

trans-(DL-Isoleucinato-*N,O*)[tris(2-aminoethyl)amine- κ^4N]cobalt(III) diperchlorate

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The racemic title compound, *trans*-[*N,N*-bis(2-aminoethyl)-1,2-ethanediamine- κ^4N](DL-isoleucinato-*N,O*)cobalt(III) diperchlorate, [Co(C₆H₁₈N₄)(C₆H₁₂NO₂)](ClO₄)₂, crystallizes in the enantiomorphous space group *P*₂₁₂₁ with *Z* = 12 (*Z'* = 3). Each of the three cations in the asymmetric unit represents a different chirality of the isoleucine ligand; two of them are *R* (or *D*) and the third is the *S* (or *L*) enantiomer. The mixture crystallizes in a so-called unbalanced crystallization, in which the cations adopt a chiral array of composition *RRS* or *SSR*, depending on the crystal selected for data collection.

Comment

Crystalline racemates may belong to one of three categories: true racemic compounds (the two enantiomers are present in equal quantities in a well defined arrangement), conglomerates (a mechanical mixture of crystals of the two pure enantiomers), and pseudoracemates or solid solutions (two enantiomers co-existing in an unordered manner in the crystal) (Jacques *et al.*, 1981). Most racemates crystallize in the first class. Here, we report a rather rare crystallization mode adopted by the title racemic complex *trans*(*N,t-N*)[Co(tren)-(DL-isoleucinato-*N,O*)](ClO₄)₂, (I), where tren is tris(2-aminoethyl)amine and *trans*(*N,t-N*) refers to one of the two possible geometric isomers in which the tertiary N atom of tren is in the position *trans* to the amide N atom of isoleucine.

The title complex crystallizes in the enantiomorphous space group *P*₂₁₂₁, with *Z* = 12 (*Z'* = 3). Each of the three cations in the asymmetric unit contains a different chirality of isoleucine. Two of them are *R* (or *D*) and the third is the *S* (or *L*) isoleucine enantiomer. The mixture crystallizes in a chiral array of composition *RRS* or *SSR*, depending on the crystal selected for data collection. This type of crystallization of racemic complexes has been documented for [Cu(PF₃)₃X] (*X* is Cl or Br), [Pt(CO)(PF₃)₃] and [Ir(NO₂)(PF₃)₃] (Albano, Bellon & Sansoni, 1969; Albano, Ricci & Sansoni, 1969;

Albano *et al.*, 1971). These substances pack in space group *P*₃ with *Z* = 9, in chiral arrays of composition $\Lambda\Lambda\Delta$ or $\Delta\Delta\Lambda$. The crystallization mode was referred to as unbalanced crystallization.

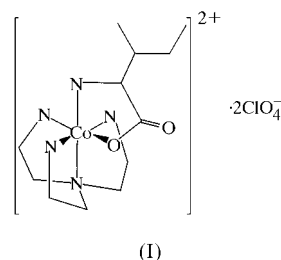


Fig. 1 shows the three independent cationic complexes in (I). The coordination geometries are very similar to each other, as well as to the reported analogues (Cai *et al.*, 2000). The differences between these three cations are the absolute configuration of the coordinated isoleucine and the conformation of the chelated five-membered rings of the tren ligand. They can be described as *S*($\delta\lambda\delta$), *R*($\delta\lambda\lambda$) and *R*($\delta\lambda\delta$) for cations 1, 2 and 3, respectively, where *R* and *S* refer to the absolute configuration of the α carbon of the isoleucine, and δ and λ refer to the absolute configurations of the five-membered chelated rings N—C—C—N of the tren ligand.

An analysis of the packing reveals double intercationic hydrogen-bonding interactions, resulting in a zigzag chain consisting of six cations denoted as Co3—Co2—Co1—Co1—Co2—Co3, with the chiralities of the ligands denoted as *R*—*R*—*S*—*S*—*R*—*R*. The six-membered chains are further linked into an infinite array by intercationic hydrogen-bonding interactions between cations of Co1, as shown in Fig. 2. The hydrogen bonds are listed in Table 1. The motifs of the intercationic hydrogen bonds can be described as a cyclic *R*₂¹(6) dimer and a finite *D*(6) chain, according to Etter's graph-set notation (Etter, 1990).

