

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

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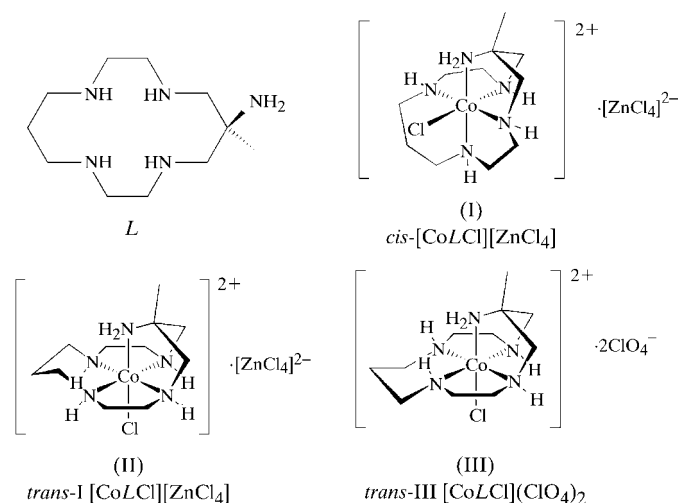
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The crystal structures of a pair of *cis* and *trans* isomers of the macrocyclic chloropentaamine title complex, as their tetrachlorozincate(II) salts, $[\text{CoCl}(\text{C}_{11}\text{H}_{27}\text{N}_5)][\text{ZnCl}_4]$, are reported. The two distinct 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*-[CoLCl](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.



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).

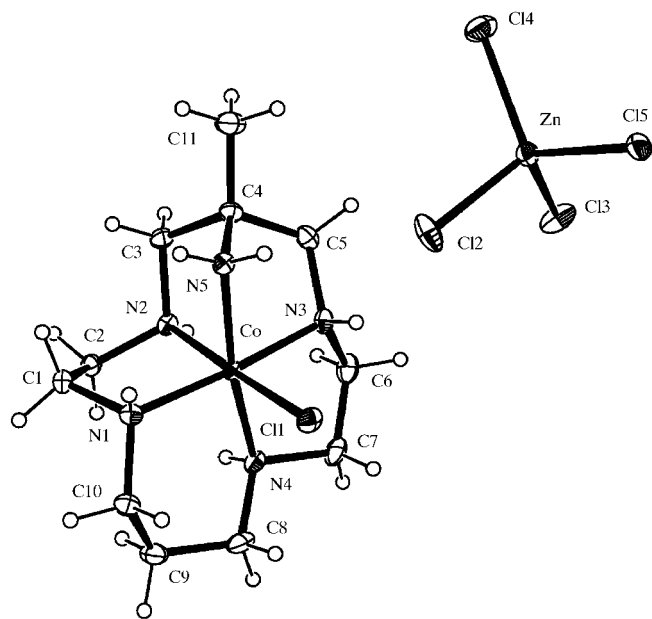


Figure 1
A view of the cation and anion of (I), with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

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-[CoLCl]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.

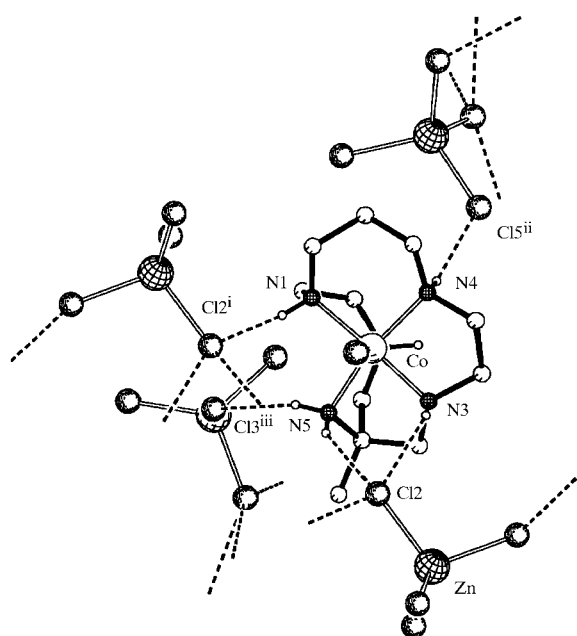


Figure 2
A view of the hydrogen-bonding in (I). Alkyl H atoms have been omitted. Symmetry codes are as given in Table 2.

