

# Tetraammine(carbonato- $\kappa^2O,O'$ )-cobalt(III) perchlorate

Singaravelu Chandra Mohan,<sup>a</sup> Samson Jegan Jennieffer,<sup>b</sup> Packianathan Thomas Muthiah<sup>b</sup> and Kandasamy Jothivenkatachalam<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Anna University – BIT Campus, Tiruchirappalli 620 024, Tamil Nadu, India, and <sup>b</sup>School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamilnadu, India  
Correspondence e-mail: jothivenkat@yahoo.com, tommtrichy@yahoo.co.in

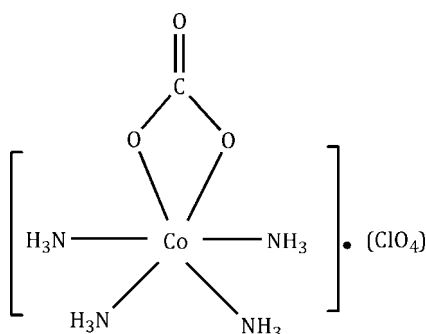
Received 20 June 2013; accepted 1 July 2013

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{Cl}-\text{O}) = 0.005$  Å; R factor = 0.042;  $wR$  factor = 0.153; data-to-parameter ratio = 21.4.

In the title complex,  $[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]\text{ClO}_4$ , both the cation and anion lie on a mirror plane. The  $\text{Co}^{\text{III}}$  ion is coordinated by two  $\text{NH}_3$  ligands and a chelating carbonato ligand in the equatorial sites and by two  $\text{NH}_3$  groups in the axial sites, forming a distorted octahedral geometry. In the crystal,  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds connect the anions and cations, forming a three-dimensional network.

## Related literature

For background to cobalt(III)-ammine complexes, see: Werner (1908) and to cobalt-carbonato complexes, see: McClintock *et al.* (2008); Cavigliasso *et al.* (2008). For their biological applications, see: Kumar & Thota (2005); Xu *et al.* (2009). For the chemistry of carbonatopentaamminecobalt(III) and carboxylatopentamminecobalt(III) complexes, see: Busset *et al.* (2007); Palaniappan *et al.* (2001); Jothivenkatachalam *et al.* (2013). For related  $\text{Co}^{\text{III}}$  complexes, see: Kim *et al.* (1998); Massoud *et al.* (2000); Sharma *et al.* (2004a,b, 2005a,b).



## Experimental

### Crystal data

$[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]\text{ClO}_4$	$V = 995.48$ (5) Å <sup>3</sup>
$M_r = 286.53$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 17.8961$ (5) Å	$\mu = 2.01$ mm <sup>-1</sup>
$b = 8.0768$ (2) Å	$T = 296$ K
$c = 6.8871$ (2) Å	$0.09 \times 0.08 \times 0.07$ mm

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer	12900 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2008)	1947 independent reflections
$T_{\text{min}} = 0.951$ , $T_{\text{max}} = 0.962$	1565 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.153$	$\Delta\rho_{\text{max}} = 1.06$ e Å <sup>-3</sup>
$S = 1.15$	$\Delta\rho_{\text{min}} = -0.75$ e Å <sup>-3</sup>
1947 reflections	
91 parameters	

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O5}$	0.89	2.52	3.371 (6)	159
$\text{N1}-\text{H1B}\cdots\text{O2}^{\text{i}}$	0.89	2.18	3.017 (3)	156
$\text{N1}-\text{H1C}\cdots\text{O3}^{\text{iii}}$	0.89	2.58	3.063 (3)	115
$\text{N1}-\text{H1C}\cdots\text{O2}^{\text{iii}}$	0.89	2.58	3.313 (3)	140
$\text{N1}-\text{H1C}\cdots\text{O1}^{\text{iv}}$	0.89	2.59	3.311 (3)	139
$\text{N4}-\text{H2}\cdots\text{O5}^{\text{ii}}$	0.75 (3)	2.44 (3)	3.145 (4)	158 (3)
$\text{N3}-\text{H4}\cdots\text{O1}^{\text{iv}}$	0.78 (3)	2.35 (2)	3.0478 (18)	151 (3)
$\text{N3}-\text{H5}\cdots\text{O2}^{\text{i}}$	0.82 (4)	2.24 (4)	3.020 (4)	158 (3)

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: POV-RAY (Persistence of Vision Team, 2004) and PLATON (Spek, 2009); software used to prepare material for publication: PLATON (Spek, 2009).

