metal-organic compounds

Cyanocobalt(III) complexes of penta- and tetradentate-coordinated macrocyclic hexaamines

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The pendent-arm macrocyclic hexaamine *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (*L*) may coordinate in tetra-, penta- or hexadentate modes, depending on the metal ion and the synthetic procedure. We report here the crystal structures of two pseudo-octahedral cobalt(III) complexes of *L*, namely sodium *trans*-cyano(*trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine)cobalt(III) triperchlorate, Na[Co(CN)($C_{13}H_{30}N_6$)](ClO$_4$)$_3$ or Na{*trans*-[Co*L*(CN)]}(ClO$_4$)$_3$, (I), where *L* is coordinated as a pentadentate ligand, and *trans*-dicyano(*trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine)cobalt(III) *trans*-dicyano(*trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diaminium)cobalt(III) tetraperchlorate tetrahydrate, [Co(CN)$_2$($C_{14}H_{32}N_6$)][Co(CN)$_2$($C_{14}H_{30}N_6$)](ClO$_4$)$_4$·4H$_2$O or *trans*-[Co*L*(CN)$_2$]*trans*-[Co(H$_2$*L*)(CN)$_2$](ClO$_4$)$_4$·4H$_2$O, (II), where the ligand binds in a tetradentate mode, with the remaining coordination sites being filled by C-bound cyano ligands. In (I), the secondary amine Co—N bond lengths lie within the range 1.944 (3)–1.969 (3) Å, while the *trans* influence of the cyano ligand lengthens the Co—N bond length of the coordinated primary amine [Co—N = 1.986 (3) Å]. The Co—CN bond length is 1.899 (3) Å. The complex cations in (II) are each located on centres of symmetry. The Co—N bond lengths in both cations are somewhat longer than in (I) and span a narrow range [1.972 (3)–1.982 (3) Å]. The two independent Co—CN bond lengths are similar [1.918 (4) and 1.926 (4) Å] but significantly longer than in the structure of (I), again a consequence of the *trans* influence of each cyano ligand.

Comment

The attachment of potentially coordinating functional groups, such as primary amines, to the periphery of macrocyclic ligands, so-called pendent-arm macrocycles, brings an added dimension to the coordination chemistry of the macrocycle. For example, the well studied macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane (cyclam) may at best occupy four

coordination sites on a given metal. However, the introduction of two exocyclic primary amines to give the analogue *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (*L*) can be achieved easily using a metal-templated synthesis
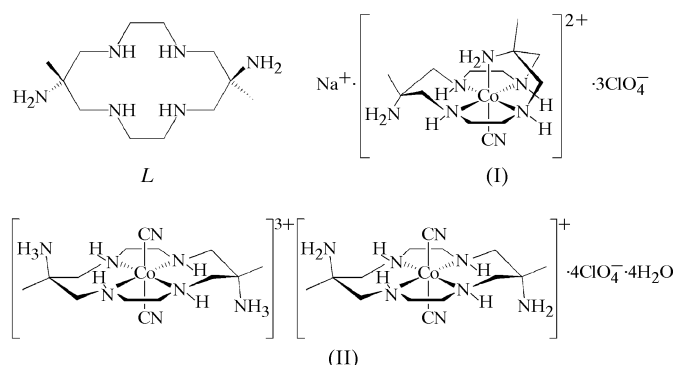
(Comba *et al.*, 1986; Bernhardt *et al.*, 1989). The *cis* isomer of *L* is also known (Bernhardt *et al.*, 1992, 1993). The ligand *L* is quite versatile and has been shown to bind in a hexadentate (Bernhardt *et al.*, 1989, 1991, 1997; Bernhardt, Comba *et al.*, 1990), pentadentate (Bernhardt, Lawrance, Comba *et al.*, 1990; Curtis *et al.*, 1992, 1993) or tetradentate (Comba *et al.*, 1986; Bernhardt, Lawrance, Patalinghug *et al.*, 1990; Bernhardt *et al.*, 1997) mode, depending on whether both, one or no primary amines are coordinated, respectively. The mode of coordination is governed by the metal ion preferences, the synthetic procedures (heat and solvent) and the presence of competing ligands. We report here the structures of two cobalt(III) complexes, one bearing the ligand bound in a pentadentate mode, *viz*. (I), and the other bound in a tetradentate mode, *viz*. (II). Cyano ligands complete the pseudo-octahedral coordination geometries. These structures are compared with related cyano complexes of Co^{III}, and also with the hexadentate-coordinated analogue [Co*L*]$^{3+}$.

