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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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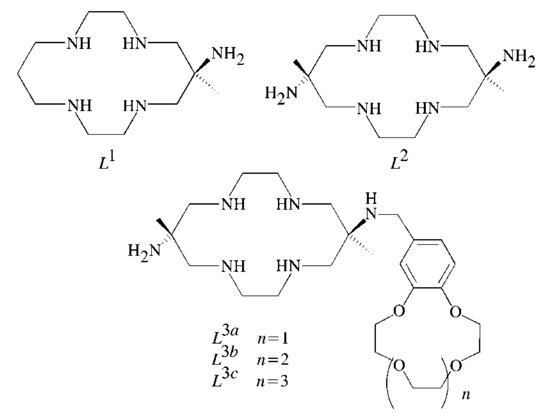
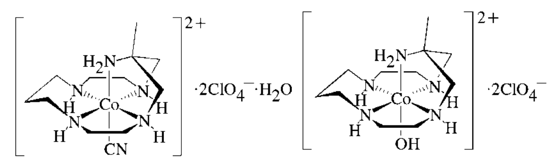
The crystal structures of a pair of closely related macrocyclic cyano- and hydroxopentaaminecobalt(III) complexes, as their perchlorate salts, are reported. Although the two complexes, $[Co(CN)(C_{11}H_{27}N_5)](ClO_4)_2 \cdot H_2O$ and $[Co(OH)(C_{11}H_{27}N_5)](ClO_4)_2$, exhibit similar conformations, 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-substitutued 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 $[CoL^1]$ moiety (Bernhardt *et al.*, 2000, 2002).

The related hexaamine 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 substituents 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.





(I) (II)

In this work, we report the crystal structures of *trans*-$[CoL^1CN](ClO_4)_2 \cdot H_2O$, (I), and *trans*-$[CoL^1OH](ClO_4)_2$, (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

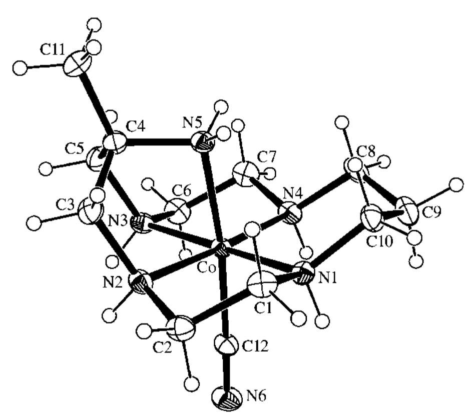


Figure 1
A view of the complex cation in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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 [CoL^1] moiety. Furthermore, in Na[CoL^{3b}CN](ClO_4)$_3$, the only other cyano-pentaaminecobalt(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).

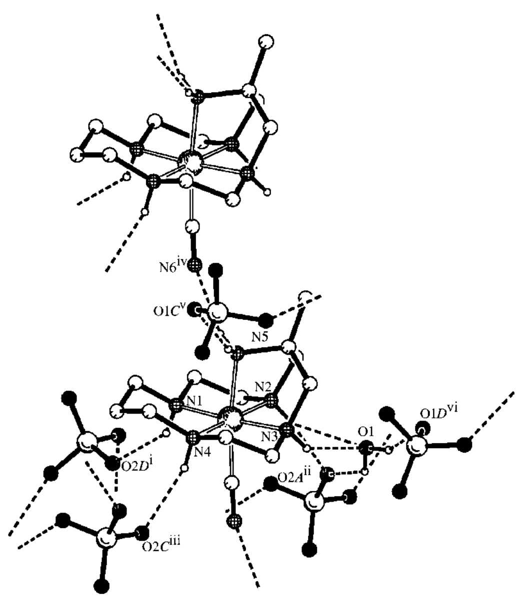


Figure 2
A plot of the hydrogen bonding in (I). Alkyl H atoms have been omitted. See Table 2 for symmetry codes.

