Geometric isomers of chloro-(6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine)cobalt(III) tetrachlorozincate(II)

Paul V. Bernhardt* and Brendan P. Macpherson

Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia
Correspondence e-mail: p.bernhardt@uq.edu.au

The crystal structures of a pair of *cis* and *trans* isomers of the macrocyclic chloropentaamine title complex, as their tetrachlorozincate(II) salts, $[CoCl(C_{11}H_{27}N_5)][ZnCl_4]$, are reported. The two distinct isomeric forms lead to significant variations in the Co—N bond lengths and, furthermore, hydrogen bonding between the complex ions is influenced by the folded (*cis*) or planar (*trans*) conformations of the coordinated ligand.

Comment

The coordination chemistry of cyclic ligands may be expanded by the attachment of coordinating functional groups to the periphery of the ring to give so-called pendant-arm macrocycles. The pendant groups may be attached to the donor atoms (in the case of amines) or to the carbon skeleton. A family of penta- and hexadentate macrocyclic amines is now extant, bearing one or two primary amines attached to macrocyclic tetraamines of various sizes. One of the most studied representatives of this family is the pentadentate cyclam derivative 6-methyl-1,4,8,11-tetraazacyclotetradecane-6-amine (*L*; Lawrance *et al.*, 1992). Like its parent cyclam, the 14-membered macrocycle *L* has the capability of coordinating in either a folded (*cis*) or a planar (*trans*) configuration, with the pendant amine providing an extra donor group and structural rigidity. Three isomeric forms of pentadentate coordinated *L* have been structurally identified, *viz.* *cis*-[CoL-Cl](ClO₄)₂ (Lawrance *et al.*, 1992) and two N-based isomeric *trans* forms. Specifically, in the *trans* form, the macrocyclic secondary amines may adopt either the *RSRS* (*trans*-I) configuration (Bernhardt *et al.*, 2000), with all amine H atoms on the same side of the macrocyclic plane, or the *RRSS* (*trans*-III) diastereomeric form, (III) (Hambley *et al.*, 1992), with two H atoms up and two down. The sixth coordination site is available for ligand substitution reactions. In this work, we report the crystal structures of *cis*- and *trans*-[CoLCl]²⁺ as their [ZnCl₄]²⁻ salts.

L

cis-[CoLCl][ZnCl₄] (I)

trans-I [CoLCl][ZnCl₄] (II)

trans-III [CoLCl](ClO₄)₂ (III)
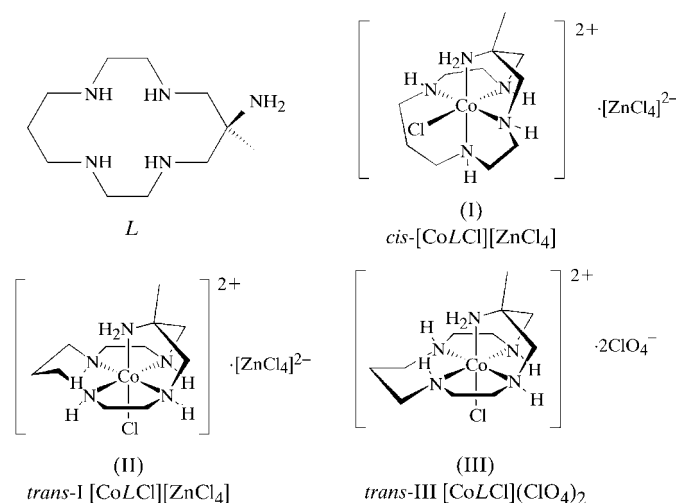
The structure of *cis*-[CoLCl][ZnCl₄], (I) (Fig. 1), reveals the folded conformation of the pentadentate coordinated macrocycle, with the Cl ligand occupying the coordination site adjacent to the primary amine. The Co—N bond lengths (Table 1) are typical of a Co^III–amine and the Co—Cl distance is also as expected. However, there are significant variations in the Co—N bonds within the complex cation, notably the Co—N3 bond of 1.940 (2) Å, which is the shortest, whereas the adjacent Co—N4 bond of 1.970 (2) Å is the longest. The corresponding coordinate bond lengths compare well with those determined for *cis*-[CoLCl](ClO₄)₂ (Lawrance *et al.*, 1992).