The structure of Na{*trans*-[Co*L*(CN)](ClO$_4$)$_3$, (I), finds all molecules on general sites. The geometry of the Co complex is shown in Fig. 1. Pentadentate coordination of the macrocycle is apparent and a C-bound cyano ligand occupies the coordination site *trans* to the single coordinated primary amine (N5). The configuration of the four macrocyclic amines is *RSRS*,
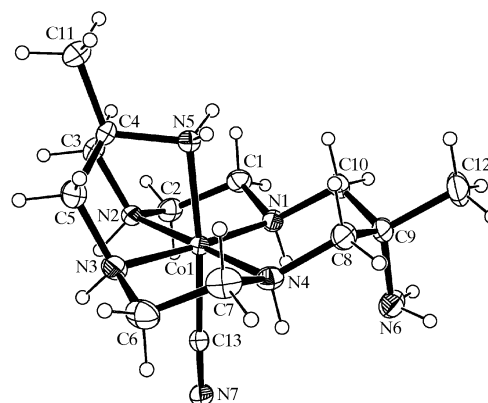

Figure 1
A plot of the complex cation of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

which is commonly referred to as *trans*-I. Interestingly, it is this N-based configurational isomer that has been observed in nearly all structurally characterized complexes of penta-dentate-coordinated *L*. The macrocyclic Co—N bond lengths (Table 1) are all similar but significantly shorter than the coordinate bond to the pendent amine N5. This is a consequence of a *trans* influence of the cyano ligand, which has been shown to elongate the *trans*-disposed Co—N bond lengths in similar compounds (Bernhardt & Hayes, 2002; Bernhardt & Macpherson, 2003). Similar *trans* influences are well known in Co^{III} chemistry, and other examples include the elongation of Co—O coordinate bonds *trans* to cyano in mixed-ligand cyano–β-diketonate–phosphine complexes (Kita *et al.*, 1988; Suzuki *et al.*, 1998).

The Na$^+$ cation is seven-coordinate and is bound to both the complex cation and the perchlorate anions in a variety of modes (Fig. 2). The Na$^+$ ion forms bonds to the cyano N atom (N7) and the dangling pendent amine (N6) in an unusual chelation mode. The remaining coordination sites are occupied by a pair of O atoms from a bidentate-coordinated perchlorate (O1*B* and O1*C*), and three monodentate-coordinated perchlorates (O2*B*, O2*A*^{ii} and O1*D*^{i}; see Table 1 for symmetry codes). Both perchlorates bridge adjacent Na$^+$ cations, with the result being a linear Na$^+$/ClO$_4^-$ coordination polymer with Co complex side chains. These side chains are crosslinked by pairs of symmetry-related perchlorate anions which form hydrogen-bonded bridges between the coordinated primary amine H atoms.

Although perchlorates 1 and 3 are well ordered, perchlorate 2 was found to be rotationally disordered about the O2*A*—Cl2 bond. Significantly, an N4—H4···O2*A* hydrogen bond and an Na1—O2*A* coordinate bond anchor this pivotal O atom, whilst the other three O atoms were refined in two different positions, with the aid of tetrahedral restraints for the minor component. The two contributors to this disorder each form bridging coordinate bonds between adjacent Na atoms (Na1—

O2*B* 88%/Na1—O2*F* 12%), although the Na—O2*F* distance in the minor component is much longer. The other O atoms, O2*C*/O2*G* and O2*D*/O2*E*, do not form any significant hydrogen bonds or coordinate bonds, which allows the anion to adopt two alterative orientations within the structure.

Given that many of the perchlorate O atoms are coordinated to the Na$^+$ ion, there are relatively few strong hydrogen-bonding interactions (Table 2). One notable interaction is a pair of symmetry-related N2—H2···N7^{iii} interactions which link the Co complexes into hydrogen-bonded dimers. The non-coordinated perchlorate O atoms participate exclusively in hydrogen bonds with the coordinated primary amine (N5), which link the above-mentioned hydrogen-bonded dimers.

