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***trans*-Cyano(6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine)-cobalt(III) bis(perchlorate) hydrate and *trans*-hydroxo(6-methyl-1,4,8,11-tetraazacyclotetradecan-6-amine)-cobalt(III) bis(perchlorate)**

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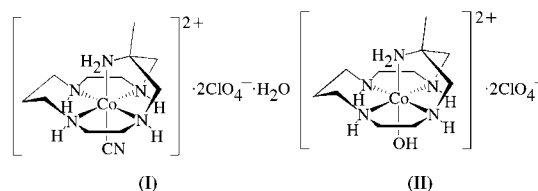
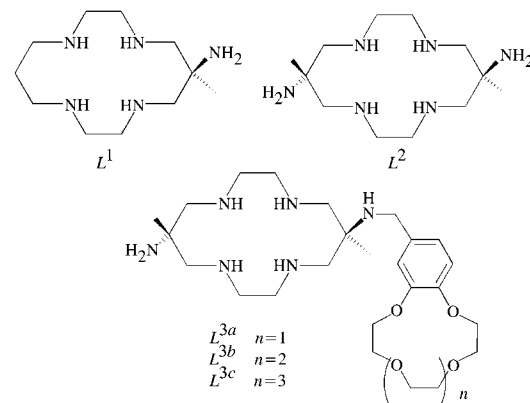
The crystal structures of a pair of closely related macrocyclic cyano- and hydroxopentaaminecobalt(III) complexes, as their perchlorate salts, are reported. Although the two complexes, $[\text{Co}(\text{CN})(\text{C}_{11}\text{H}_{27}\text{N}_5)](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and $[\text{Co}(\text{OH})(\text{C}_{11}\text{H}_{27}\text{N}_5)](\text{ClO}_4)_2$, exhibit similar conformations, significant differences in the Co–N bond lengths arise from the influence of the sixth ligand (cyano as opposed to hydroxo). The ensuing hydrogen-bonding patterns are also distinctly different. Disorder in the perchlorate anions was clearly resolved and this was rationalized on the basis of distinct hydrogen-bonding motifs involving the anion O atoms and the N–H and O–H donors.

Comment

The pendant amino-substituted cyclam 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine (L^1) has the capability of binding as a pentadentate ligand *via* its four secondary amine and single primary amine N-donors. The ligand may coordinate in a folded (*cis*) (Lawrance *et al.*, 1992) or planar (*trans*) configuration (Hambley *et al.*, 1992). Within the *trans* form, there are two possible N-based isomeric forms, *viz.* *RSRS* (*trans*-I) (Bernhardt *et al.*, 2000), with all amine H atoms on the same side of the macrocyclic plane, and *RRSS* (*trans*-III) (Hambley *et al.*, 1992), with two H atoms up and two down. In six-coordinate complexes of L^1 , the *trans*-I form has been most commonly encountered in complexes bearing the $[\text{CoL}^1]$ moiety (Bernhardt *et al.*, 2000, 2002).

The related hexamine L^2 may bind in a hexadentate (Bernhardt *et al.*, 1989, 1991; Bernhardt, Comba *et al.*, 1990), pentadentate (Bernhardt, Lawrance, Comba *et al.*, 1990; Curtis *et al.*, 1993) or tetradentate (Curtis *et al.*, 1992; Bernhardt, Lawrance, Patalinghug *et al.*, 1990) mode, depending on the protonation state of the pendant amines and the preferred coordination geometry of the metal ion. When bulky substi-

tuent are attached to one of the pendant amines of L^2 (e.g. L^{3a-c}), coordination of the substituted amine is disfavoured on steric grounds (Bernhardt & Hayes, 2002). Pentadentate coordination by ligands such as L^{3a-c} has obvious parallels with the chemistry of L^1 .



In this work, we report the crystal structures of *trans*- $[\text{CoL}^1\text{CN}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, (I), and *trans*- $[\text{CoL}^1\text{OH}](\text{ClO}_4)_2$, (II), where both complexes are in the *trans*-I configuration. These structures represent rare examples of structurally characterized cyano- and hydroxopentaaminecobalt(III) complexes.

