in the [(OH$_2$)Co{(DO)(DOH)bn}(ethyl)]$^+$ complex, with the two carbon atoms C16 and C17 bent down toward the imidazole ring.

The imidazole rings of the two independent molecules in the asymmetric unit are joined by hydrogen bonds with the two ClO_4^- anions (Fig. 2). The H atoms covalently bonded to N16 and N26 of the two imidazole rings form bifurcated hydrogen bonds to O13 and O23 of the anions. Because of the hydrogen bonding to N16 and N26, the imidazole rings in the two molecules are oriented in opposite directions relative to the equatorial ligand. However, in both molecules the plane of the imidazole ring bisects the diimine chelate rings as shown in Fig. 3. This orientation of the imidazole ring appears to result from the steric effect of the carbon atoms in the butane bridge of the equatorial ligand.

TABLE 2. Fractional atomic coordinates and equivalent isotropic displacement coefficients for the non-hydrogen atoms of [(imidazole)Co{(DO)(DOH)bn}(ethyl)]ClO_4

Atom	x	y	z	U_{eq}[a]
Co(1)	0.164(2)	−0.0524(1)	0.233(1)	0.0464(4)
N(11)	0.049(2)	−0.0931(8)	0.299(1)	0.067(3)
N(12)	0.031(2)	0.0260(8)	0.169(1)	0.070(3)
N(13)	0.284(2)	−0.0240(8)	0.167(1)	0.066(3)
N(14)	0.279(2)	−0.1348(8)	0.300(1)	0.070(3)
N(15)	0.216(2)	0.0616(6)	0.325(1)	0.049(2)
N(16)	0.324(2)	0.1702(7)	0.414(1)	0.063(3)
O(11)	0.073(2)	−0.1554(8)	0.372(1)	0.101(4)
O(12)	0.269(2)	−0.1906(8)	0.371(1)	0.100(4)
C(11)	−0.146(2)	−0.085(2)	0.324(2)	0.118(8)
C(12)	−0.053(2)	−0.057(1)	0.276(2)	0.073(4)
C(13)	−0.062(2)	0.008(1)	0.203(2)	0.067(4)
C(15)	0.033(3)	0.083(3)	0.093(2)	0.16(1)
C(16)	0.103(5)	0.168(2)	0.097(3)	0.21(2)
C(17)	0.227(4)	0.157(1)	0.111(2)	0.18(1)
C(18)	0.273(2)	0.045(2)	0.087(1)	0.097(6)
C(110)	0.378(2)	−0.070(1)	0.195(2)	0.075(4)
C(111)	0.382(2)	−0.134(1)	0.273(2)	0.079(5)
C(112)	0.480(2)	−0.201(1)	0.317(2)	0.122(8)
C(113)	−0.176(2)	0.061(2)	0.167(2)	0.109(6)
C(114)	0.488(2)	−0.066(2)	0.158(2)	0.116(8)
C(115)	0.109(2)	−0.170(1)	0.146(2)	0.073(4)
C(116)	0.144(2)	−0.274(1)	0.175(2)	0.101(6)
C(117)	0.146(2)	0.129(1)	0.362(2)	0.072(4)
C(118)	0.215(2)	0.196(1)	0.416(2)	0.075(4)
C(119)	0.321(2)	0.090(1)	0.359(1)	0.061(4)
Co(2)	0.831(2)	0.5615(1)	0.777(1)	0.0465(4)
N(21)	0.756(2)	0.6463(7)	0.682(1)	0.059(3)
N(22)	0.683(2)	0.5769(7)	0.814(1)	0.060(3)
N(23)	0.914(2)	0.4707(6)	0.871(1)	0.052(2)
N(24)	0.977(2)	0.5649(7)	0.746(1)	0.053(2)
N(25)	0.784(2)	0.4374(7)	0.696(1)	0.052(3)
N(26)	0.678(2)	0.3258(8)	0.608(1)	0.062(3)
O(21)	0.807(2)	0.6799(7)	0.617(1)	0.073(3)
O(22)	0.997(2)	0.6181(7)	0.673(1)	0.077(3)
C(21)	0.579(2)	0.734(1)	0.607(2)	0.095(5)
C(22)	0.648(2)	0.6691(9)	0.681(1)	0.067(3)
C(23)	0.609(2)	0.6308(9)	0.758(1)	0.061(3)
C(25)	0.664(2)	0.549(1)	0.904(1)	0.067(3)
C(26)	0.649(2)	0.432(1)	0.915(2)	0.084(5)
C(27)	0.743(2)	0.371(1)	0.900(1)	0.072(4)
C(28)	0.867(2)	0.4109(9)	0.937(1)	0.069(3)
C(210)	1.022(2)	0.4656(7)	0.870(1)	0.056(3)
C(211)	1.062(2)	0.5216(9)	0.797(1)	0.059(3)
C(212)	1.181(2)	0.526(1)	0.783(2)	0.089(5)
C(213)	0.487(2)	0.650(1)	0.772(2)	0.092(5)
C(214)	1.108(2)	0.402(1)	0.936(2)	0.082(4)
C(215)	0.878(2)	0.690(1)	0.847(2)	0.075(4)
C(216)	0.950(2)	0.6848(9)	0.937(1)	0.076(4)
C(217)	0.851(2)	0.360(1)	0.675(2)	0.076(4)
C(218)	0.788(2)	0.293(1)	0.622(2)	0.075(4)
C(219)	0.678(2)	0.4151(9)	0.652(2)	0.063(4)
Cl(1)	0.638(2)	0.0963(2)	0.430(1)	0.0625(5)
O(13)	0.582(2)	0.1775(5)	0.464(1)	0.086(2)
O(14)	0.757(2)	0.1018(7)	0.464(1)	0.098(3)
O(15)	0.618(2)	0.1017(6)	0.335(1)	0.124(4)
O(16)	0.595(2)	0.0042(4)	0.456(1)	0.130(4)
Cl(2)	0.375(2)	0.4184(2)	0.558(1)	0.0667(6)
O(23)	0.429(2)	0.3293(4)	0.537(1)	0.126(4)
O(24)	0.256(2)	0.4101(8)	0.526(1)	0.088(2)
O(25)	0.417(2)	0.5016(5)	0.516(1)	0.22(1)
O(26)	0.396(2)	0.4328(8)	0.652(1)	0.138(5)