The structure of the tetradentate-coordinated macrocyclic complex *trans*-[Co*L*(CN)$_2$]*trans*-[Co(H$_2$*L*)(CN)$_2$](ClO$_4$)$_4$·4H$_2$O, (II), comprises two independent complex cations, each on a centre of symmetry, in addition to perchlorate anions and water molecules on general sites. Both unique perchlorate anions were found to be disordered. Both complex cations exhibit a tetragonally compressed octahedral coordination geometry.

Analysis of difference maps during refinement revealed that atom N31 bears three H atoms, *i.e.* the complex containing atom Co1 (cation 1) is in its diprotonated form, *trans*-[Co(H$_2$*L*)(CN)$_2$]$^{3+}$ (Fig. 3), while atom N32 of cation 2
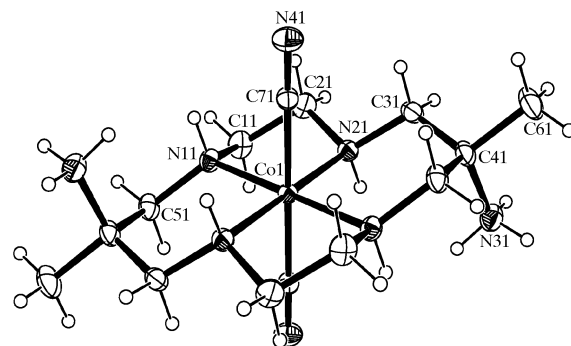
Figure 3
A plot of the cation *trans*-[Co(H$_2$*L*)(CN)$_2$]$^{3+}$ in (II) formed with the diprotonated macrocycle, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Figure 2
A plot of the Na$^+$ cation coordination in (I). See Table 1 for symmetry codes.

Figure 4
A plot of the cation *trans*-[Co*L*(CN)$_2$]$^+$ in (II) formed with the unprotonated macrocycle, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.
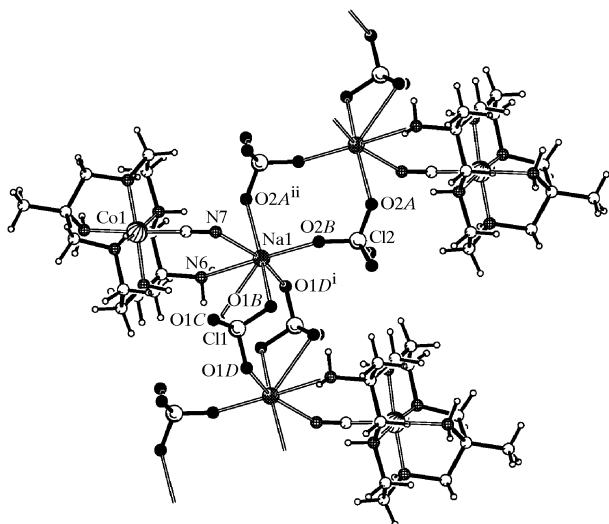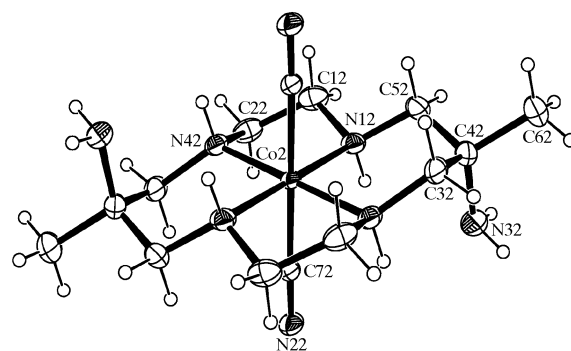
possesses only two H atoms, corresponding to the formula *trans*-[Co*L*(CN)$_2$]$^+$ (Fig. 4). This is consistent with two whole perchlorate anions in the asymmetric unit. In both complex cations, the macrocycle is coordinated in the so-called *trans*-III configuration of N-atom donors, and the pendent amines are *cis* to the adjacent secondary amine H atoms.