The structure of (I) (Fig. 1) reveals the expected scorpionate conformation of the macrocyclic ligand, with the pendant amine tail coordinating above the CoN_4 plane and *trans* to the cyano ligand. The *trans*-I N-based isomer is apparent. As expected, the Co–CN coordinate bond is the shortest (Table 1). The four secondary amine coordinate bonds are similar, and the Co–N bond to the pendant amine is significantly longer. For comparison, in all other high-resolution crystal structures of Co^{III} complexes containing the

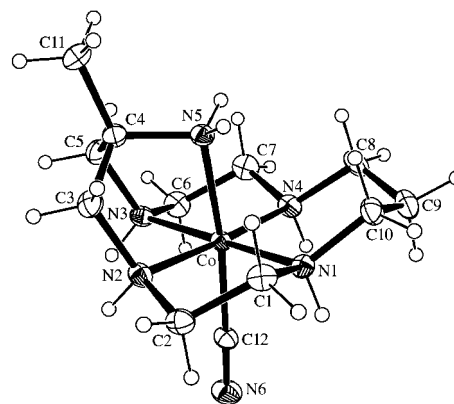


Figure 1

A view of the complex cation in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

pentadentate-coordinated L^1 moiety, including derivatives such as L^{3a-c} , the five Co—N bonds lie within a relatively narrow range (1.94–1.96 Å). In (I), there is a significant increase in the average Co—N bond length; upon closer inspection, the four in-plane Co—N bonds span the range 1.956 (3)–1.975 (3) Å, while the bond to the pendant amine is significantly longer [1.990 (2) Å]. This axial elongation may be attributed to the *trans* influence of the cyano ligand, as no significant differences between the bond lengths involving the secondary or primary amines have been seen in chloro (Bernhardt *et al.*, 2000; Bernhardt & Macpherson, 2003), N-bound ferrocyanide (Bernhardt *et al.*, 2000) or ferricyanide (Bernhardt *et al.*, 2002) complexes bearing the $[\text{Co}L^1]$ moiety. Furthermore, in $\text{Na}[\text{Co}L^{3b}\text{CN}](\text{ClO}_4)_3$, the only other cyanopentaamminecobalt(III) complex to be structurally characterized to date, a similar *trans* influence of the cyano ligand on the pendant amine coordinate bond length [2.001 (5) Å] was observed (Bernhardt & Hayes, 2002).

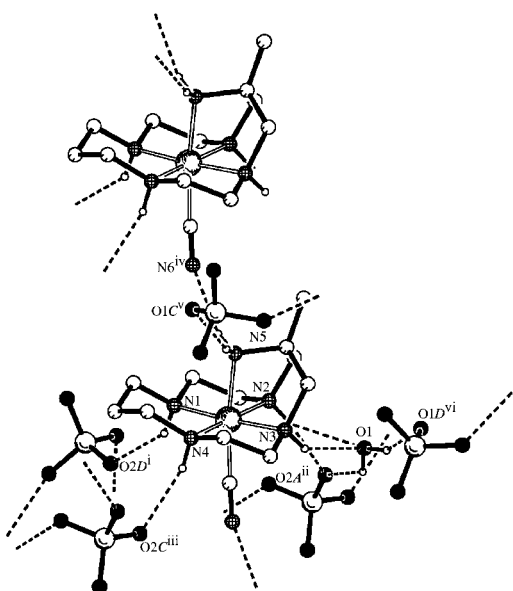


Figure 2
 A plot of the hydrogen bonding in (I). Alkyl H atoms have been omitted. See Table 2 for symmetry codes.

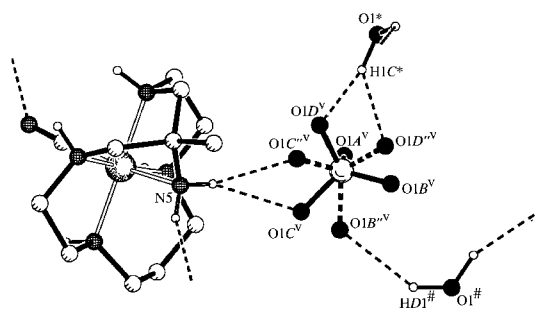


Figure 3
 A plot of the perchlorate disorder in (I). Alkyl H atoms have been omitted. See Table 2 for the perchlorate symmetry code. Atoms labelled with an asterisk (*) are at the symmetry position $(1 - x, \frac{1}{2} + y, 1 - z)$ and atoms labelled with a hash sign (#) are at the symmetry position $(x - 1, y + 1, z)$.