The [ZnCl₄]²⁻ anion in (I) exhibits a distorted tetrahedral geometry, with significant variations in the Zn—Cl bond lengths (Table 1). The coordination angles also reveal a distortion from ideal tetrahedral symmetry. These distortions are related to hydrogen-bonding interactions with the amine H atoms of the coordinated macrocycle (Table 2). The Cl ligands Cl2, Cl3 and Cl5 participate in hydrogen bonds with most of the amine H atoms, except that attached to atom N2, which makes no significant hydrogen-bonding contacts (Fig. 2). Interestingly, atom Cl2 forms a trifurcated hydrogen-bonded motif involving amine H atoms from two separate complex cations. There is no correlation between the number of hydrogen-bonding interactions involving each acceptor and the respective Zn—Cl bond length.

The structure of *trans*-I-[CoLCl][ZnCl₄], (II) (Fig. 3), has also been determined. The macrocyclic secondary amines encircle the metal centre and the pendant primary amine occupies the coordination site *trans* to the Cl ligand. In contrast with the structure of the *cis* isomer, (I), the Co—N bonds in (II) (Table 3) span a narrower range, while the Co—Cl bond length is significantly longer. The bond lengths determined match those reported for *trans*-I-[CoLCl](ClO₄)₂ (Bernhardt *et al.*, 2000). In addition, the bond lengths are not markedly different from those in the N-based diastereomer *trans*-III-[CoLCl](ClO₄)₂, (III) (Hambley *et al.*, 1992).
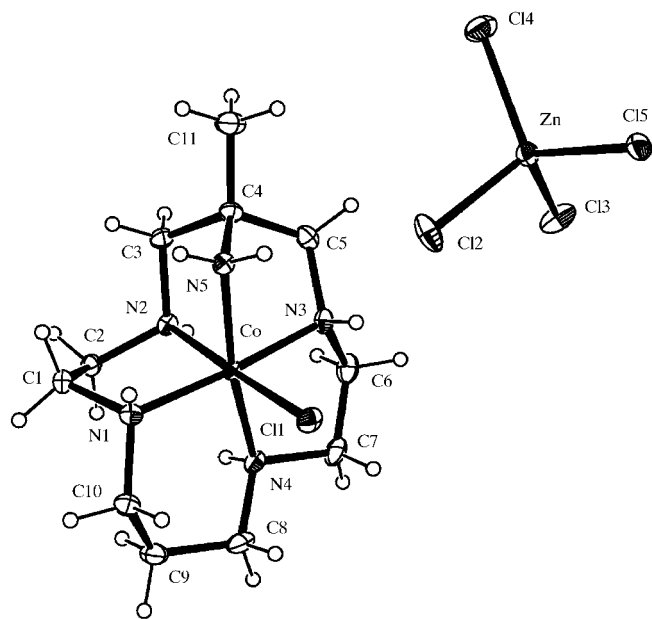
Figure 1
A view of the cation and anion of (I), with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Molecular mechanics calculations (Bernhardt *et al.*, 2002) have reproduced the variations in Co—N and Co—Cl bond lengths observed in *cis*-, *trans*-I- and *trans*-III-[Co*L*Cl]$^{2+}$. The folded *cis* configuration is best able to accommodate an expansion of the Co—N bond lengths, whereas the *trans* isomers tend to enforce shorter coordinate bond lengths. These calculations agree with the reported crystal structures of these complexes.
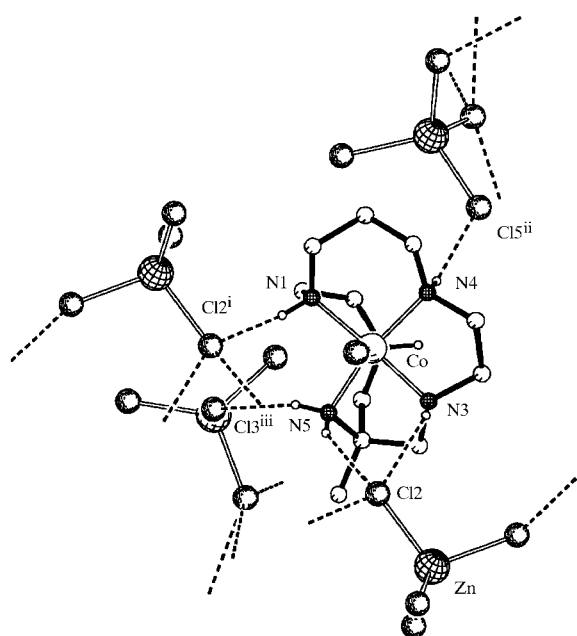

