Synthesis and structure determination of racemic (Δ/Λ)-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, $[Co(C_2H_8N_2)_3]Cl_3.\{[Na(H_2O)_6]Cl\}_{0.5}$, 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 $[Co(en)_3]^{3+}$ cation with distorted octahedral geometry after the application of crystal symmetry. The sodium cation (site symmetry $\bar{3}$), has a single water molecule bound to it in the asymmetric unit and yields a distorted, octahedrally coordinated hydrated $[Na(H_2O)_6]^+$ cation after the application of symmetry. One of the chloride ions lies on a general position and the other has $\bar{3}$ 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), $[Co(en)_3]^{3+}$, 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 $[Co(en)_3]^{3+}$ 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.
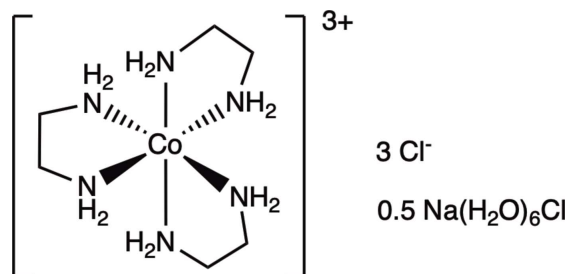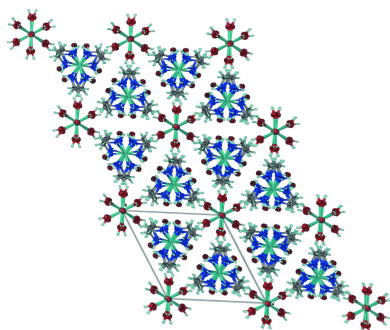
2. Structural commentary

The title compound crystallizes in the centrosymmetric trigonal space group $P\bar{3}c1$ (Fig. 1). The asymmetric unit consists of a trivalent cobalt atom residing on a threefold axis chelated by an ethylene diamine (en; $C_2H_8N_2$) ligand. Two Cl anions, one occupying a general position and the other lying on a $\bar{3}$ axis are also present. One Na cation, also positioned on a $\bar{3}$ axis, with a water molecule (general position) bound to it are also observed. After application of crystal symmetry, the $[Co(en)_3]^{3+}$ and $[Na(H_2O)_6]^+$ 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 $C-H\cdots O$, $N-H\cdots Cl$ and $O-H\cdots Cl$ hydrogen bonds between the $[Co(en)_3]^{3+}$ and $[Na(H_2O)_6]^+$ cations and the chloride anions. Unlike the structure of enantiopure Λ-[tris(ethylenediamine)cobalt(III) trichloride]·0.5NaCl·3H$_2$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 $\Lambda\delta\delta\delta$ and the $\Delta\lambda\lambda\lambda$ 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
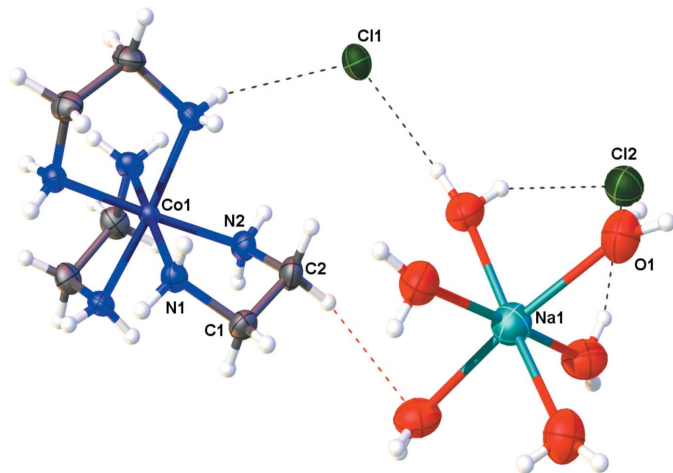

Figure 2
Face-sharing octahedra looking into the *ac* plane encompassing the Na(H$_2$O)$_6^+$ cations and six water molecules hydrogen bonded to Cl2 that form a herringbone pattern with respect to one another. Anisotropic displacement ellipsoids have been set to the 50% probability level. Dashed lines represent hydrogen bonds.