[a] Equivalent isotropic U_{eq} (Å^2) defined as one third of the trace of the orthogonalized U_{ij} tensor.

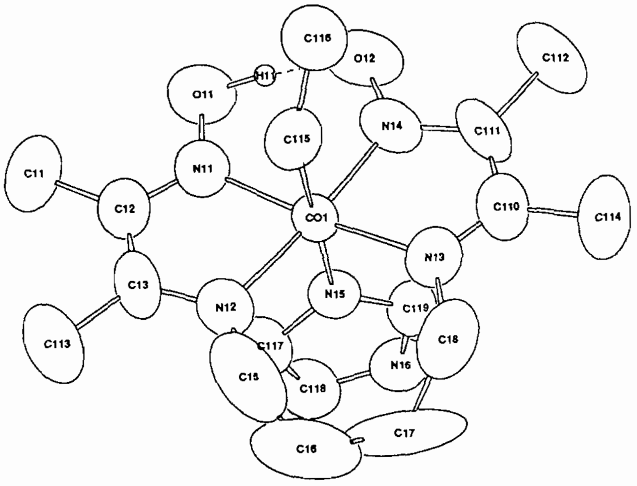

Fig. 1. An ORTEP view of the [(imidazole)Co{(DO)(DOH)bn}(ethyl)]$^+$ cation (molecule 1), showing thermal ellipsoids at the 50% probability level. The oxime H atom which closes the equatorial ligand with a hydrogen bond is shown; other H atoms have been omitted for clarity.

Bond lengths and bond angles for the two independent molecules in the asymmetric unit are shown in Figs. 4 and 5. The Co–C bond lengths in the two molecules are similar to the 2.03(2) Å length in coenzyme B_{12} [4a], although the axial Co–N distance is considerably shorter than the 2.24 Å distance in the coenzyme. The Co–C$_\alpha$–C$_\beta$ angles are larger than the normal tetrahedral angle, and the C–C bond distances in the ethyl ligand are contracted relative to the normal single bond distance.

As in the other complexes of this series, the macrocyclic equatorial ring is folded*. The two halves of the ring may be bent upward in a V shape toward the alkyl group (positive α value) or downward, away from the alkyl ligand (negative α value). In the [(OH$_2$)Co{(DO)(DOH)bn}(ethyl)]$^+$ complex, α was -6.0 and the (DO)(DOH)bn ligand was bent downward toward the water ligand [12]. In the [(imidazole)Co{(DO)(DOH)bn}(ethyl)]ClO$_4$ structure the values of α are 4(1) and 9(1)°, showing that the equatorial ligand is bent upward (Fig. 6) toward the alkyl group in both molecules, but to a significantly different degree.

The high thermal factors of carbon atoms of the butyl bridge (C15–C18, C25–C28) indicate positional disorder in this part of the molecule. The crystal structure may, in fact, indicate the dynamic characteristics of the complex in solution. The two different molecules in the asymmetric unit show 'snapshots' of two different conformations for the molecule. As shown in Fig. 3, the alkyl ligand is oriented in two different ways in the two independent molecules: in molecule 1 the alkyl ligand lies over N14; in molecule 2 the ethyl group lies over N13. The orientation of the alkyl

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*Two similar planes through the diimine portions of the macrocyclic ring are chosen: plane 1 (N11, C12, C13, N12) and plane 2 (N13, C110, C111, N14). The angle α represents the deviation from planarity of the two halves of the macrocyclic ring.