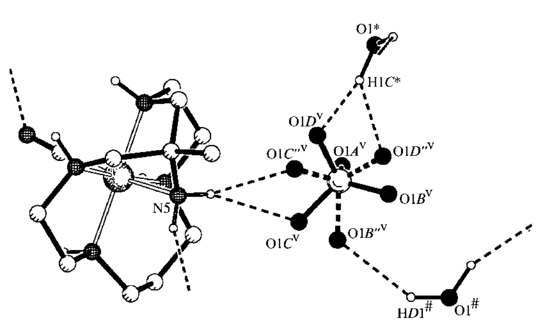


Figure 3
A plot of the perchlorate disorder in (I). Alkyl H atoms have been omitted. See Table 2 for the perchlorate symmetry code. Atoms labelled with an asterisk (*) are at the symmetry position $(1 - x, \frac{1}{2} + y, 1 - z)$ and atoms labelled with a hash sign (#) are at the symmetry position $(x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

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 O1*B*, O1*C* and O1*D* (O1*B''*, O1*C''* and O1*D''*) was resolved and two distinct orientations of the anion were identified, related by a *ca* 70° rotation of the anion about the Cl1—O1*A* 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 O1*C* and O1*D* 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 O1*B''* as acceptor for a water molecule, whereas atom O1*B* 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

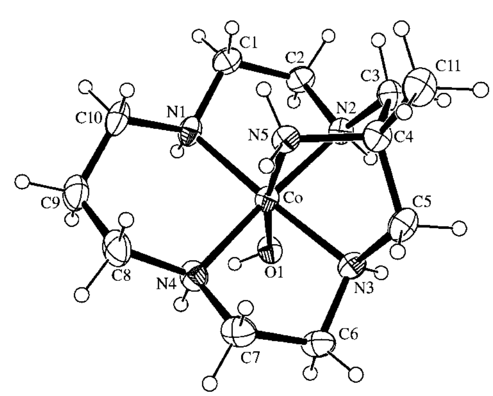


Figure 4
A view of the complex cation in (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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) (O1*B*/O1*C*/O1*D* and O1*B*″/O1*C*″/O1*D*″, and O2*B*/O2*C*/O2*D* and O2*B*″/O2*C*″/O2*D*″). 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 Cl1—O1*A*. In the major orientation, atoms O1*B* and O1*D* accept strong hydrogen bonds from N4—H4 and O1—H1*C*. In the minor contributor, only atom O2*D*″ is hydrogen bonded, in a bifurcated motif with both N4—H4 and O1—H1*C*. Anion 2 bridges the pendant amines of adjacent cations. Rotation about Cl2—O2*A*, 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 complexes bearing the [CoL^1] or pentadentate-coordinated [CoL^2] moiety. Perchlorate disorder was resolved and rationalized on the basis of distinct hydrogen-bonding patterns.

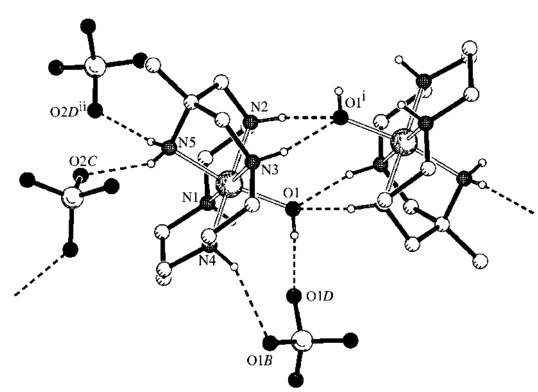


Figure 5
A plot of the hydrogen bonding in (II). Alkyl H atoms have been omitted. See Table 4 for symmetry codes.

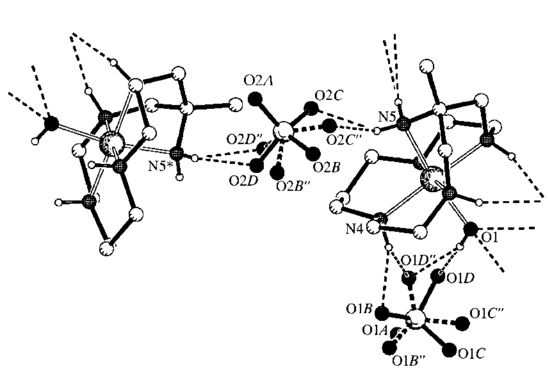


Figure 6
A plot of the perchlorate disorder in (II). Alkyl H atoms have been omitted. The atom labelled with an asterisk (*) is at the symmetry position ($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$).

Experimental

The precursor *trans*-I-[CoL^1Cl]$(ClO_4)_2$ (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 $NaClO_4$ solution of the complex. The hydroxo analogue, (II), was prepared by base hydrolysis of *trans*-I-[CoL^1Cl]$(ClO_4)_2$ (pH = 10) at room temperature, followed by slow evaporation of the solution at this pH.