KJV thanks the Department of Science and Technology (DST), Government of India, New Delhi, for financial support (sanction No. SR/FT/CS-042/2008). The authors thank the DST India (FIST programme) for the use of the diffractometer at the School of Chemistry, Bharathidasan University, Tiruchirappalli, Tamilnadu, India.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5627).

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## supplementary materials

*Acta Cryst.* (2013). E69, i45–i46 [doi:10.1107/S1600536813018187]

**Tetraammine(carbonato- $\kappa^2$ O,O')cobalt(III) perchlorate**

**Singaravelu Chandra Mohan, Samson Jegan Jenniefer, Packianathan Thomas Muthiah and Kandasamy Jothivenkatachalam**

**Comment**

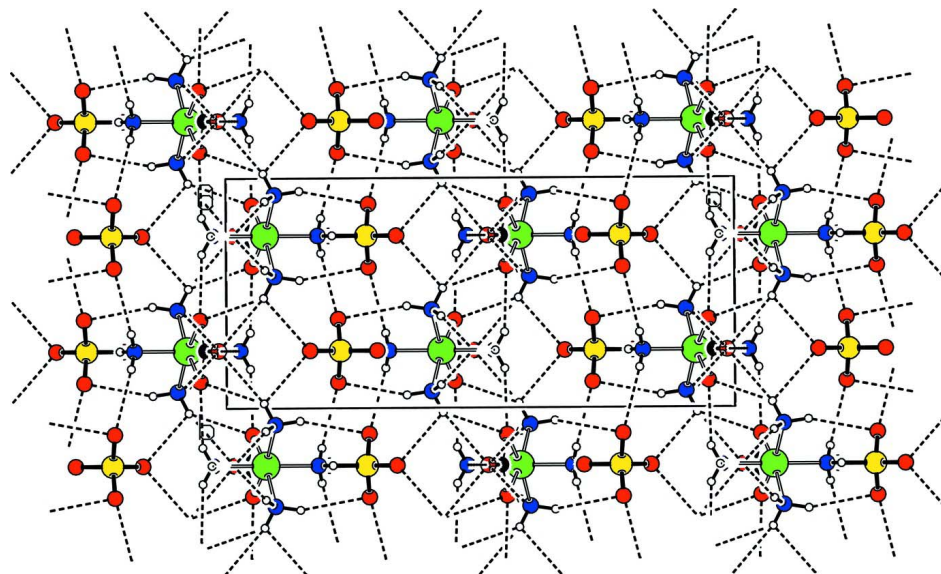
Cobalt(III) ammine complexes are well known and were widely studied by Werner (1908). In aqueous medium, the chelated ring of a bicarbonate complex is opened and protonation occurs due to hydrolysis which leads to instability. The less stability of a carbonato complex in acidic aqueous medium not only leads to protonation but also makes a site for metallation (McClintock *et al.*, 2008; Cavigliasso *et al.*, 2008). The carbonato complex also plays a vital role in photocleavage of proteins with high preference and it assists the new models of transition metal complexes for the photocleavage (Kumar & Thota, 2005). The P—O bonds present in the phosphodiester of DNA have been cleaved hydrolytically by the imitative of chelated carbonato complexes (Xu *et al.*, 2009). Recently the carbonate radical generation by photochemical reaction of carbonatopentaamminecobalt(III) complex was also reported (Busset *et al.*, 2007). The photochemical reactions of carboxylatopentamminecobalt(III) complexes lead to the reduction of metal centre and the formation of oxidized ligands, which may lead to the synthesis of value added products (Palaniappan *et al.*, 2001; Jothivenkatachalam *et al.*, 2013).