In our previous papers, we predicted (Cai *et al.*, 2000, 2001) and then validated (Hu *et al.*, 2001) that the series of [Co(N4)(DL-aminoacido)]²⁺ complexes, where N4 is a tetradentate ligand such as tren or trisethylenetetraamine (trien), is a system that tends to favour conglomerate crystallization. For most of the investigated racemic [Co(N4)(aminoacido)]²⁺ complexes, intercationic hydrogen-bonding interactions generally exist which bring cations of the same chirality together into helical chains. The spiral or helical chaining arrangement remains the same for both the racemic and enantiomeric complexes, regardless of whether the racemic complexes crystallize as a racemate or a conglomerate. Since the hydrogen-bonding pattern observed in the racemic crystal is the same as that observed in the enantiomeric form, we refer to it as the 'chiral recognition motif' of these systems. It is interesting to note that for (I), we observe a hydrogen-bonding motif which links only the Co1 cations together into an infinite helical arrangement, having hydrogen-bond parameters close to the average values reported, *i.e.* N \cdots O 2.875 Å and N—H \cdots O 155.3° for the first hydrogen bond, and N \cdots O 2.965 Å and N—H \cdots O 133.2° for

the second (Hu *et al.*, 2001). There are no direct contacts between cations centred on Co2 or Co3.

We have documented herein another unique and uncommon crystallization mode. There is another class of crystalline $[\text{Co}(\text{tren})(\text{DL-aminoacidato})]^{2+}$ compounds referred to as conglomeratic solids (Yamanari & Fuyuhiko, 1996; Hu *et al.*, 2001), in which the D- and L- amino acids occupy the same enantiomorphic crystalline lattice in an unbalanced fashion. Together with the kryptoracemate identified previously (Bernal *et al.*, 1995, 1996; Cai *et al.*, 1998), it is clear that the