Hydrogen bonding is a feature of the structure of (I) (Fig. 2). The complex cations are arranged into a linear polymeric hydrogen-bonded array, with the pendant amino group as donor and the cyano ligand as acceptor (Table 2). All remaining N—H groups participate in hydrogen bonds to either the perchlorate anions or the water molecule. Of note is the bifurcated hydrogen bond formed between the water atom O1 and the pair of adjacent secondary amines (N2 and N3).

Disorder in the positions of perchlorate atoms O1B, O1C and O1D (O1B', O1C' and O1D') was resolved and two distinct orientations of the anion were identified, related by a *ca* 70° rotation of the anion about the C11—O1A bond. The complementary occupancies of the two contributors were 83 and 17%, and no geometric restraints were used in the refinement. The hydrogen bonds present in these two orientations are illustrated in Fig. 3. In the major contributor, atoms O1C and O1D participate in strong hydrogen-bonding interactions with the pendant amine and the water molecule (Table 2). Although these two interactions remain in the alternate minor orientation, they are somewhat more acute and hence weaker. To compensate for this misalignment, the minor contributor gains an extra hydrogen bond, with atom O1B' as acceptor for a water molecule, whereas atom O1B has no partner in the major form.

The structure of (II) (Fig. 4) has also been determined. The conformation of the macrocycle is identical to that seen in (I), but the Co—N bond lengths (Table 3) now lie within the normal range for Co^{III} complexes of L^1 and pentadentate-coordinated L^2 , and the Co—N5 bond length is not particularly long.

Substitution of cyano (a hydrogen-bond acceptor) with hydroxo (both a donor and an acceptor) results in a quite different hydrogen-bonding pattern for (II) (Fig. 5). Unlike the polymeric hydrogen-bonded chain seen in (I), the cations in (II) form centrosymmetric dimers, with the hydroxo O atom of one cation participating in a bifurcated hydrogen bond with the secondary amine groups N2 and N3 on an adjacent complex (Table 4). This motif is reminiscent of that seen in (I), where the water molecule plays the role of acceptor in place of

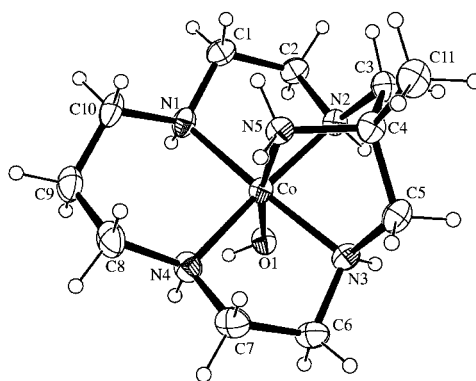


Figure 4
 A view of the complex cation in (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

the hydroxo ligand. All other amine H atoms (except that attached to N1) and the hydroxo ligand participate in hydrogen bonding with the perchlorate anions.

Disorder was identified in both perchlorate anions in (II) (O1B/O1C/O1D and O1B''/O1C''/O1D'', and O2B/O2C/O2D and O2B''/O2C''/O2D''). The contributors were again refined with complementary occupancies (91 and 9%) without geometrical restraints. The two contributors (Fig. 6) to disorder in anion 1 are related by a *ca* 40° rotation about C11—O1A. In the major orientation, atoms O1B and O1D accept strong hydrogen bonds from N4—H4 and O1—H1C. In the minor contributor, only atom O2D'' is hydrogen bonded, in a bifurcated motif with both N4—H4 and O1—H1C. Anion 2 bridges the pendant amines of adjacent cations. Rotation about C12—O2A, again by *ca* 40°, generates the two contributors, each of which forms a pair of hydrogen bonds of similar strength to two different complex cations.

In conclusion, some interesting variations in the structures of two closely related macrocyclic pentaamine complexes of Co^{III} have been identified. Introduction of a cyano ligand into the sixth coordination site, (I), leads to a lengthening of the Co—N bonds and a significant extension of the Co—N bond *trans* to the cyano ligand. By comparison, the coordinate bonds in the hydroxo analogue, (II), are typical of other

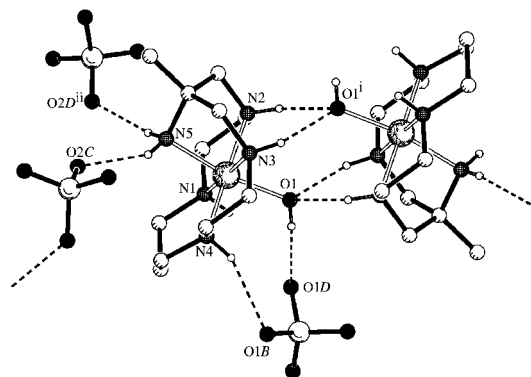


Figure 5
A plot of the hydrogen bonding in (II). Alkyl H atoms have been omitted. See Table 4 for symmetry codes.