The coordinate bond lengths and angles of *trans*-[Co(H$_2$*L*)(CN)$_2$]$^{3+}$ and *trans*-[Co*L*(CN)$_2$]$^+$ are very similar (Table 3). The Co—N bond lengths are significantly longer than those found in pentadentate-coordinated (I) and also in the hexadentate-coordinated analogue [Co*L*]$^{3+}$, which span the range 1.937 (2)–1.955 (3) Å (Bernhardt *et al.*, 1989; Bernhardt & Jones, 1998). This reflects a greater flexibility in the tetradentate-coordinated ligands in (II), as opposed to the rigidity imposed by coordination of the pendent amines in one or two axial sites. Indeed, it has been shown that hexadentate-coordinated complexes of *L* invariably exhibit abnormally short *M*—N bond lengths (Bernhardt *et al.*, 1989, 1991; Bernhardt, Comba *et al.*, 1990), and this has been reproduced by molecular mechanics calculations (Bernhardt & Comba, 1991).

The Co—CN coordinate bond lengths in (II) [1.918 (4) and 1.926 (4) Å] are lengthened significantly in comparison with that found in (I) [1.899 (3) Å]. As mentioned above, the cyano ligand exhibits a strong *trans* influence and in this case leads to a mutual weakening of the *trans* axially coordinated cyano ligands.

Although the coordination environments of the two independent cations of (II) are very similar, there are some notable disparities in the two sets of macrocyclic bond angles, particularly in the vicinity of the pendent amine/aminium group. This is most readily seen in the angles subtended at the tertiary atoms C41 (cation 1) and C42 (cation 2) by the methyl and aminium/amine substituents. The N31—C41—C61 angle in the diprotonated cation *trans*-[Co(H$_2$*L*)(CN)$_2$]$^{3+}$ [105.7 (4)°] is contracted considerably from its ideal tetrahedral value. In contrast, the corresponding N32—C42—C62 angle in the unprotonated cation *trans*-[Co*L*(CN)$_2$]$^+$ [113.7 (4)°] is more obtuse than its ideal value. A comparison of Figs. 3 and 4 enables the effects of these distortions to be seen clearly. Although both atoms N31 and N32 are axially disposed, the aminium group in cation 1 (Fig. 3) is evidently distorted from an ideal axial orientation. It appears that

repulsions between the secondary amine H atoms and the adjacent aminium H atom in *trans*-[Co(H$_2$*L*)(CN)$_2$]$^{3+}$ force the pendent aminium group away from the cyano ligand and consequently towards the geminal methyl group. In the absence of this H atom {in *trans*-[Co*L*(CN)$_2$]$^+$}, no repulsive force is present and a weak attractive hydrogen bond between the pendent amine and the two adjacent secondary amine H atoms appears to draw the pendent amine closer to the axially coordinated ligand, thus opening up the N32—C42—C62 angle.

Intermolecular hydrogen bonds abound in (II), involving both complex cations, water molecules and perchlorate anions. Of note are the hydrogen bonds linking the two complex cations (Fig. 5). As seen in the structure of *trans*-[Co*L*(CN)]$^{2+}$, the terminal N atoms of the cyano ligands accept hydrogen bonds from the macrocyclic secondary amine of the adjacent complex cation. These are augmented by weaker (acute) hydrogen bonds from the aminium group (N31) on cation 1.

In conclusion, a pair of cobalt(III) complexes each bearing the hexaamine macrocycle *L* in a penta- or tetradentate coordinated form have been structurally characterized. The cyano ligands coordinate in the coordination sites left vacant by the pendent amines. The restraints imposed by coordination of the pendent amine in (I) lead to shorter Co—N bond lengths, and a *trans* influence of the cyano ligand is seen in both (I) and (II), which results in an elongation of the Co—N or Co—CN coordinate bond relative to bond lengths where an amine is coordinated in the *trans* position.

Experimental

In a well ventilated fume hood, a solution of CoCl$_2$·6H$_2$O (0.23 g) and *L*·6HCl (0.5 g) in water (40 ml) was prepared; the pH was immediately raised to 6 with dilute NaOH to give a red solution. After stirring for 2 min, NaCN (0.15 g; *Caution!* extremely toxic) was added and the mixture was stirred at 333 K for 1 h, whereupon the colour of the solution changed to yellow. The mixture was diluted to 200 ml and charged on a column of Sephadex C25 cation-exchange resin (10 × 2 cm). Three well separated yellow bands eluted in the order *trans*-[Co*L*(CN)$_2$]$^+$ (0.1 *M* NaClO$_4$), *trans*-[Co*L*(CN)]$^{2+}$ (0.2 *M* NaClO$_4$) and [Co*L*]$^{3+}$ (0.5 *M* NaClO$_4$). The compound *trans*-[Co*L*(CN)$_2$]*trans*-[Co(H$_2$*L*)(CN)$_2$](ClO$_4$)$_4$·4H$_2$O crystallized from the first band after concentration to *ca* 20 ml and acidification to pH 3. Na{*trans*-[Co*L*(CN)]}(ClO$_4$)$_3$ crystallized from a concentrated solution of band 2 at pH 7. These crystals were filtered off and dried in air. The complex obtained from the third band, [Co*L*](ClO$_4$)$_3$, has been described previously (Bernhardt *et al.*, 1989).

