Synthesis and structure determination of racemic (\(\Delta/\Lambda\))-tris(ethylenediamine)cobalt(III) trichloride hemi(hexaaquasodium chloride)

Linden H. Conrad-Marut, a Eric W. Reinheimer b and Adam R. Johnson a *

a Department of Chemistry, Harvey Mudd College, 301 Platt Avenue, Claremont, CA 91711-5990, USA, and b Rigaku Americas Corporation, 9009 New Trails Dr., The Woodlands, TX 77381, USA. *Correspondence e-mail: adam_johnson@hmc.edu

The synthesis and crystal structure of the title racemic compound, \([\text{Co(C_2H_8N_2)_3}]\text{Cl}_3 \cdot [\text{Na(H}_2\text{O)}_6]\text{Cl}]_{0.5}\), are reported. The trivalent cobalt atom, which resides on a crystallographic threefold axis, is chelated by a single ethylene diamine (en) ligand and yields the tris-chelate \([\text{Co(en)}_3]^{3+}\) cation with distorted octahedral geometry after the application of crystal symmetry. The sodium cation (site symmetry 3), has a single water molecule bound to it in the asymmetric unit and yields a distorted, octahedrally coordinated hydrated \([\text{Na(H}_2\text{O)}_6]^+\) cation after the application of symmetry. One of the chloride ions lies on a general position and the other has 3 site symmetry. An extensive array of C—H⋯O, N—H⋯Cl and O—H⋯Cl hydrogen bonds exists between the ethylene diamine ligands, the water molecules of hydration, and the anions present, thereby furnishing solid-state stability.

1. Chemical context

The coordination complex-cation tris-ethylenediamine cobalt(III), \([\text{Co(en)}_3]^{3+}\), was influential in Werner’s development of the structure of transition-metal complexes as it could be resolved into its two enantiomers by selective crystallization using tartrate anions, thus helping to demonstrate the octahedral geometry of the metal ion (Werner, 1912). As such, the synthesis of members of this family of complexes is a common undergraduate laboratory experiment (Work & McReynolds, 1946; Broomhead et al., 1960; Girolami et al., 1999; McClellan & Cass, 2015).

The synthesis and structural characterization of many members of this family of complexes, both racemic and resolved, have been undertaken over the years. In all cases, the \([\text{Co(en)}_3]^{3+}\) complex cation was found to have trigonally distorted octahedral symmetry, as expected, and the structures usually have significant hydrogen-bonding interactions involving the ethylene diamine ligands, the water molecules of hydration, and the anions present.
2. Structural commentary

The title compound crystallizes in the centrosymmetric trigonal space group $P\overline{3}c1$ (Fig. 1). The asymmetric unit consists of a trivalent cobalt atom residing on a threefold axis chelated by an ethylene diamine (en; C$_2$H$_8$N$_2$) ligand. Two Cl anions, one occupying a general position and the other lying on a 3 axis are also present. One Na cation, also positioned on a 3 axis, with a water molecule (general position) bound to it are also observed. After application of crystal symmetry, the [Co(en)$_3$]$^{3+}$ and [Na(H$_2$O)$_6$]$^+$ cationic complexes that result each adopt distorted octahedral geometries.

Within the chelating en ligand, given the $sp^3$-hybridization of the C atoms and an expected tetrahedral coordination environment around those C atoms, bond angles around each should be near the expected 109.5°. The values obtained from the crystal structure [minimum = 106.33 (15)°; maximum = 111.2 (12)°] indicate a degree of distortion.

Solid-state integrity is maintained by an array of C—H⋯O, N—H⋯Cl and O—H⋯Cl hydrogen bonds between the [Co(en)$_3$]$^{3+}$ and [Na(H$_2$O)$_6$]$^+$ cations and the chloride anions. Unlike the structure of enantiopure $[\text{tris}$($\text{ethylenediamine}$)$\text{cobalt(III)}$] trichloride $0.5\text{NaCl}$ $3\text{H}_{2}\text{O}$ (Nakatsu et al., 1957; Farrugia et al., 2000), where the sodium cations and chloride anions showed signs of disorder, no features suggestive of disorder are observed in the structure of the racemate.