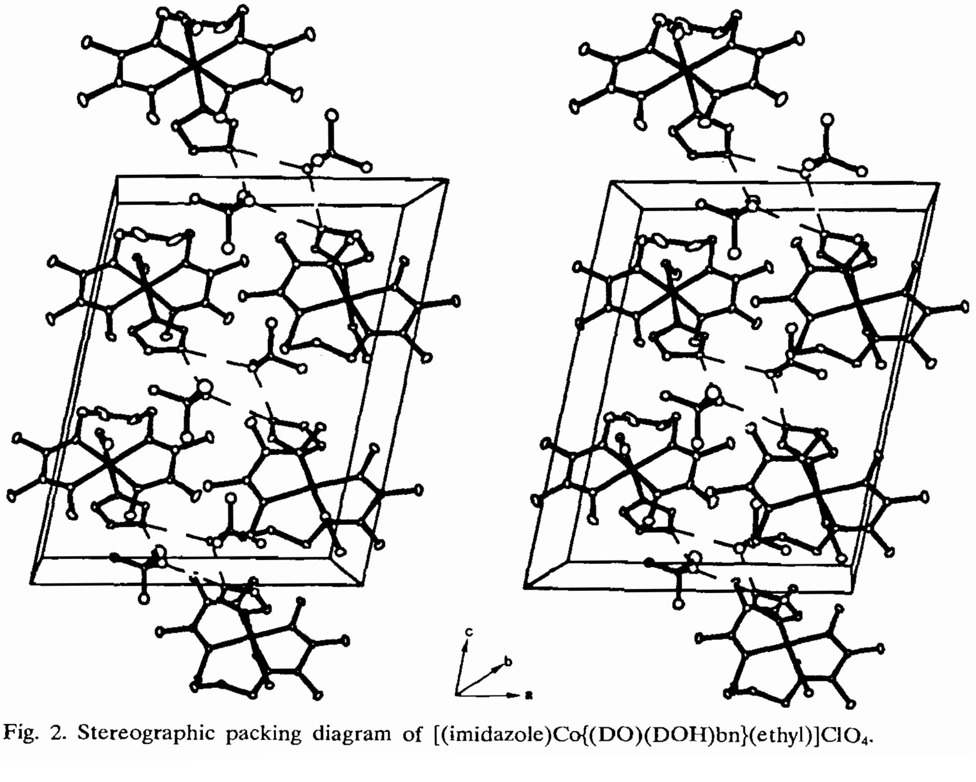

Fig. 2. Stereographic packing diagram of [(imidazole)Co{(DO)(DOH)bn}(ethyl)]ClO$_4$.

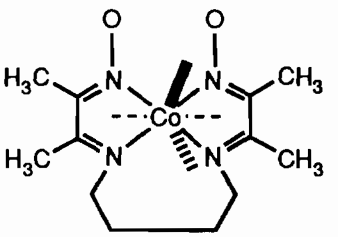

Fig. 3. Orientation of the alkyl ligand in the two molecules of [(imidazole)Co{(DO)(DOH)bn}(ethyl)]ClO$_4$. The molecule is viewed down the C–Co bond. The plane of the imidazole ligand is shown as a dashed line.

