

## Tris(ethylenediamine-*N,N'*)cobalt(III) oxalate perchlorate dihydrate

Jiwen Cai,<sup>a\*</sup> Yufei Zhang,<sup>a</sup> Xiaopeng Hu<sup>b</sup> and Xiaolong Feng<sup>a</sup>

<sup>a</sup>Instrumentation Analysis and Research Center, Zhongshan University, Guangzhou 510275, People's Republic of China, and <sup>b</sup>Department of Chemistry, Zhongshan University, Guangzhou 510275, People's Republic of China  
Correspondence e-mail: puscjw@zsu.edu.cn

Received 5 January 2000

Accepted 24 February 2000

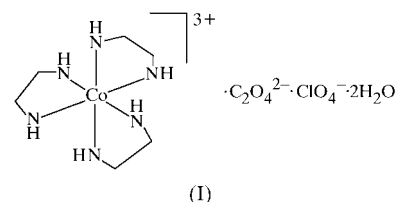
The crystallization behavior of the title compound,  $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{C}_2\text{O}_4)(\text{ClO}_4)\cdot 2\text{H}_2\text{O}$ , has been studied in order to evaluate the effect of the counter-anion on the crystalline structures of  $[\text{Co}(\text{en})_3](\text{C}_2\text{O}_4)\cdot X$  ( $\text{en}$  = ethylenediamine). Two-dimensional intermolecular hydrogen-bonding networks are formed between the amine protons of the  $[\text{Co}(\text{en})_3]^{3+}$  cations and the O atoms of the oxalate anions. Perchlorate and water molecules fill in the channels between the two-dimensional networks and form hydrogen-bonding interactions with the two-dimensional layers, thus constructing a three-dimensional hydrogen-bonding network.

### Comment

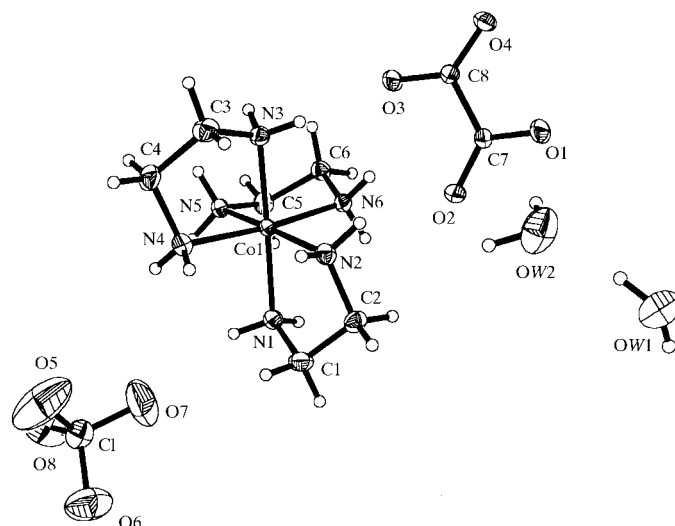
In preceding papers (Bernal *et al.*, 1995, 1996; Cai *et al.*, 1998), we reported a series of  $\text{Co}^{\text{III}}$ -amine complexes crystallized in enantiomorphic space groups whose asymmetric units are racemic pairs, a phenomenon defined as kryptoracemic crystallization. The kryptoracemic crystallization pathway is rather rarely adopted by coordination racemates (Bernal *et al.*, 1995, 1996, 1997; Cai *et al.*, 1998; Rodriguez *et al.*, 1996; Haupt & Huber, 1978), and is poorly documented and investigated. In order for a kryptoracemic crystallization mode to occur, the number of molecules in the unit cell,  $Z$ , must be an even multiple of the number of general positions of the space group and, while some atoms may share a non-crystallographic pseudo-inversion center, the degree to which they conform to such an inversion center varies for different sets of atoms.