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 Cl2 accepts six, symmetry-equivalent O1—H1$E\cdots$Cl2 hydrogen bonds (Table 1) and forms a distorted Cl(H$_2$O)$_6$ octahedron. Along the *c*-axis, the orientation of the sodium and Cl2 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-

Figure 1
Anisotropic displacement ellipsoid plot of **1** with ellipsoids set to the 50% probability level. Atoms in the asymmetric unit are labeled. Dashed lines represent hydrogen bonds.
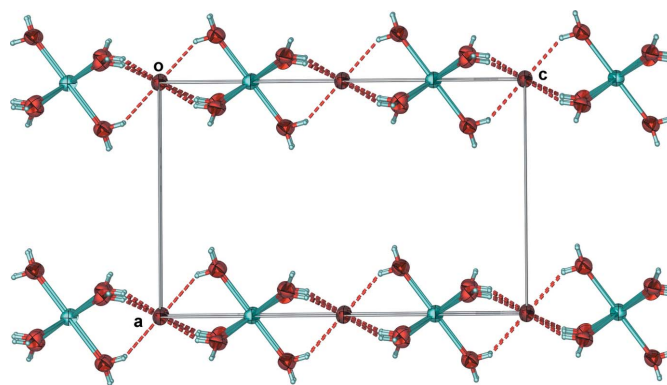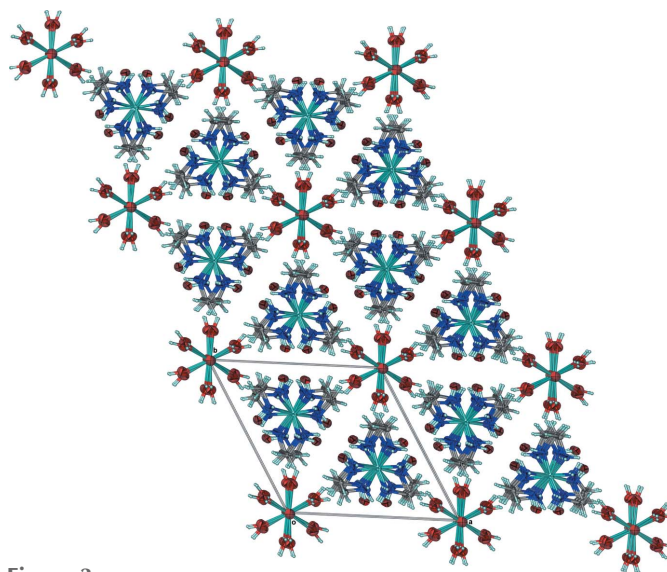

Figure 3
Packing of **1** relative to the *ab* plane. Collectively, the symmetry elements make the structure of **1** an excellent example of the *p6mm* two-dimensional space group. Anisotropic displacement ellipsoids have been set to the 50% probability level.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A···Cl1[i]	0.84 (2)	2.57 (2)	3.3586 (13)	156.7 (18)
N1—H1B···Cl1[ii]	0.81 (2)	2.75 (2)	3.4317 (13)	142.0 (19)
N2—H2A···Cl1[iii]	0.84 (2)	2.50 (2)	3.3286 (14)	172 (2)
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···O1[iv]	0.92 (2)	2.59 (2)	3.361 (2)	142.1 (17)

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

state 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 reported to have the trigonal space group $P\bar{3}c1$; however, no additional structural details were reported (Dingle & Ballhausen, 1967). This salt was later crystallized as the non-stoichiometric hydrate (2.8 water molecules per cobalt center) with long chains of hydrogen-bonded water molecules that precluded interactions between the incorporated water molecules and the ethylene diamine ligands (Whuler *et al.*, 1975). This same salt was later crystallized as the tetrahydrate and included a one-dimensional water chain perpendicular to the [001] direction. The solid was vacuum dried to form void channels that could incorporate guest molecules (Takamizawa *et al.*, 2008).