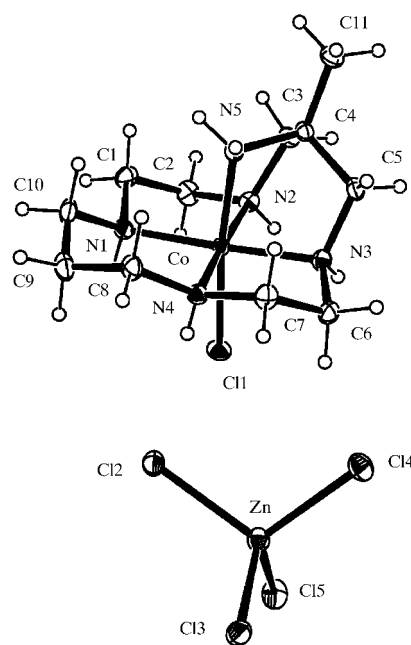


Figure 3
A view of the cation and anion of (II), with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii.

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 [ZnCl₄]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 chloropentaamine-cobalt(III) complexes have each been crystallized as their tetrachlorozincate salts. The coordination geometries of the cations are the same as reported for the

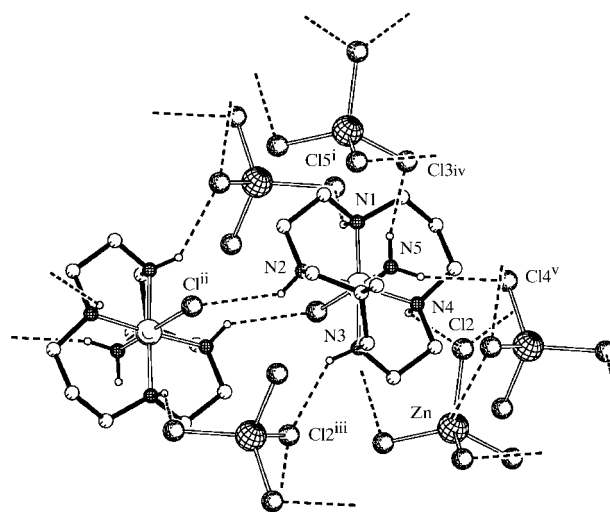


Figure 4
A view of the hydrogen-bonding in (II). Alkyl H atoms have been omitted. Symmetry codes are as given in Table 4.

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 CoCl₂·6H₂O with L·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 ZnCl₂·6H₂O. The *trans*-I-[CoLCl]²⁺ cation may be made selectively by reacting equimolar amounts of Na₃[Co(CO₃)₃]·3H₂O and L·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 ZnCl₂·6H₂O to an HCl solution.

Compound (I)

Crystal data

[CoCl(C₁₁H₂₇N₅)] [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) Å³
Z = 8
D_x = 1.829 Mg m⁻³

Mo *Kα* radiation
 Cell parameters from 25 reflections
 θ = 11.3–12.7°
 μ = 2.80 mm⁻¹
T = 296 (2) K
 Prism, red
 0.6 × 0.5 × 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* > 2σ(*I*)
 θ_{\max} = 25.0°
h = 0 → 13
k = 0 → 16
l = 0 → 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 $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.001
 $\Delta\rho_{\max} = 0.56 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.00173 (8)

Table 2

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...Cl2 ⁱ	0.91	2.33	3.214 (2)	164
N3—H3...Cl2	0.91	2.60	3.341 (2)	139
N4—H4...Cl5 ⁱⁱ	0.91	2.48	3.272 (2)	145
N5—H5C...Cl3 ⁱⁱⁱ	0.90	2.66	3.494 (2)	155
N5—H5D...Cl2	0.90	2.67	3.458 (2)	147
N5—H5D...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(C₁₁H₂₇N₅)] [ZnCl₄]
M_r = 530.93
 Monoclinic, *P2₁/c*
a = 11.9431 (9) Å
b = 12.167 (1) Å
c = 13.9670 (7) Å
 β = 99.165 (7)°
V = 2003.7 (2) Å³
Z = 4

D_x = 1.76 Mg m⁻³
 Mo *Kα* radiation
 Cell parameters from 25 reflections
 θ = 11.3–13.9°
 μ = 2.70 mm⁻¹
T = 296 (2) K
 Prism, red
 0.5 × 0.5 × 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* > 2σ(*I*)

*R*_{int} = 0.024
 θ_{\max} = 25.0°
h = 0 → 14
k = 0 → 14
l = -16 → 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)		

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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.80 \text{ e } \text{\AA}^{-3}$

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: TA1423). Services for accessing these data are described at the back of the journal.

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) 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 ($N-H = 0.90-0.91 \text{ \AA}$ and $C-H = 0.96-0.97 \text{ \AA}$).

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*

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