Figure 2
A view of the hydrogen-bonding in (I). Alkyl H atoms have been omitted. Symmetry codes are as given in Table 2.
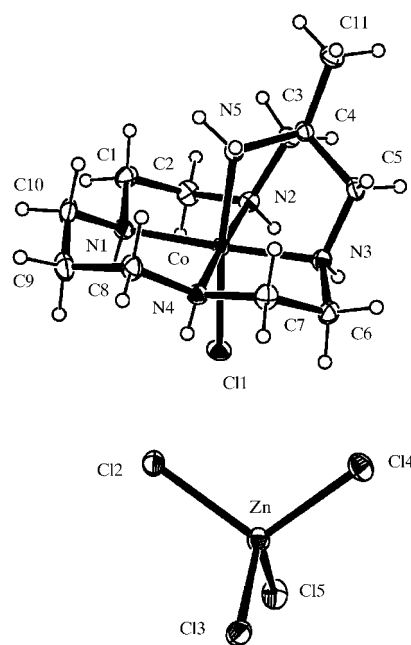

Figure 3
A view of the cation and anion of (II), with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

Hydrogen bonding between the amine H atoms and the Cl ligands is again a feature in (II). Unlike the *cis* isomer, (I), each amine H atom participates in a hydrogen bond with a Cl ligand from either a [ZnCl$_4$]$^{2-}$ anion or an adjacent complex cation (Fig. 4 and Table 4). Although atom Cl1 is in proximity to the four macrocyclic NH groups, the N—H···Cl angles are too acute (<120°) to be considered significant hydrogen bonds.

In conclusion, a pair of *cis* and *trans* isomeric chloro-pentaamine–cobalt(III) complexes have each been crystallized as their tetrachlorozincate salts. The coordination geometries of the cations are the same as reported for the
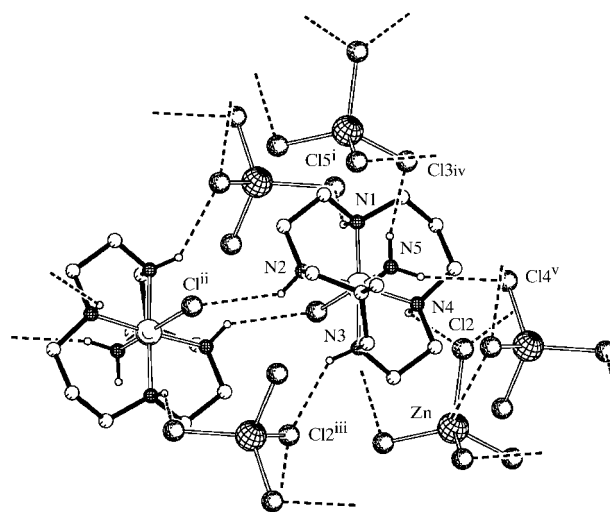