The crystal structure of the title complex is composed of one  $[\text{CoCO}_3(\text{NH}_3)_4]^+$  cation and a  $\text{ClO}_4^-$  anion in a 1:1 molar ratio. A mirror plane bisects the cation as well as the perchlorate anion, hence half a cation and an anion form the asymmetric unit. The molecular structure of the title complex is shown in Fig. 1. The  $\text{Co}^{\text{III}}$  ion is coordinated by two  $\text{NH}_3$  ligands and a chelating carbonato ligand equatorially, by two  $\text{NH}_3$  groups axially. Unlike other  $d^6$  octahedral  $\text{Co}(\text{II})$  complexes the title complex shows a distortion from ideal octahedral geometry. This can be noted by the deviation of  $\text{O1—Co—O1}^i$  bond angle of  $68.41(7)^\circ$  from the ideal octahedral bond angle of  $90^\circ$ . This is due to the steric restriction of the carbonato ligand in the formation of four membered chelate ring. The observed  $\text{O—Co—O}$  bond angle is similar to those observed in related  $[\text{Co}(\text{CO}_3)(\text{N})_4]^+$  species (Kim *et al.*, 1998; Massoud *et al.*, 2000). The chelating  $\text{CO}_3^{2-}$  has a slight influence on the  $\text{N1—Co—N1}^i$  bond angle *trans* to the  $\text{O1—Co—O1}^i$  angle. The  $\text{N1—Co—N1}^i$  bond angle is  $94.22(8)^\circ$ . The  $\text{Co—N}$  bond distances observed for the complex under investigation is similar to those reported earlier  $[\text{CoCO}_3(\text{L}2)]\text{ClO}_4$ ,  $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^+$ ,  $[\text{Co}(\text{NH}_3)_6]_3^{3+}$ , (Massoud *et al.*, 2000; Sharma *et al.*, 2004*a,b*; Sharma *et al.*, 2005*a,b*). In the crystal,  $\text{N—H}\cdots\text{O}$  hydrogen bonds connect anions and cations to form a three-dimensional network (Fig. 2).

**Experimental**

Carbonatotetraamminecobalt(III) perchlorate was synthesized by the treatment of sodium bicarbonate with aquapentaamminecobalt(III) perchlorate dissolved in small amount of hot water. The pH of the reaction mixture is adjusted to pH 8 by varying sodium bicarbonate and refluxed at 333K for 4 h and kept in cool place. The purple colored carbonatotetraamminecobalt(III) perchlorate precipitate then settled. The resulting solution was filtered and was dissolved in minimum amount of hot water, and then allowed to crystallize by slow evaporation at ambient temperature. Fine




**Figure 2**

The packing of the complex viewed along the *c* axis, showing N—H...O hydrogen bonds as dashed lines.

### Tetraammine(carbonato- $\kappa^2O,O'$ )cobalt(III) perchlorate

#### Crystal data

[Co(CO<sub>3</sub>)(NH<sub>3</sub>)<sub>4</sub>]ClO<sub>4</sub>

$M_r = 286.53$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 17.8961 (5) \text{ \AA}$

$b = 8.0768 (2) \text{ \AA}$

$c = 6.8871 (2) \text{ \AA}$

$V = 995.48 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 584$

$D_x = 1.912 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1947 reflections

$\theta = 2.3\text{--}33.0^\circ$

$\mu = 2.01 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate, purple

$0.09 \times 0.08 \times 0.07 \text{ mm}$

#### Data collection

Bruker SMART APEXII CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2008)

$T_{\min} = 0.951$ ,  $T_{\max} = 0.962$

12900 measured reflections

1947 independent reflections

1565 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 33.0^\circ$ ,  $\theta_{\min} = 2.3^\circ$

$h = -27 \rightarrow 27$

$k = -11 \rightarrow 12$

$l = -10 \rightarrow 10$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.153$

$S = 1.15$

1947 reflections

91 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H atoms treated by a mixture of independent  
and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 1.06 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.75 \text{ e } \text{\AA}^{-3}$$