Like racemic [Co(en)$_3$]Cl$_3$, other chemically-similar salts have been crystallized that demonstrate hydrogen-bonding arrays involving the ethylenediamine ligands, interstitial water molecules, and the counter-ions. These included the Λ-enantiomer of the monohydrate Cl and I salts, which crystallize in the tetragonal space group $P4_32_12$, in 1969 and 2001, respectively (Iwata *et al.*, 1969; Matsuki *et al.*, 2001). The structure of the bromide salt of the Δ-enantiomer, Δ-[Co(en)$_3$]Br$_3$·H$_2$O, was carried out in 1962, though the absolute structure could not be determined by anomalous dispersion at that time (Nakatsu, 1962). The structure of the right-handed helical enantiomer, Δ-[Co(en)$_3$]I$_3$·H$_2$O was finally reported in 2019 and crystallizes in the orthorhombic space group $P2_12_12_1$ (Grant *et al.*, 2019).

More complex counter-ions have also been utilized in racemic and purely enantiomeric salts with [Co(en)$_3$]$^{3+}$. The structures of the nitrate salts, obtained both as a racemic crystal in the $Pca2_1$ space group (Oldenbourg, 1998) and as the Λ-enantiomer in the $P4_12_12$ space group (Witiak *et al.*, 1972) were reported. Racemic crystals [Co(en)$_3$][Cr(CN)$_5$(NO)]·2H$_2$O (Enemark *et al.*, 1970) and [Co(en)$_3$]$_2$[CdCl$_6$]Cl$_2$·2H$_2$O (Veal & Hodgson, 1972) were also reported, which crystallize in the monoclinic space group $P2_1/c$. The complex racemic hydrogen phosphate salt [Co(en)$_3$]$_2$[HPO$_4$]$_3$·9H$_2$O was determined to exist in the orthorhombic space group *Pnma* (Raymond & Duesler, 1971).

Table 2
Experimental details.

Crystal data	
Chemical formula	[Co(C$_2$H$_8$N$_2$)$_3$]Cl$_3$·{[Na(H$_2$O)$_6$]Cl}$_{0.5}$
M_r	428.86
Crystal system, space group	Trigonal, $P\bar{3}c1$
Temperature (K)	293
a, c (Å)	11.4290 (2), 15.5815 (2)
V (Å^3)	1762.61 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.53
Crystal size (mm)	0.39 × 0.29 × 0.22
Data collection	
Diffractometer	XtaLAB Mini II
Absorption correction	Analytical (*CrysAlis PRO*; Rigaku OD, 2020)
T_{min}, T_{max}	0.664, 0.794
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	65362, 1860, 1643
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.722
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.072, 1.06
No. of reflections	1860
No. of parameters	99
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.76

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

In this latter-most structure, it has been proposed that the significant hydrogen bonding involving the en ligands, the counter-ion and the water molecules of hydration is directly responsible for this material's circular dichroism spectrum (Raymond & Duesler, 1971).

As the student laboratory preparation usually involves the synthesis of the racemic double salt [Co(en)$_3$]·Cl$_3$·0.5NaCl·3H$_2$O (McClellan & Cass, 2015; Girolami *et al.*, 1999), we were surprised to not find its structure reported in the Cambridge Structural Database. As mentioned previously, the structure of the Λ-enantiomer of the complex was first reported in 1957 (Nakatsu *et al.*, 1957) and later redetermined in 2000 (Farrugia *et al.*, 2000).