Compound (I)

Crystal data

[Co(CN)($C_{11}H_{27}N_5$)]$(ClO_4)_2\cdot H_2O$
M_r = 531.24
Monoclinic, $P2_1$
a = 7.4158 (5) Å
b = 8.9373 (8) Å
c = 16.228 (2) Å
β = 100.218 (7)°
V = 1058.49 (18) Å^3
Z = 2
D_x = 1.667 Mg m^{-3}
Mo $K\alpha$ 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 $\omega/2\theta$ 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 $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 25.0°
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 10$
$l = -19 \rightarrow 19$
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
$w = 1/[\sigma^2(F_o^2) + (0.0567P)^2 + 0.0357P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}
Extinction correction: *SHELXL*97
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).

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

$[Co(OH)(C_{11}H_{27}N_5)](ClO_4)_2$	$D_x = 1.71$ Mg m^{-3}
$M_r = 504.21$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 23 reflections
$a = 14.817$ (5) Å	$\theta = 11.2$–13.4°
$b = 9.535$ (2) Å	$\mu = 1.21$ mm^{-1}
$c = 15.409$ (8) Å	$T = 293$ (2) K
$\beta = 115.91$ (3)°	Prism, red
$V = 1958.1$ (13) Å^3	0.5 × 0.3 × 0.3 mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 25.0°$
Non-profiled ω scans	$h = 0 \rightarrow 17$
3569 measured reflections	$k = 0 \rightarrow 11$
3430 independent reflections	$l = -18 \rightarrow 16$
2406 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{int} = 0.071$	frequency: 120 min
	intensity decay: −8%

Refinement

Refinement on F^2	H-atom parameters constrained
$R(F) = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.142$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.70$ e Å^{-3}
3430 reflections	$\Delta\rho_{min} = -0.69$ e Å^{-3}
278 parameters	

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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).

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

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

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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.

References

Bernhardt, P. V., Comba, P., Curtis, N. F., Hambley, T. W., Lawrance, G. A., Maeder, M. & Siriwardena, A. (1990). *Inorg. Chem.* **29**, 3208–3213.
Bernhardt, P. V. & Hayes, E. J. (2002). *Inorg. Chem.* **41**, 2892–2902.
Bernhardt, P. V., Lawrance, G. A., Comba, P., Martin, L. L. & Hambley, T. W. (1990). *J. Chem. Soc. Dalton Trans.* pp. 2859–2862.
Bernhardt, P. V., Lawrance, G. A. & Hambley, T. W. (1989). *J. Chem. Soc. Dalton Trans.* pp. 1059–1065.
Bernhardt, P. V., Lawrance, G. A., Maeder, M., Rossignoli, M. & Hambley, T. W. (1991). *J. Chem. Soc. Dalton Trans.* pp. 1167–1170.
Bernhardt, P. V., Lawrance, G. A., Patalinghug, W. C., Skelton, B. W., White, A. H., Curtis, N. F. & Siriwardena, A. (1990). *J. Chem. Soc. Dalton Trans.* pp. 2853–2858.
Bernhardt, P. V. & Macpherson, B. P. (2003). *Acta Cryst.* C**59**, m467–m470.
Bernhardt, P. V., Macpherson, B. P. & Martinez, M. (2000). *Inorg. Chem.* **39**, 5203–5208.
Bernhardt, P. V., Macpherson, B. P. & Martinez, M. (2002). *J. Chem. Soc. Dalton Trans.* pp. 1435–1441.
Curtis, N. F., Gainsford, G. J., Siriwardena, A. & Weatherburn, D. C. (1993). *Aust. J. Chem.* **46**, 755–786.
Curtis, N. F., Robinson, W. T. & Weatherburn, D. C. (1992). *Aust. J. Chem.* **45**, 1663–1680.
Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hambley, T. W., Lawrance, G. A., Martinez, M., Skelton, B. W. & White, A. H. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1643–1648.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.
Lawrance, G. A., Manning, T. M., Maeder, M., Martinez, M., O'Leary, M. A., Patalinghug, W. C., Skelton, B. W. & White, A. H. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1635–1641.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1985). *SHELXS*86. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXL*97. Release 97-2. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.