Compound (I)

Crystal data

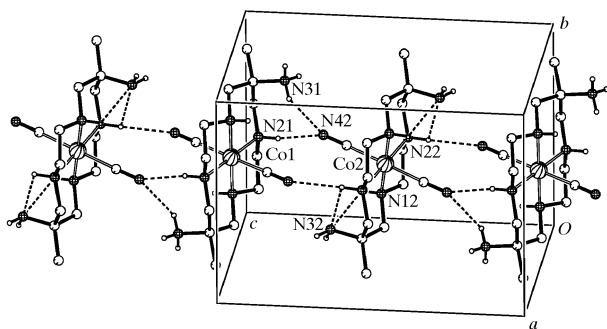|	
Na[Co(CN)(C$_{13}$H$_{30}$N$_6$)](ClO$_4$)$_3$	$Z = 2$
$M_r = 664.71$	$D_x = 1.706$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.405$ (2) Å	Cell parameters from 25
$b = 10.683$ (2) Å	reflections
$c = 14.211$ (2) Å	$\theta = 11.3$–14.1°
$\alpha = 94.02$ (1)°	$\mu = 1.06$ mm^{-1}
$\beta = 100.62$ (2)°	$T = 294$ (2) K
$\gamma = 111.21$ (1)°	Prism, yellow
$V = 1293.7$ (4) Å^3	0.27 × 0.27 × 0.07 mm

Figure 5
A plot of the hydrogen bonding (dashed lines) in (II). Alkyl H atoms have been omitted.

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	3275 reflections with $I > 2\sigma(I)$
Non-profiled $\omega/2\theta$ scans	$R_{int} = 0.018$
Absorption correction: ψ scan (North *et al.*, 1968) (number of ψ scan sets used was 4; θ correction was applied; averaged transmission function was used; no Fourier smoothing was applied) $T_{min} = 0.799$, $T_{max} = 0.928$	$\theta_{max} = 25.0°$
	$h = 0 \rightarrow 11$
	$k = -12 \rightarrow 11$
	$l = -16 \rightarrow 16$
	3 standard reflections frequency: 120 min intensity decay: 7%
4846 measured reflections	
4546 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 1.1231P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4546 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
348 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected interatomic distances (Å) for (I).

Co1—N1	1.949 (3)	O1B—Na1	2.663 (4)
Co1—N2	1.944 (3)	O1C—Na1	2.746 (4)
Co1—N3	1.953 (3)	O1D—Na1^i	2.383 (3)
Co1—N4	1.969 (3)	O2A—Na1^{ii}	2.480 (4)
Co1—N5	1.986 (3)	O2B—Na1	2.331 (5)
C13—Co1	1.899 (4)	O2F—Na1	2.99 (3)
N6—Na1	2.920 (4)	O2G—Na1	3.01 (3)
N7—Na1	2.574 (3)		

Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $-x + 1, -y, -z + 2$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1C	0.91	2.10	2.985 (4)	163
N2—H2$\cdots$N7^{iii}	0.91	2.08	2.983 (4)	172
N3—H3$\cdots$O1A^{iii}	0.91	2.53	3.149 (5)	126
N3—H3$\cdots$N7^{iii}	0.91	2.56	3.384 (5)	151
N4—H4$\cdots$O2A^{ii}	0.91	2.25	3.137 (4)	163
N5—H5C$\cdots$O3D	0.90	2.34	3.193 (5)	159
N5—H5C$\cdots$O3A	0.90	2.66	3.246 (6)	124
N5—H5D$\cdots$O3C^{iv}	0.90	2.26	3.144 (5)	167
N6—H6D$\cdots$O1B^i	0.90	2.60	3.281 (5)	133

Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $-x + 1, -y, -z + 2$; (iii) $-x + 1, -y + 1, -z + 2$; (iv) $-x, -y + 1, -z + 1$.