Figure 4
A view of the hydrogen-bonding in (II). Alkyl H atoms have been omitted. Symmetry codes are as given in Table 4.

perchlorate salts of the respective isomers. Hydrogen bonding with the complex anions in this work has been found to be dependent on the isomeric form of the complex cation. In particular, the *cis* isomer, (I), possesses an unmatched hydrogen-bond donor (N2—H2) and acceptor (Cl4). In contrast, in the structure of the *trans* isomer, (II), all potential donors and acceptors are involved in hydrogen bonding.

Experimental

Reaction of $CoCl_2 \cdot 6H_2O$ with $L \cdot 5HCl$ in aerated aqueous solution gives predominantly *cis*-$[CoLCl]^{2+}$, which may be separated from other products by cation exchange chromatography, as described by Lawrance *et al.* (1992). The *cis*-[CoLCl][ZnCl4] complex, (I), was crystallized from a concentrated HCl solution by addition of excess $ZnCl_2 \cdot 6H_2O$. The *trans*-I-$[CoLCl]^{2+}$ cation may be made selectively by reacting equimolar amounts of $Na_3[Co(CO_3)_3] \cdot 3H_2O$ and $L \cdot 5HCl$, as reported by Bernhardt *et al.* (2000). Following purification by column chromatography, the complex was crystallized as *trans*-I-[CoLCl][ZnCl4], (II), by addition of excess $ZnCl_2 \cdot 6H_2O$ to an HCl solution.

Compound (I)

Crystal data

[CoCl($C_{11}H_{27}N_5$)][ZnCl4]
$M_r = 530.93$
Orthorhombic, *Pcab*
$a = 11.619 (1)$ Å
$b = 14.109 (3)$ Å
$c = 23.517 (3)$ Å
$V = 3855.2 (10)$ Å^3
$Z = 8$
$D_x = 1.829$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.3–12.7°$
$\mu = 2.80$ mm^{-1}
$T = 296 (2)$ K
Prism, red
$0.6 \times 0.5 \times 0.5$ mm

Data collection

Enraf–Nonius TurboCAD4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.284$, $T_{max} = 0.335$
3385 measured reflections
3385 independent reflections

2970 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 27$
3 standard reflections
  frequency: 120 min
  intensity decay: 1%

Table 1
Selected geometric parameters (Å, °) for (I).

Co—N1	1.961 (2)	Co—Cl1	2.2404 (6)
Co—N2	1.966 (2)	Zn—Cl3	2.2516 (7)
Co—N3	1.940 (2)	Zn—Cl2	2.2636 (7)
Co—N4	1.970 (2)	Zn—Cl4	2.2839 (8)
Co—N5	1.953 (2)	Zn—Cl5	2.3057 (7)
N1—Co—N2	87.37 (8)	N3—Co—Cl1	90.40 (6)
N1—Co—N3	175.99 (8)	N4—Co—N5	168.29 (8)
N1—Co—N4	95.38 (8)	N4—Co—Cl1	91.83 (6)
N1—Co—N5	95.64 (8)	N5—Co—Cl1	91.65 (6)
N1—Co—Cl1	92.32 (6)	Cl2—Zn—Cl3	105.98 (3)
N2—Co—N3	89.75 (8)	Cl2—Zn—Cl4	112.47 (3)
N2—Co—N4	91.42 (8)	Cl2—Zn—Cl5	104.43 (3)
N2—Co—N5	85.17 (8)	Cl3—Zn—Cl4	108.53 (3)
N2—Co—Cl1	176.76 (6)	Cl3—Zn—Cl5	113.48 (3)
N3—Co—N4	87.49 (8)	Cl4—Zn—Cl5	111.84 (3)
N3—Co—N5	81.32 (8)		