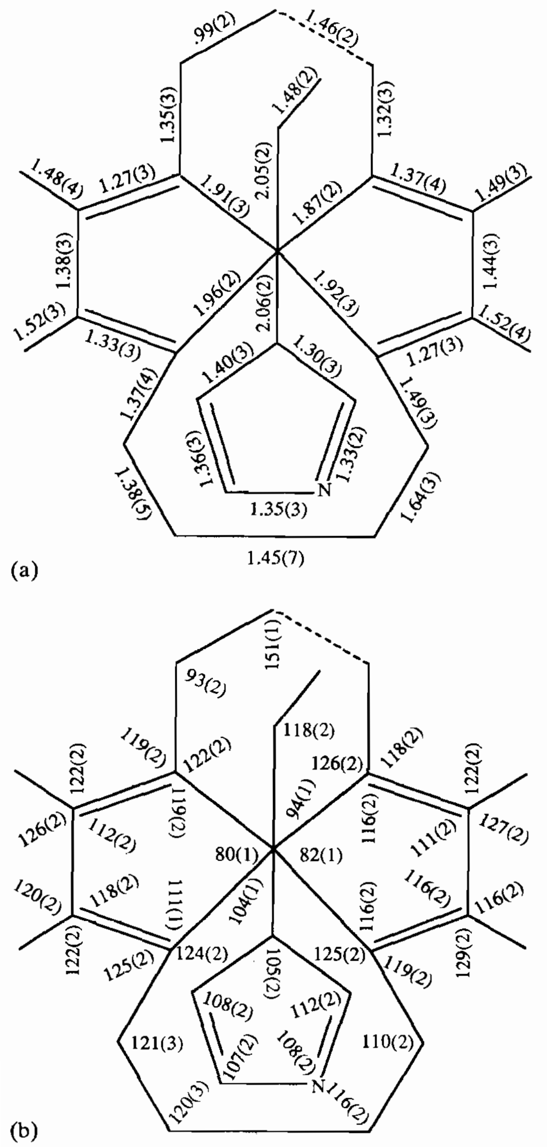

Fig. 4. Diagrams of molecule 1 of [(imidazole)Co-{(DO)(DOH)bn}(ethyl)]ClO$_4$ showing (a) bond lengths and (b) angles, with e.s.d.s of the least significant digits given in parentheses.

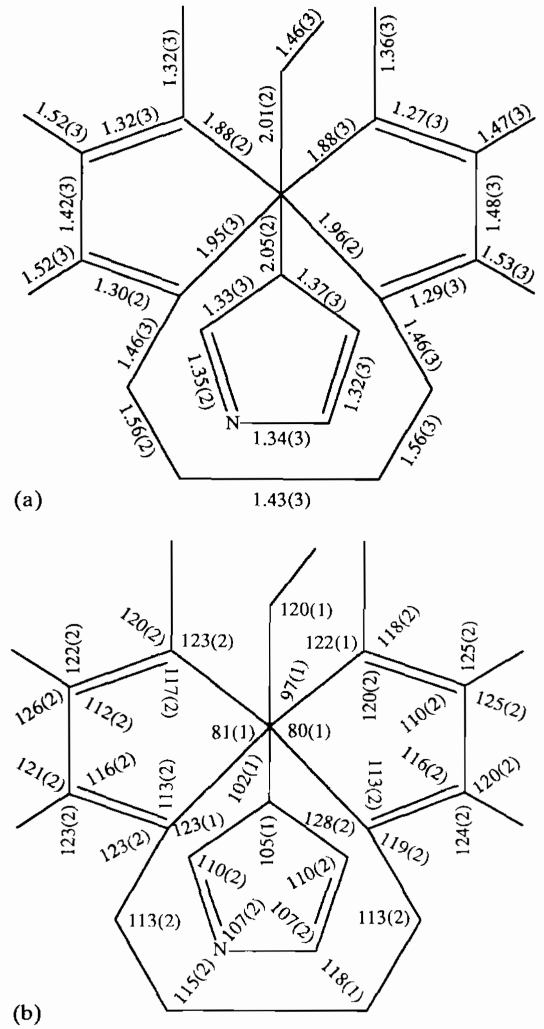

Fig. 5. Diagrams of molecule 2 of [(imidazole)Co{(DO)-(DOH)bn}(ethyl)]ClO$_4$ showing (a) bond lengths and (b) angles, with e.s.d.s of the least significant digits given in parentheses.

ligand appears to be related to the twist of the seven-membered chelate ring of the equatorial ligand. In molecule 1, the atoms Co1, N12, N13, C15 and C18 are coplanar within ±0.04(4) Å. In molecule 2, C28 is pushed below the equatorial plane by 0.28(3) Å, away from the alkyl ligand which is oriented above it, and C25 is twisted up above the equatorial plane by 0.45(3) Å.

Supplementary material

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

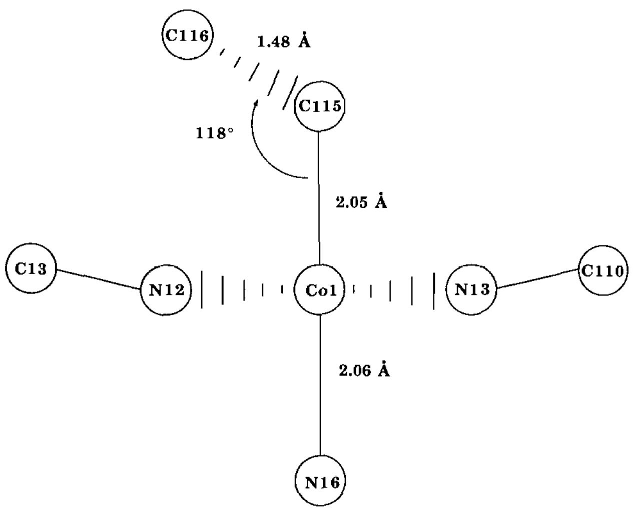

Fig. 6. Buckling or folding of the equatorial ligand in [(imidazole)Co{(DO)(DOH)bn}(ethyl)]ClO_4. The fold angles are 4(1) and 9(1)° in the two molecules in the asymmetric unit.

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