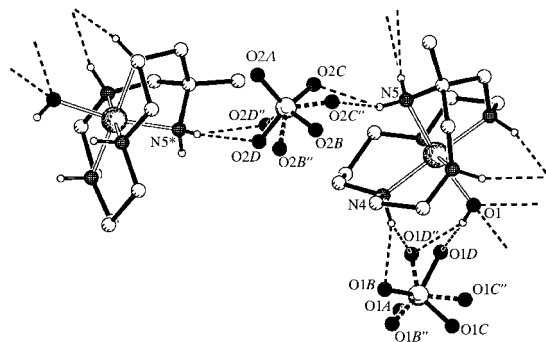


Figure 6
A plot of the perchlorate disorder in (II). Alkyl H atoms have been omitted. The atom labelled with an asterisk (*) is at the symmetry position $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

complexes bearing the [CoL¹] or pentadentate-coordinated [CoL²] moiety. Perchlorate disorder was resolved and rationalized on the basis of distinct hydrogen-bonding patterns.

Experimental

The precursor *trans*-I-[CoL¹Cl](ClO₄)₂ (Bernhardt *et al.*, 2000) was converted to the cyano complex by stirring an aqueous solution of the complex at 298 K for 2 h in the presence of a stoichiometric amount of KCN in a well ventilated fume hood. The compound was purified by cation-exchange chromatography and then crystallised as (I) by slow evaporation of a concentrated NaClO₄ solution of the complex. The hydroxo analogue, (II), was prepared by base hydrolysis of *trans*-I-[CoL¹Cl](ClO₄)₂ (pH = 10) at room temperature, followed by slow evaporation of the solution at this pH.

Compound (I)

Crystal data

[Co(CN)(C₁₁H₂₇N₅)](ClO₄)₂·H₂O
M_r = 531.24
 Monoclinic, *P*₂₁
a = 7.4158 (5) Å
b = 8.9373 (8) Å
c = 16.228 (2) Å
 β = 100.218 (7)°
V = 1058.49 (18) Å³
Z = 2

D_x = 1.667 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 25 reflections
 θ = 10.8–14.2°
 μ = 1.12 mm⁻¹
T = 293 (2) K
 Prism, yellow
 0.5 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled ω/2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.686, *T_{max}* = 0.799
 2789 measured reflections
 2240 independent reflections
 2111 reflections with *I* > 2σ(*I*)

R_{int} = 0.028
 θ_{max} = 25.0°
h = -1 → 8
k = -1 → 10
l = -19 → 19
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on *F*²
R(*F*) = 0.029
wR(*F*²) = 0.075
S = 1.11
 2240 reflections
 285 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0567*P*)² + 0.0357*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001
 Δρ_{max} = 0.29 e Å⁻³
 Δρ_{min} = -0.46 e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.046 (3)
 Absolute structure: Flack (1983), 193 Friedel pairs
 Flack parameter = 0.036 (15)

Table 1

Selected geometric parameters (Å, °) for (I).