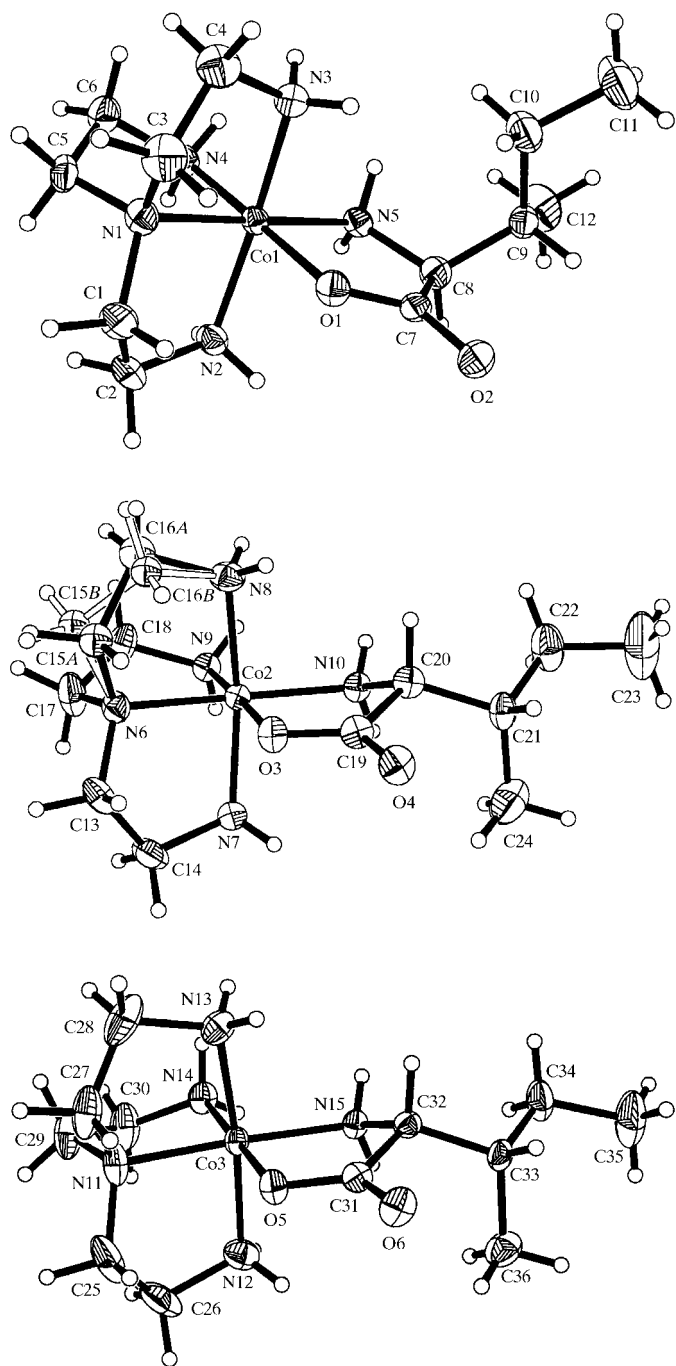


Figure 1
The conformations of the three independent cations of (I), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

three categories used to identify the nature of crystalline racemates are not sufficient to cover all the crystallization modes which can be adopted by racemic compounds.

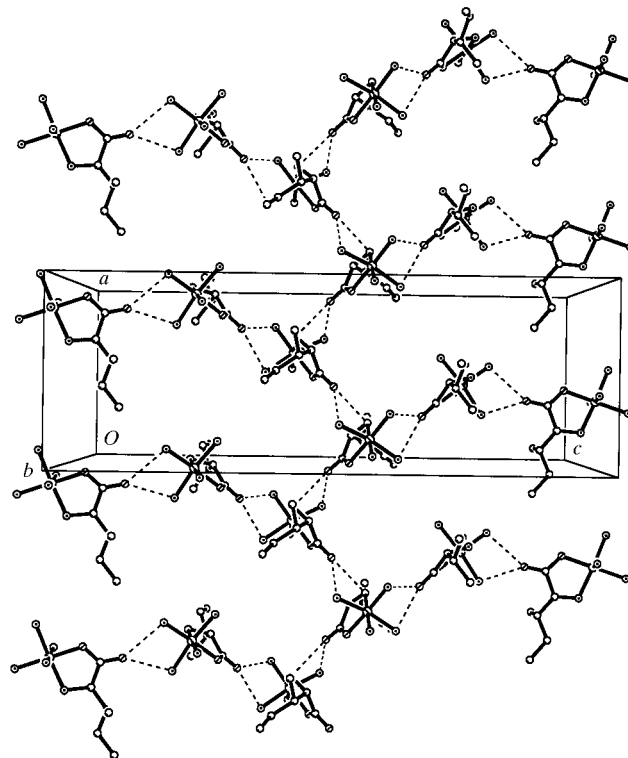


Figure 2
The packing arrangement of the cations in (I). The perchlorate anions, the C atoms of the tren ligands and all the H atoms have been omitted for clarity.

Experimental

To an aqueous solution of *cis*- $[\text{Co}(\text{tren})\text{Cl}_2]\text{Cl}$, a 10% aqueous solution of NaOH was added with stirring until the pH was 7.5–8.0. An equimolar amount of DL-isoleucine was added and the pH was again adjusted to 7.5–8.0. After heating at 333 K for several hours in a water bath, the colour changed to orange, and the solution was then cooled to room temperature and filtered. NaClO_4 was added to the resulting solution. Crystals of (I) suitable for X-ray diffraction data collection were obtained from this solution.