3. Supramolecular features

The en-chelated, trivalent cobalt atom in the title compound lies on a threefold axis housed within the (021) plane. As a result of crystal symmetry, the full [Co(en)$_3$]$^{3+}$ cation is generated and shows both the $\Delta\delta\delta\delta$ and the $\Delta\alpha\alpha\alpha\alpha$ configurations with distorted octahedral geometry (Jensen, 1970). By virtue of its residing on a threefold axis, the net +1 charge that results from the Co atom is balanced by a fully occupied Cl anion occupying a general position. Typically, changes in conformation of the en ligand can be attributed to hydrogen bonding; however, all en conformations in both Co(en)$_3$ and Cr(en)$_3$ cations demonstrate similar energies (Veal & Hodgson, 1972; Enemark et al., 1970; Raymond et al., 1968a,b; Raymond & Ibers, 1968). Analogous to the many structures encompassing the [Co(en)$_3$]$^{3+}$ cation, hydrogen-bonded arrays are prevalent in the solid-state structure between the en ligands and both water molecules and chloride anions (Table 1).

It is notable that Cl$_2$ accepts six, symmetry-equivalent O1—H1E⋯Cl2 hydrogen bonds (Table 1) and forms a distorted Cl$_2$(H$_2$O)$_6$ octahedron. Along the c-axis, the orientation of the sodium and Cl$_2$ octahedra with respect to one another forms a herringbone-type pattern when looking into the $ac$ plane (Fig. 2). Collectively, the symmetry elements within the solid-
The structure of racemic [Co(en)]$_3$Cl$_3$ was reported to have the trigonal space group $P31c1$; however, no additional structural details were reported (Dingle & Ballhausen, 1967). This salt was later crystallized as the non-stoichiometric hydrate (6.75 g, 170 mmol) were next added slowly while the solution was stirred. Each pellet initially turned blue and then completely dispersion at that time (Nakatsu, 1962). The structure of the racemate make it an excellent illustration of the $P6mm$ two-dimensional space group when looking towards the ab plane (Fig. 3).

4. Database survey

The structure of racemic [Co(en)$_3$]Cl$_3$ was prepared following the method of Girolami (Girolami et al., 1999) and later modified by Cass (McClellan & Cass, 2015). Into a 100 ml beaker, CoCl$_2$·6H$_2$O (6.0 g, 25 mmol, finely ground using a mortar and pestle) was added dropwise until the pH was approximately 7–7.5, then completely dissolved within a few minutes. The pH was then tested using litmus paper and determined to be 8. Hydrochloric acid (6 M) was added dropwise until the pH was approximately 7–7.5.
which changed the color of the solution to rusty orange. A hydrogen peroxide solution (20 ml of 3% solution) was added dropwise over a couple of minutes and the solution became dark orange. The solution was slowly brought to a boil while stirring. The stir bar was removed and the beaker placed into an ice bath for 30 minutes to cool. The crystals were collected through filtration and washed with 95% ethanol (50 ml) and subsequently diethyl ether (20 ml) to yield a bright-orange powder (6.754 g, 18.6 mmol, 74.5%). Large single crystals (ca 3 x 3 x 3 mm) of 1 were grown by slow evaporation from water and cut to size using a razor blade.

6. Refinement

Crystal data, data collection and structure refinement details for 1 are summarized in Table 2. With the exception of atom H1E, which was constrained to ride on the water O atom (O1), all other H atoms were located in the difference-Fourier map and freely refined with 0.91 < C—H < 0.99 Å, 0.81 < N—H < 0.84 Å, and O—H = 0.89 Å.

Funding information

Funding for this research was provided by: Harvey Mudd College.