Co—N1	1.963 (2)	Co—N4	1.975 (3)
Co—N2	1.956 (3)	Co—N5	1.990 (2)
Co—N3	1.960 (3)	Co—C12	1.901 (3)
N1—Co—N2	87.82 (14)	N2—Co—C12	91.22 (14)
N1—Co—N3	175.76 (14)	N3—Co—N4	87.73 (13)
N1—Co—N4	95.88 (14)	N3—Co—N5	84.84 (11)
N1—Co—N5	92.67 (10)	N3—Co—C12	90.17 (12)
N1—Co—C12	92.04 (12)	N4—Co—N5	94.06 (15)
N2—Co—N3	88.52 (12)	N4—Co—C12	90.02 (14)
N2—Co—N4	176.06 (13)	N5—Co—C12	173.41 (15)
N2—Co—N5	84.37 (15)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O2D ⁱ	0.91	2.18	2.954 (4)	142
N2—H2...O1	0.91	2.37	3.122 (4)	140
N2—H2...O2A ⁱⁱ	0.91	2.40	3.185 (5)	145
N3—H3...O1	0.91	2.18	2.965 (5)	144
N4—H4...O2C ⁱⁱⁱ	0.91	2.23	3.115 (5)	163
N5—H5C...N6 ^{iv}	0.90	2.23	3.073 (4)	156
N5—H5D...O1C ^v	0.90	2.17	2.99 (2)	150
N5—H5D...O1C ^v	0.90	2.33	3.173 (8)	155
O1—H1C...O1D ^{vi}	0.97	2.02	2.930 (7)	156
O1—H1C...O1D ^{vi}	0.97	2.33	3.11 (4)	137
O1—H1D...O2A ⁱⁱ	0.98	2.07	2.819 (5)	132
O1—H1D...O1B ^{vii}	0.98	2.35	3.12 (3)	136

Symmetry codes: (i) $1-x, \frac{1}{2}+y, 2-z$; (ii) $1+x, y, z$; (iii) $1+x, 1+y, z$; (iv) $x-1, y, z$; (v) $x, 1+y, z$; (vi) $1-x, \frac{1}{2}+y, 1-z$.

Compound (II)

Crystal data

[Co(OH)(C₁₁H₂₇N₅)](ClO₄)₂
M_r = 504.21
 Monoclinic, *P*₂₁/*n*
a = 14.817 (5) Å
b = 9.535 (2) Å
c = 15.409 (8) Å
 β = 115.91 (3)°
V = 1958.1 (13) Å³
Z = 4

D_x = 1.71 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 23 reflections
 θ = 11.2–13.4°
 μ = 1.21 mm⁻¹
T = 293 (2) K
 Prism, red
 0.5 × 0.3 × 0.3 mm

Data collection

Enraf–Nonius CAD-4
 diffractometer
 Non-profiled ω scans
 3569 measured reflections
 3430 independent reflections
 2406 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.071

θ_{\max} = 25.0°
 h = 0 → 17
 k = 0 → 11
 l = -18 → 16
 3 standard reflections
 frequency: 120 min
 intensity decay: -8%

Refinement

Refinement on *F*²
R(*F*) = 0.049
wR(*F*²) = 0.142
S = 1.03
 3430 reflections
 278 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0915P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.70 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{Å}^{-3}$

For both compounds, data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve struc-

Table 3
Selected geometric parameters (Å, °) for (II).

Co—N1	1.958 (4)	Co—N4	1.954 (4)
Co—N2	1.943 (4)	Co—N5	1.976 (4)
Co—N3	1.940 (4)	Co—O1	1.892 (3)
N1—Co—N2	88.25 (15)	N2—Co—O1	88.66 (14)
N1—Co—N3	176.51 (16)	N3—Co—N4	88.03 (16)
N1—Co—N4	95.42 (16)	N3—Co—N5	84.92 (15)
N1—Co—N5	95.21 (15)	N3—Co—O1	87.41 (14)
N1—Co—O1	92.01 (14)	N4—Co—N5	95.95 (15)
N2—Co—N3	88.29 (15)	N4—Co—O1	90.97 (15)
N2—Co—N4	176.32 (16)	N5—Co—O1	169.48 (14)
N2—Co—N5	83.94 (15)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2...O1 ⁱ	0.91	2.04	2.892 (5)	156
N3—H3...O1 ⁱ	0.91	2.02	2.878 (5)	157
N4—H4...O1B	0.91	2.46	3.301 (7)	155
N5—H5C...O2D ⁱⁱ	0.90	2.24	3.04 (4)	148
N5—H5C...O2D ⁱⁱ	0.90	2.26	3.128 (7)	163
N5—H5D...O2C	0.90	2.13	2.935 (6)	148
N5—H5D...O2C ^v	0.90	2.14	2.97 (5)	153
O1—H1C...O1D	0.76	2.16	2.879 (5)	158
O1—H1C...O1D ^v	0.76	2.22	2.94 (5)	159
N4—H4...O1D ^v	0.91	2.45	3.18 (6)	137

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

ture: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1425). Services for accessing these data are described at the back of the journal.

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