In the crystal structures of the racemates  $[\text{Co}(\text{en})_3](\text{C}_2\text{O}_4)\cdot X\cdot 3\text{H}_2\text{O}$  ( $X = \text{Cl}^-$ ,  $\text{Br}^-$ ) and  $\{[\text{Co}(\text{en})_3](\text{C}_2\text{O}_4)\text{I}\}_2\cdot 3\text{H}_2\text{O}$ , the iodide crystallizes in the enantiomorphic space group  $P2_12_12_1$  with a racemic pair of  $[\text{Co}(\text{en})_3]^{3+}$  in the asymmetric unit, while both the chloride and bromide crystallize in the centrosymmetric space group  $C2/c$  (Bernal *et al.*, 1995). Counter-anions were claimed to be crucial for controlling the crystallization pathway adopted by these complexes. In order to support further the conclusion made in the previous paper, as well as to explore the structural factors that lead to the

kryptoracemic crystallization mode, a crystal structure analysis of the title compound, (I), was conducted.



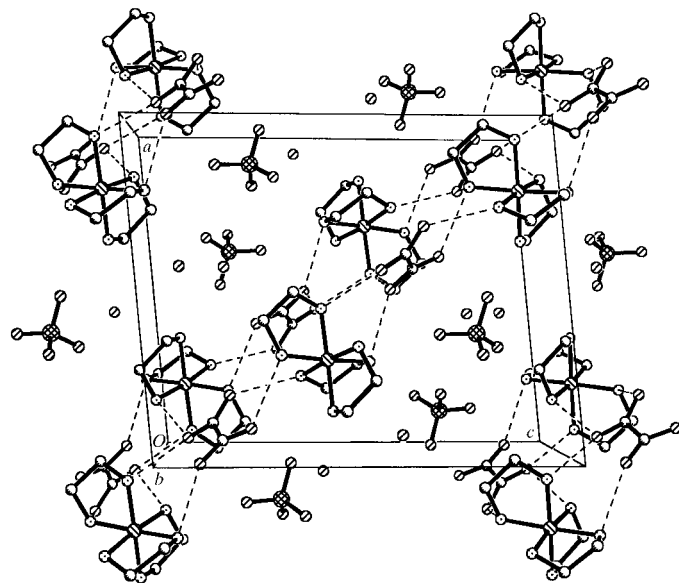
The geometry of the  $[\text{Co}(\text{en})_3]^{3+}$  moiety in the perchlorate is very similar to that in the iodide. The absolute configuration of the  $\text{Co}^{\text{III}}$  center is  $\Lambda(\delta\delta\delta)$  and  $\Delta(\lambda\lambda\lambda)$ , which is the highest energy conformation (Saito, 1985; Cotton & Wilkinson, 1988). The  $\text{Co}-\text{N}$  distances range from 1.9560 (15) to 1.9772 (17) Å, and the inter-ligand  $\text{N}-\text{Co}-\text{N}$  angles are in the range  $85.34(7)-93.86(7)^\circ$  for *cis*- and  $173.90(7)-174.79(7)^\circ$  for *trans*-N atoms. A layer-type structure is found in which each oxalate anion is involved with four  $\text{Co}^{\text{III}}$  complex cations through extensive hydrogen-bonding interactions formed between the oxalate-O atoms and the amine-H atoms of the en ligands, thus constructing a dense two-dimensional network as shown in Fig. 2. The complex cations running along the  $b$  axis in the same string have the same chirality, while cations in adjacent strings have opposite chirality. One can see that the perchlorate anions and water molecules pack between the layers formed by the complex cations and oxalate anions, and thus hold the layers together through intermolecular hydrogen bonds which form between the complex cations and the perchlorate anions, as well as between the oxalate anions and water molecules. In the iodide structure, a layer of helical strings composed of the same chirality of complex cations is found, and the strings are linked to each other by the oxalate and iodide anions and the waters of hydration. Adjacent layers are related by a non-crystallographic pseudo-inversion center, thus resulting in kryptoracemic crystallization. The packing feature of perchlorate is more similar to that adopted by the



**Figure 1**

The molecular structure of (I) showing 30% probability displacement ellipsoids.

chloride and bromide. In all three of these centrosymmetric structures, layer-type structures are constructed only by the complex cations and the oxalate anions, rather than involving all the moieties as observed in the kryptoracemic iodide. This packing similarity is also indicated by the fact that they all have very similar reported densities, which are 1.571, 1.695 and



**Figure 2**  
The packing of molecules of (I) viewed down the *b* axis. H atoms have been omitted and only cation–oxalate hydrogen bonds are depicted for clarity.