Refinement

Refinement on F^2
$R(F) = 0.022$
$wR(F^2) = 0.056$
$S = 1.07$
3385 reflections
209 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 3.6352P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00173 (8)

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$\cdots$Cl2^i	0.91	2.33	3.214 (2)	164
N3—H3$\cdots$Cl2	0.91	2.60	3.341 (2)	139
N4—H4$\cdots$Cl5^{ii}	0.91	2.48	3.272 (2)	145
N5—H5$C\cdots$Cl3^{iii}	0.90	2.66	3.494 (2)	155
N5—H5$D\cdots$Cl2	0.90	2.67	3.458 (2)	147
N5—H5$D\cdots$Cl1^i	0.90	2.85	3.462 (2)	127

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

Compound (II)

Crystal data

[CoCl($C_{11}H_{27}N_5$)][ZnCl4]
$M_r = 530.93$
Monoclinic, $P2_1/c$
$a = 11.9431 (9)$ Å
$b = 12.167 (1)$ Å
$c = 13.9670 (7)$ Å
$\beta = 99.165 (7)°$
$V = 2003.7 (2)$ Å^3
$Z = 4$

$D_x = 1.76$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.3–13.9°$
$\mu = 2.70$ mm^{-1}
$T = 296 (2)$ K
Prism, red
$0.5 \times 0.5 \times 0.1$ mm

Data collection

Enraf–Nonius TurboCAD4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.346$, $T_{max} = 0.774$
3698 measured reflections
3518 independent reflections
2570 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections
  frequency: 120 min
  intensity decay: 6%

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

Co—N1	1.958 (3)	Co—Cl1	2.256 (1)
Co—N2	1.944 (3)	Zn—Cl2	2.2880 (11)
Co—N3	1.955 (3)	Zn—Cl3	2.2969 (11)
Co—N4	1.957 (3)	Zn—Cl4	2.2723 (11)
Co—N5	1.961 (3)	Zn—Cl5	2.2420 (11)
N1—Co—N2	87.70 (13)	N3—Co—Cl1	90.37 (9)
N1—Co—N3	176.58 (13)	N4—Co—N5	94.65 (13)
N1—Co—N4	96.04 (13)	N4—Co—Cl1	90.60 (9)
N1—Co—N5	94.34 (13)	N5—Co—Cl1	172.58 (9)
N1—Co—Cl1	90.30 (10)	Cl2—Zn—Cl3	108.68 (4)
N2—Co—N3	88.95 (12)	Cl2—Zn—Cl4	108.70 (4)
N2—Co—N4	176.17 (12)	Cl2—Zn—Cl5	108.79 (4)
N2—Co—N5	84.20 (12)	Cl3—Zn—Cl4	106.37 (4)
N2—Co—Cl1	90.22 (9)	Cl3—Zn—Cl5	110.79 (4)
N3—Co—N4	87.30 (12)	Cl4—Zn—Cl5	113.39 (4)
N3—Co—N5	84.66 (12)		

metal-organic compounds

Refinement

Refinement on F^2
$R(F) = 0.034$
$wR(F^2) = 0.095$
$S = 1.03$
3518 reflections
208 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.6197P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$\cdots$Cl5^i	0.91	2.60	3.393 (3)	146
N2—H2$\cdots$Cl1^{ii}	0.91	2.58	3.316 (3)	139
N3—H3$\cdots$Cl2^{iii}	0.91	2.54	3.256 (3)	135
N4—H4$\cdots$Cl2	0.91	2.75	3.395 (3)	129
N5—H5C$\cdots$Cl3^{iv}	0.90	2.49	3.327 (3)	156
N5—H5D$\cdots$Cl4^v	0.90	2.57	3.420 (3)	159

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $-x, -y, 1 - z$; (iii) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x, 1 + y, z$; (v) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

All H atoms were included at estimated positions and constrained using a riding model (N—H = 0.90–0.91 Å and C—H = 0.96–0.97 Å).

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).

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