References

Broomhead, J. A., Dwyer, F. P., Hogarth, J. W. & Sievers, R. E. (1960). Inorg. Synth. pp. 183–186.
Dingle, R. & Ballhausen, C. J. (1967). Mat. Fys. Medd. Dan. Vid. Selsk. 35, 3–26.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). J. Appl. Cryst. 42, 339–341.
Enemark, J. H., Quinby, M. S., Reed, L. L., Steuck, M. J. & Walthers, K. K. (1970). Inorg. Chem. 9, 2397–2403.
Farrugia, L. J., Peacock, R. D. & Stewart, B. (2000). Acta Cryst. C56, 149–151.
Girolami, G. S., Rauchfuss, T. B. & Angelici, R. J. (1999). Synthesis and Technique in Inorganic Chemistry, 3rd ed. Sausalito, California: University Science Books.
Grant, G. J., Noll, B. C. & Lee, J. P. (2019). Z. Anorg. Allg. Chem. 645, 1011–1014.
Iwata, M., Nakatsu, K. & Saito, Y. (1969). Acta Cryst. B25, 2562–2571.
Jensen, K. A. (1970). Inorg. Chem. 9, 1–5.
Matsuki, R., Shiro, M., Asahi, T. & Asai, H. (2001). Acta Cryst. E57, m448–m450.
McClellan, M. J. & Cass, M. E. (2015). J. Chem. Educ. 92, 1766–1770.
Nakatsu, K. (1962). Bull. Chem. Soc. Jpn, 35, 832–839.
Nakatsu, K., Shiro, M., Saito, Y. & Kuroya, H. (1957). Bull. Chem. Soc. Jpn, 30, 158–164.
Oldenbourg, D. G. (1998). Z. Kristallogr. Krist. 213, 161–167.
Raymond, K. N., Cortfield, P. W. R. & Ibers, J. A. (1968a). Inorg. Chem. 7, 842–844.
Raymond, K. N., Cortfield, P. W. R. & Ibers, J. A. (1968b). Inorg. Chem. 7, 1362–1372.
Raymond, K. N. & Duesler, E. N. (1971). Inorg. Chem. 10, 1486–1492.
Raymond, K. N. & Ibers, J. A. (1968). Inorg. Chem. 7, 2333–2338.
Rigaku OD (2020). CrysAlis PRO. Rigaku Oxford Diffraction, Tokyo, Japan.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Takamizawa, S., Akatsuka, T. & Ueda, T. (2008). Angew. Chem. Int. Ed. 47, 1689–1692.
Veal, J. T. & Hodgson, D. J. (1972). Inorg. Chem. 11, 597–600.
Werner, A. (1912). Ber. Dtsch. Chem. Ges. 45, 121–130.
Whuler, A., Brouty, C., Spinat, P. & Herpin, P. (1975). Acta Cryst. B31, 2069–2076.
Witiak, D., Clardy, J. C. & Martin, D. S. (1972). Acta Cryst. B28, 2694–2699.
Work, J. B. & McReynolds, J. P. (1946). Inorg. Synth. pp. 221–222.
Synthesis and structure determination of racemic (Δ/Λ)-tris(ethylenediamine)-cobalt(III) trichloride hemi(hexaaquasodium chloride)

Linden H. Conrad-Marut, Eric W. Reinheimer and Adam R. Johnson

Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2020); cell refinement: CrysAlis PRO (Rigaku OD, 2020); data reduction: CrysAlis PRO (Rigaku OD, 2020); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

(Δ/Λ)-tris(ethylenediamine)cobalt(III) trichloride hemi(hexaaquasodium chloride)

Crystal data

[Co(C2H8N2)3]Cl3·{[Na(H2O)6]Cl}0.5

Mr = 428.86
Trigonal, P3c1
a = 11.4290 (2) Å
c = 15.5815 (2) Å
V = 1762.61 (7) Å³
Z = 4

Tmin = 0.664, Tmax = 0.794

Data collection

XtaLAB Mini II

diffraclometer

Radiation source: fine-focus sealed X-ray tube,
Rigaku (Mo) X-ray Source

Graphite monochromator

Detector resolution: 10.0000 pixels mm⁻¹
ω scans

Absorption correction: analytical
(Chemical Crystallography and Diffractometry, 2002)

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.027
wR(F²) = 0.072
S = 1.06

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F²) + (0.0373P)² + 0.9272P]

where P = (F² + 2Fc²)/3

(Δ/σ)max = 0.001
Δρmax = 0.47 e Å⁻³
Δρmin = −0.76 e Å⁻³
Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|Atom| x | y | z | U(eq) |
|----|----|----|----|-------|
|Co1 | 0.3333 | 0.6667 | 0.88151 (2) | 0.01756 (9) |
|Cl1 | 0.10242 (4) | 0.61265 (4) | 0.62517 (2) | 0.03423 (11) |
|Cl2 | 0.0000 | 1.0000 | 0.5000 | 0.0546 (3) |
|Na1 | 0.0000 | 1.0000 | 0.7500 | 0.0543 (5) |
|N1 | 0.29983 (13) | 0.51120 (12) | 0.95321 (8) | 0.0244 (2) |
|N2 | 0.18593 (13) | 0.53380 (13) | 0.80958 (8) | 0.0273 (2) |
|O1 | 0.08849 (18) | 0.88917 (17) | 0.65619 (12) | 0.0592 (4) |
|H1E | 0.0758 | 0.9001 | 0.6015 | 0.089* |
|C1 | 0.17218 (16) | 0.39077 (15) | 0.92577 (10) | 0.0302 (3) |
|C2 | 0.16421 (17) | 0.39746 (16) | 0.82971 (10) | 0.0316 (3) |
|H2C | 0.235 (2) | 0.386 (2) | 0.8014 (13) | 0.036 (5)* |
|H1A | 0.363 (2) | 0.494 (2) | 0.9459 (13) | 0.036 (5)* |
|H1C | 0.171 (2) | 0.310 (2) | 0.9475 (15) | 0.042 (6)* |
|H1D | 0.103 (2) | 0.396 (2) | 0.9513 (13) | 0.033 (5)* |
|H2D | 0.081 (2) | 0.332 (2) | 0.8111 (13) | 0.040 (6)* |
|H2A | 0.114 (2) | 0.533 (2) | 0.8215 (14) | 0.038 (5)* |
|H1B | 0.291 (2) | 0.519 (2) | 1.0044 (14) | 0.038 (5)* |
|H2B | 0.198 (2) | 0.546 (2) | 0.7578 (14) | 0.042 (6)* |
|H1F | 0.105 (4) | 0.824 (4) | 0.639 (2) | 0.096 (11)* |