1.668 Mg m<sup>-3</sup> for the chloride, bromide and perchlorate, respectively, while for the iodide, the calculated density, 1.930 Mg m<sup>-3</sup>, is much higher. The perchlorate anion is much bulkier than the chloride and bromide and thus displaces one water of hydration.

To sum up what we observe here and in other series of complexes we have investigated, such as [Co(tren)(NO<sub>2</sub>)<sub>2</sub>]X {tren = tris(2-aminoethyl)amine, X = [Br(ClO<sub>4</sub>)<sub>0.5</sub><sup>-</sup>·0.5H<sub>2</sub>O, Br<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>]}, in which the double salt crystallizes as a kryptoracemate and the two parent salts as true racemates (Bernal *et al.*, 1996), and *cis*-[Co(dmtrien)(NO<sub>2</sub>)<sub>2</sub>]X (dmtrien = 3,6-dimethyl-3,6-diazaoctane-1,8-diamine, X = Cl<sup>-</sup>·0.5H<sub>2</sub>O, I<sup>-</sup>), in which the chloride crystallizes as a kryptoracemate and the iodide as a true racemate (Cai *et al.*, 1998), the kryptoracemic crystallization phenomenon of these series of complexes depends on the nature of the counter-anions. However, there is no clear relationship with the nature of the counter-anions and the crystallization pathway of the racemic complexes cannot be predicted.

## Experimental

To an aqueous solution of [Co(en)<sub>3</sub>]Cl<sub>3</sub>, equal amounts (molar) of NaClO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)·H<sub>2</sub>O were added under stirring until dissolved. The resulting solution was kept at room temperature. Crystals suitable for X-ray analysis were obtained after a few days.

## Crystal data

[Co(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>](C<sub>2</sub>O<sub>4</sub>)(ClO<sub>4</sub>)·2H<sub>2</sub>O  
*M<sub>r</sub>* = 462.74  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 12.5502 (7) Å  
*b* = 9.5832 (5) Å  
*c* = 15.3950 (8) Å  
 β = 95.7340 (10)°  
*V* = 1842.31 (17) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.668 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from global unit-cell refinement  
 θ = 2.00–27.02°  
 μ = 1.138 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, red  
 0.30 × 0.30 × 0.20 mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 φ and ω scans  
 Absorption correction: empirical (Blessing, 1995)  
*T*<sub>min</sub> = 0.727, *T*<sub>max</sub> = 0.804  
 10 764 measured reflections  
 4017 independent reflections

3256 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.021  
 θ<sub>max</sub> = 27.02°  
*h* = -15 → 16  
*k* = -5 → 12  
*l* = -19 → 19  
 Intensity decay: none

## Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.031  
*wR*(*F*<sup>2</sup>) = 0.090  
*S* = 1.024  
 4017 reflections  
 235 parameters  
 H atoms constrained

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0652*P*)<sup>2</sup> + 0.2357*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.006  
 Δρ<sub>max</sub> = 0.46 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.37 e Å<sup>-3</sup>

**Table 1**

Hydrogen-bonding geometry (Å, °).