Compound (II)

Crystal data

[Co(CN)$_2$(C$_{14}$H$_{32}$N$_6$)]- [Co(CN)$_2$(C$_{14}$H$_{30}$N$_6$)]- (ClO$_4$)$_4\cdot$4H$_2$O	$D_x = 1.603$ Mg m^{-3}
$M_r = 1210.66$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 25 reflections
$a = 9.0697$ (3) Å	$\theta = 11.2–13.8°$
$b = 10.5362$ (5) Å	$\mu = 0.96$ mm^{-1}
$c = 13.3674$ (9) Å	$T = 294$ (2) K
$\alpha = 87.805$ (6)°	Prism, yellow
$\beta = 82.909$ (7)°	$0.5 \times 0.2 \times 0.2$ mm
$\gamma = 81.743$ (5)°	
$V = 1254.21$ (11) Å^3	
$Z = 1$	

Data collection

Enraf–Nonius CAD-4 diffractometer	3690 reflections with $I > 2\sigma(I)$
Non-profiled $\omega/2\theta$ scans	$R_{int} = 0.029$
Absorption correction: ψ scan (North *et al.*, 1968) (Number of ψ scan sets used was 4; θ correction was applied; averaged transmission function was used; no Fourier smoothing was applied) $T_{min} = 0.791$, $T_{max} = 0.806$	$\theta_{max} = 25.0°$
	$h = 0 \rightarrow 10$
	$k = -12 \rightarrow 12$
	$l = -15 \rightarrow 15$
	3 standard reflections frequency: 120 min intensity decay: 0%
4719 measured reflections	
4412 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 2.931P]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.166$	
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
4412 reflections	$\Delta\rho_{max} = 1.20$ e Å^{-3}
327 parameters	$\Delta\rho_{min} = -0.96$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL97* (Sheldrick, 1997)
	Extinction coefficient: 0.044 (4)

Table 3
Selected interatomic distances (Å) for (II).

N11—Co1	1.972 (3)	N12—Co2	1.977 (4)
N21—Co1	1.981 (3)	N22—Co2	1.982 (3)
C71—Co1	1.926 (4)	C72—Co2	1.918 (4)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1A$\cdots$N41	0.89	2.03	2.898 (6)	167
O1—H1B$\cdots$O1G^i	0.88	2.03	2.912 (14)	172
O2—H2B$\cdots$O1^i	0.89	2.05	2.776 (9)	138
N11—H11$\cdots$O2C^{ii}	0.91	2.12	3.024 (7)	175
N21—H21$\cdots$N42	0.91	2.00	2.885 (5)	165
N31—H31C$\cdots$O2	0.89	1.82	2.708 (6)	177
N31—H31E$\cdots$O2A	0.89	2.49	3.153 (8)	132
N31—H31E$\cdots$O1D^{iii}	0.89	2.29	3.035 (12)	141
N31—H31E$\cdots$O1F^{iii}	0.89	2.65	3.388 (15)	141
N12—H12$\cdots$O1C	0.91	2.19	3.048 (10)	158

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $x, y + 1, z$.

Water H atoms were identified from difference maps and their positional and displacement parameters were restrained during subsequent refinement cycles, with O—H = 0.89 (1) Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The H atoms of the pendent amines and aminium groups in both structures were first identified from difference maps and then constrained, with N—H = 0.89 Å and $U_{iso}(H) = 1.5U_{eq}(N)$. All alkyl H atoms were treated as riding, with C—H distances ranging from 0.93 to 0.97 Å and with $U_{iso}(H) = 1.5$ (methyl H atoms) or 1.2 (all other atoms) times $U_{eq}(C)$. Perchlorate disorder was apparent in both structures. In (I), atoms O2B, O2C and O2D were refined in two positions with complementary occupancies and with the aid of tetrahedral restraints. In (II), both perchlorate anions were disordered. All O atoms attached to atom Cl1 were identified in two positions and refined with complementary occupancies. In the second anion, a pseudo-mirror plane passing through atoms O2A, O2B and O2C resulted in two different positions for the Cl atom and the remaining O atom. Again, tetrahedral restraints were included. All

minor components of the disorder were refined with isotropic displacement parameters.

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 structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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