5. Synthesis and crystallization

The title complex **1** 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 dissolved in water (20 mL) with stirring. Upon addition of ethylenediamine dihydrochloride (13.3 g, 100 mmol), the solution became pink and cloudy. Sodium hydroxide pellets (6.75 g, 170 mmol) were next added slowly while the solution stirred. Each pellet initially turned blue and 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 × 3 ×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 H1*E*, 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.

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.* C**56**, 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., Nakatzu, K. & Saito, Y. (1969). *Acta Cryst.* B**25**, 2562–2571.

Jensen, K. A. (1970). *Inorg. Chem.* **9**, 1–5.

Matsuki, R., Shiro, M., Asahi, T. & Asai, H. (2001). *Acta Cryst.* E**57**, 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., Corfield, P. W. R. & Ibers, J. A. (1968*a*). *Inorg. Chem.* **7**, 842–844.

Raymond, K. N., Corfield, P. W. R. & Ibers, J. A. (1968*b*). *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. (2015*a*). *Acta Cryst.* A**71**, 3–8.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 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.* B**31**, 2069–2076.

Witiak, D., Clardy, J. C. & Martin, D. S. (1972). *Acta Cryst.* B**28**, 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

$[Co(C_2H_8N_2)_3]Cl_3 \cdot \{[Na(H_2O)_6]Cl\}_{0.5}$	$D_x = 1.616$ Mg m^{-3}
$M_r = 428.86$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $P\bar{3}c1$	Cell parameters from 30262 reflections
$a = 11.4290$ (2) Å	$\theta = 2.1$–$30.7°$
$c = 15.5815$ (2) Å	$\mu = 1.53$ mm^{-1}
$V = 1762.61$ (7) Å^3	$T = 293$ K
$Z = 4$	Block, clear light orange
$F(000) = 896$	$0.39 \times 0.29 \times 0.22$ mm

Data collection

XtaLAB Mini II diffractometer	$T_{min} = 0.664$, $T_{max} = 0.794$
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source	65362 measured reflections
	1860 independent reflections
Graphite monochromator	1643 reflections with $I > 2\sigma(I)$
Detector resolution: 10.0000 pixels mm^{-1}	$R_{int} = 0.027$
ω scans	$\theta_{max} = 30.9°$, $\theta_{min} = 2.6°$
Absorption correction: analytical (CrysalisPro; Rigaku OD, 2020)	$h = -16 \rightarrow 16$
	$k = -16 \rightarrow 16$
	$l = -22 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.027$	
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.9272P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
1860 reflections	$(\Delta/\sigma)_{max} = 0.001$
99 parameters	$\Delta\rho_{max} = 0.47$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.76$ e Å^{-3}
Primary atom site location: dual	

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)

	x	*y*	*z*	U_{iso}*/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)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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, º)

Co1—N1ⁱ	1.9676 (12)	N1—H1A	0.84 (2)
Co1—N1ⁱⁱ	1.9676 (12)	N1—H1B	0.81 (2)
Co1—N1	1.9677 (12)	N2—C2	1.484 (2)
Co1—N2ⁱ	1.9601 (12)	N2—H2A	0.84 (2)