<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–H1A...O4 <sup>i</sup>	0.90	2.16	2.848 (2)	133
N1–H1A...O7	0.90	2.59	3.276 (4)	133
N1–H1B...O1 <sup>ii</sup>	0.90	2.23	3.112 (3)	165
N2–H2A...O2	0.90	2.10	2.887 (2)	146
N2–H2A...O8 <sup>iii</sup>	0.90	2.50	3.130 (3)	128
N2–H2B...OW1 <sup>iv</sup>	0.90	2.17	3.045 (3)	165
N3–H3A...O3	0.90	2.24	2.960 (2)	137
N3–H3A...O8 <sup>iii</sup>	0.90	2.55	3.270 (3)	138
N3–H3B...O3 <sup>v</sup>	0.90	1.97	2.852 (2)	166
N4–H4A...O1 <sup>i</sup>	0.90	2.34	3.127 (2)	146
N4–H4B...OW1 <sup>iv</sup>	0.90	2.21	3.043 (3)	154
N5–H5A...O1 <sup>i</sup>	0.90	2.11	2.885 (2)	143
N5–H5A...O4 <sup>i</sup>	0.90	2.32	3.079 (2)	141
N5–H5B...O4 <sup>v</sup>	0.90	2.08	2.953 (2)	164
N6–H6A...O3	0.90	2.12	2.927 (2)	149
N6–H6A...O2	0.90	2.29	2.992 (2)	134
N6–H6B...O2 <sup>ii</sup>	0.90	2.02	2.908 (2)	167
OW1–HW1...OW2	0.95	1.79	2.732 (3)	172
OW1–HW2...O6 <sup>vi</sup>	0.84	2.37	3.071 (4)	141
OW2–HW3...O1	0.91	1.96	2.850 (3)	167
OW2–HW4...O6 <sup>vii</sup>	0.94	2.40	3.287 (4)	157

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

All H atoms of the en ligands were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters. The H atoms of the water molecules were found in the final difference Fourier map and refined as riding atoms. The distance C7–C8 of 1.551 (3) Å of the oxalate anion is within the range reported for analogous structures (Bernal *et al.*, 1995; Fuertes *et al.*, 1988; Myrczek, 1997), in which the corresponding distances range from 1.54 to 1.60 Å.

Data collection: *SMART* (Bruker, 1998a); cell refinement: *SMART*; 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, 1998b); software used to prepare material for publication: *SHELXTL*.

This work is supported by the National Nature Science Foundation of China (No. 29801006).

---

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1103). Services for accessing these data are described at the back of the journal.

---

## References

- Bernal, I., Cai, J., Massoud, S. S., Watkins, S. F. & Fronczek, F. (1996). *J. Coord. Chem.* **38**, 165–181.
- Bernal, I., Cai, J. & Myrczek, J. (1995). *Acta Chim. Hung.* **132**, 451–474.
- Bernal, I., Somoza, F. & Banh, V. (1997). *J. Coord. Chem.* **42**, 1–10.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruker (1998a). *SMART*. Version 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1998b). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SAINT+*. Version 6.0. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cai, J., Myrczek, J., Chun, H. & Bernal, I. (1998). *J. Chem. Soc. Dalton Trans.* pp. 4155–4160.
- Cotton, F. A. & Wilkinson, G. (1988). *Advanced Inorganic Chemistry*, pp. 55–56. New York: Wiley Interscience.
- Fuertes, A., Miravittles, C., Ibáñez, R., Martínez-Tamayo, E. & Beltrán-Porter, A. (1988). *Acta Cryst.* **C44**, 417–421.
- Haupt, H. J. & Huber, F. (1978). *Z. Anorg. Allg. Chem.* **442**, 31–40.
- Myrczek, J. (1997). *Pol. J. Chem.* **71**, 844–847.
- Rodríguez, M.-C., Morgenstern-Badarau, I., Cesario, M., Guilhem, J., Keita, B. & Nadjó, L. (1996). *Inorg. Chem.* **35**, 7804–7810.
- Saito, Y. (1985). *Stereochemistry of Optically Active Transition Metal Complexes*, American Chemical Society Symposium Series 119, pp. 13–42. Washington, DC: American Chemical Society.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.