Atomic displacement parameters (Å²)

|Atom| U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|----|-----|-----|-----|-----|-----|-----|
|Co1 | 0.01928 (11) | 0.01928 (11) | 0.01412 (13) | 0.00964 (5) | 0.000 | 0.000 |
|Cl1 | 0.03216 (19) | 0.0423 (2) | 0.02759 (18) | 0.01808 (16) | 0.00203 (13) | 0.00448 (14) |
|Cl2 | 0.0568 (5) | 0.0568 (5) | 0.0501 (7) | 0.0284 (2) | 0.000 | 0.000 |
|Na1 | 0.0515 (7) | 0.0515 (7) | 0.0598 (13) | 0.0258 (4) | 0.000 | 0.000 |
|N1 | 0.0287 (6) | 0.0247 (5) | 0.0207 (5) | 0.0141 (5) | −0.0015 (4) | 0.0011 (4) |
|N2 | 0.0278 (6) | 0.0296 (6) | 0.0222 (5) | 0.0126 (5) | −0.0053 (4) | −0.0026 (4) |
|O1 | 0.0636 (10) | 0.0485 (9) | 0.0674 (10) | 0.0295 (8) | −0.0137 (8) | −0.0076 (8) |
|C1 | 0.0318 (7) | 0.0225 (6) | 0.0299 (7) | 0.0088 (5) | 0.0024 (5) | 0.0017 (5) |
|C2 | 0.0340 (7) | 0.0246 (6) | 0.0289 (7) | 0.0092 (6) | −0.0045 (6) | −0.0067 (5) |

Geometric parameters (Å, °)

|Atom| Bond Distance| Bond Angle |
|----|---------------|------------|
|Co1—N1 | 1.9676 (12) | N1—H1A | 0.84 (2) |
|Co1—N1 | 1.9676 (12) | N1—H1B | 0.81 (2) |
|Co1—N1 | 1.9677 (12) | N2—C2 | 1.484 (2) |
|Co1—N2 | 1.9601 (12) | N2—H2A | 0.84 (2) |
### Hydrogen-bond geometry (Å, °)

| D—H···A     | D—H | H···A | D···A     | D—H···A |
|-------------|------|-------|-----------|---------|
| N1—H1A···Cl1viii | 0.84 (2) | 2.57 (2) | 3.3586 (13) | 156.7 (18) |
| N1—H1B···Cl1ix | 0.81 (2) | 2.75 (2) | 3.4317 (13) | 142.0 (19) |
| N2—H2A···Cl1vii | 0.84 (2) | 2.50 (2) | 3.3286 (14) | 172 (2) |

Symmetry codes: (i) \(-x+y, -x+1, z\); (ii) \(-y+1, x-y+1, z\); (iii) \(-y+1, x-y+2, z\); (iv) \(x-y+1, -y+2, -z+3/2\); (v) \(y-1, x+1, z\); (vi) \(-x+y-1, -x+1, z\); (vii) \(-x, -x+y, -z+3/2\).
|       | d (Å)  | r (Å)  | D (°)  |          |
|-------|--------|--------|--------|----------|
| N2—H2B···Cl1 | 0.82 (2) | 2.62 (2) | 3.2925 (13) | 140.6 (19) |
| O1—H1E···Cl2 | 0.88 | 2.35 | 3.1354 (18) | 147 |
| O1—H1F···Cl1 | 0.89 (4) | 2.41 (4) | 3.2787 (18) | 164 (3) |
| C2—H2D···O1x | 0.92 (2) | 2.59 (2) | 3.361 (2) | 142.1 (17) |

Symmetry codes: (vii) −x, −x+y, −z+3/2; (viii) x−y+1, −y+1, −z+3/2; (ix) x, x−y+1, z+1/2; (x) −y+1, x, −z+3/2.