Co1—N2^{ii}	1.9601 (12)	N2—H2B	0.82 (2)
Co1—N2	1.9600 (12)	O1—H1E	0.8837
Na1—O1^{iii}	2.4586 (19)	O1—H1F	0.89 (4)
Na1—O1^{iv}	2.4586 (19)	C1—C2	1.504 (2)
Na1—O1^{v}	2.4587 (19)	C1—H1C	0.97 (2)
Na1—O1	2.4586 (19)	C1—H1D	0.91 (2)
Na1—O1^{vi}	2.4586 (19)	C2—H2C	0.99 (2)
Na1—O1^{vii}	2.4586 (19)	C2—H2D	0.92 (2)
N1—C1	1.4825 (19)		
N1^{i}—Co1—N1^{ii}	90.94 (5)	O1^{iii}—Na1—O1^{v}	96.03 (8)
N1^{i}—Co1—N1	90.94 (5)	Co1—N1—H1A	109.1 (14)
N1^{ii}—Co1—N1	90.94 (5)	Co1—N1—H1B	115.9 (15)
N2^{i}—Co1—N1^{i}	85.48 (5)	C1—N1—Co1	109.36 (9)
N2—Co1—N1^{ii}	174.50 (5)	C1—N1—H1A	108.0 (14)
N2—Co1—N1	85.48 (5)	C1—N1—H1B	105.5 (16)
N2—Co1—N1^{i}	93.29 (6)	H1A—N1—H1B	109 (2)
N2^{i}—Co1—N1	174.50 (5)	Co1—N2—H2A	109.7 (15)
N2^{ii}—Co1—N1^{i}	174.50 (6)	Co1—N2—H2B	115.3 (15)
N2^{ii}—Co1—N1	93.29 (6)	C2—N2—Co1	108.69 (9)
N2^{i}—Co1—N1^{ii}	93.29 (6)	C2—N2—H2A	107.2 (16)
N2^{ii}—Co1—N1^{ii}	85.48 (5)	C2—N2—H2B	108.5 (15)
N2^{i}—Co1—N2^{ii}	90.55 (6)	H2A—N2—H2B	107 (2)
N2^{i}—Co1—N2	90.55 (6)	Na1—O1—H1E	111.2
N2—Co1—N2^{ii}	90.55 (6)	Na1—O1—H1F	156 (2)
O1^{iv}—Na1—O1^{v}	88.27 (6)	H1E—O1—H1F	87.3
O1^{iv}—Na1—O1	96.03 (8)	N1—C1—C2	107.24 (12)
O1—Na1—O1^{v}	174.05 (8)	N1—C1—H1C	108.8 (14)
O1^{vi}—Na1—O1^{iv}	174.05 (8)	N1—C1—H1D	107.4 (13)
O1^{vi}—Na1—O1^{v}	87.75 (8)	C2—C1—H1C	115.0 (13)
O1^{vii}—Na1—O1^{iv}	88.27 (6)	C2—C1—H1D	110.8 (13)
O1^{vii}—Na1—O1	87.75 (8)	H1C—C1—H1D	107.4 (18)
O1^{vi}—Na1—O1^{iii}	88.27 (6)	N2—C2—C1	106.33 (12)
O1^{iii}—Na1—O1	88.27 (6)	N2—C2—H2C	109.2 (13)
O1^{vii}—Na1—O1^{iii}	174.05 (8)	N2—C2—H2D	110.3 (13)
O1^{vii}—Na1—O1^{v}	88.27 (6)	C1—C2—H2C	111.2 (12)
O1^{iv}—Na1—O1^{iii}	87.75 (9)	C1—C2—H2D	109.8 (13)
O1^{vi}—Na1—O1	88.27 (6)	H2C—C2—H2D	110.0 (18)
O1^{vi}—Na1—O1^{vii}	96.03 (8)		

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+3/2; (vi) −x+y−1, −x+1, z; (vii) −x, −x+y, −z+3/2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···Cl1^{viii}	0.84 (2)	2.57 (2)	3.3586 (13)	156.7 (18)
N1—H1*B*···Cl1^{ix}	0.81 (2)	2.75 (2)	3.4317 (13)	142.0 (19)
N2—H2*A*···Cl1^{vii}	0.84 (2)	2.50 (2)	3.3286 (14)	172 (2)

N2—H2*B*···Cl1	0.82 (2)	2.62 (2)	3.2925 (13)	140.6 (19)
O1—H1*E*···Cl2	0.88	2.35	3.1354 (18)	147
O1—H1*F*···Cl1	0.89 (4)	2.41 (4)	3.2787 (18)	164 (3)
C2—H2*D*···O1[x]	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.