Crystal data

$[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)(\text{C}_6\text{H}_{12}\text{NO}_2)](\text{ClO}_4)_2$
 $M_r = 534.24$
 Orthorhombic, $P2_12_12_1$
 $a = 9.4330$ (12) Å
 $b = 25.266$ (3) Å
 $c = 27.258$ (4) Å
 $V = 6496.4$ (14) Å³
 $Z = 12$
 $D_x = 1.639$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 989 reflections
 $\theta = 3.78$ – 26.37°
 $\mu = 1.098$ mm⁻¹
 $T = 293$ (2) K
 Plate, orange
 $0.24 \times 0.12 \times 0.05$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.779$, $T_{\max} = 0.947$
 36 842 measured reflections

7309 independent reflections (plus 5923 Friedel-related reflections)
 10 595 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 26.37^\circ$
 $h = -11 \rightarrow 11$
 $k = -24 \rightarrow 31$
 $l = -33 \rightarrow 34$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.2357P]$
$R(F) = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\max} = 0.042$
$S = 1.003$	$\Delta\rho_{\max} = 0.72 \text{ e } \text{\AA}^{-3}$
13 232 reflections	$\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$
811 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.005 (13)

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2C··O2 ⁱ	0.90	2.20	2.728 (5)	117
N2—H2C··O13 ⁱⁱ	0.90	2.45	3.205 (7)	142
N2—H2D··O9 ⁱⁱⁱ	0.90	2.39	3.272 (10)	167
N3—H3C··O8 ^{iv}	0.90	2.53	3.270 (6)	139
N3—H3D··O4 ^v	0.90	2.11	2.914 (5)	148
N4—H4C··O4 ^v	0.90	2.12	2.930 (5)	149
N4—H4C··O7 ⁱⁱ	0.90	2.58	3.057 (7)	114
N4—H4D··O13 ⁱⁱ	0.90	2.17	3.030 (6)	159
N5—H5C··O2 ⁱ	0.90	2.04	2.828 (5)	146
N5—H5D··O4 ^v	0.90	2.28	3.045 (5)	142
N7—H7A··O6 ^{vi}	0.90	2.10	2.905 (5)	148
N7—H7B··O21	0.90	2.20	3.003 (7)	149
N8—H8B··O8 ^{vii}	0.90	2.30	3.082 (6)	146
N8—H8B··O10 ^{vii}	0.90	2.50	3.305 (11)	149
N8—H8C··O20 ^{viii}	0.90	2.16	3.000 (8)	155
N9—H9B··O20 ^{viii}	0.90	2.34	3.165 (8)	152
N9—H9C··O6 ^{vi}	0.90	2.08	2.912 (5)	154
N9—H9C··O26 ^{viii}	0.90	2.53	3.109 (10)	123
N10—H10C··O26 ^{viii}	0.90	2.16	2.837 (6)	131
N10—H10D··O20 ^{viii}	0.90	2.53	3.326 (10)	148
N10—H10D··O22 ^{viii}	0.90	2.61	3.472 (8)	160
N12—H12D··O27	0.90	2.14	3.036 (6)	171
N12—H12D··O28	0.90	2.61	3.227 (8)	126
N12—H12E··O14 ^{ix}	0.90	2.13	2.971 (7)	156
N13—H13C··O23 ^{vi}	0.90	2.13	2.998 (7)	163
N13—H13D··O25	0.90	2.55	3.145 (10)	124
N13—H13D··O22	0.90	2.64	3.349 (9)	136
N14—H14C··O22	0.90	2.28	3.123 (8)	155
N14—H14D··O27	0.90	2.42	3.163 (7)	140
N14—H14D··O30	0.90	2.46	3.318 (8)	159
N15—H15E··O28	0.90	2.23	3.103 (6)	165
N15—H15F··O24	0.90	2.07	2.960 (6)	169

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

All H atoms were placed in idealized positions (N—H = 0.90 \AA , and C—H = 0.98, 0.97 and 0.96 \AA for CH, CH₂ and CH₃, respectively) and were refined as riding with relative isotropic parameters. Some of

the O atoms of the perchlorate anions were disordered and caused high displacement parameters. Atoms C15 and C16 were disordered and were refined isotropically over two positions, denoted *A* and *B* in Fig. 1.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT+* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1160). Services for accessing these data are described at the back of the journal.

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