*Special details*

**Geometry.** Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement.** Refinement on  $F^2$  for ALL reflections except those flagged by the user for potential systematic errors. Weighted  $R$ -factors  $wR$  and all goodnesses of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The observed criterion of  $F^2 > \sigma(F^2)$  is used only for calculating  $-R$ -factor-obs *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.07671 (2)	0.25000	0.88852 (5)	0.0258 (1)
O1	0.05126 (10)	0.1164 (2)	1.10933 (19)	0.0324 (5)
O2	0.01415 (17)	0.25000	1.3801 (3)	0.0486 (9)
N1	0.09597 (12)	0.0723 (2)	0.7015 (3)	0.0362 (5)
N3	-0.02722 (17)	0.25000	0.8052 (4)	0.0328 (8)
N4	0.18057 (18)	0.25000	0.9753 (5)	0.0380 (9)
C1	0.03851 (18)	0.25000	1.2100 (4)	0.0319 (8)
Cl2	0.27539 (5)	0.25000	0.48795 (14)	0.0426 (3)
O3	0.3348 (3)	0.25000	0.3518 (8)	0.0950 (17)
O4	0.2027 (3)	0.25000	0.4051 (6)	0.149 (4)
O5	0.2799 (3)	0.1123 (4)	0.6072 (7)	0.131 (2)
H1A	0.14500	0.05620	0.69100	0.0540*
H1B	0.07740	0.10050	0.58620	0.0540*
H1C	0.07430	-0.02060	0.74220	0.0540*
H2	0.1869 (18)	0.174 (4)	1.035 (5)	0.052 (10)*
H3	0.209 (3)	0.25000	0.904 (8)	0.062 (19)*
H4	-0.0472 (17)	0.171 (3)	0.843 (4)	0.032 (7)*
H5	-0.029 (2)	0.25000	0.686 (6)	0.023 (8)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0320 (3)	0.0241 (2)	0.0213 (2)	0.0000	-0.0021 (1)	0.0000
O1	0.0417 (9)	0.0285 (8)	0.0269 (7)	-0.0032 (7)	-0.0017 (5)	0.0027 (5)
O2	0.0462 (14)	0.077 (2)	0.0227 (10)	0.0000	0.0028 (8)	0.0000
N1	0.0450 (10)	0.0319 (9)	0.0318 (8)	0.0014 (8)	0.0007 (8)	-0.0035 (7)
N3	0.0368 (13)	0.0343 (14)	0.0272 (12)	0.0000	-0.0029 (10)	0.0000
N4	0.0369 (14)	0.0407 (18)	0.0364 (14)	0.0000	-0.0037 (12)	0.0000
C1	0.0336 (13)	0.0392 (16)	0.0230 (11)	0.0000	-0.0044 (10)	0.0000
Cl2	0.0418 (4)	0.0377 (5)	0.0482 (5)	0.0000	0.0064 (3)	0.0000
O3	0.102 (3)	0.068 (3)	0.115 (3)	0.0000	0.076 (3)	0.0000
O4	0.066 (3)	0.324 (11)	0.056 (3)	0.0000	-0.0011 (19)	0.0000
O5	0.162 (4)	0.0684 (19)	0.161 (4)	0.041 (2)	0.070 (3)	0.054 (2)

Geometric parameters (Å, °)

Co1—O1	1.9195 (15)	O2—C1	1.250 (4)
Co1—N1	1.9590 (19)	N1—H1A	0.8900
Co1—N3	1.947 (3)	N1—H1B	0.8900
Co1—N4	1.952 (3)	N1—H1C	0.8900
Co1—O1 <sup>i</sup>	1.9195 (15)	N3—H4	0.78 (3)
Co1—N1 <sup>i</sup>	1.9590 (19)	N3—H5	0.82 (4)
Cl2—O5 <sup>i</sup>	1.385 (4)	N3—H4 <sup>i</sup>	0.78 (3)
Cl2—O3	1.418 (6)	N4—H3	0.71 (5)
Cl2—O4	1.421 (5)	N4—H2 <sup>i</sup>	0.75 (3)
Cl2—O5	1.385 (4)	N4—H2	0.75 (3)
O1—C1	1.303 (2)		
Co1...O2 <sup>ii</sup>	3.676 (2)	N3...O1	2.743 (3)
Co1...O1 <sup>iii</sup>	3.7420 (17)	N3...N1 <sup>i</sup>	2.726 (3)
Co1...O1 <sup>iv</sup>	3.7420 (17)	N3...O2 <sup>ii</sup>	3.020 (4)
Co1...O2 <sup>v</sup>	3.676 (2)	N3...N1	2.726 (3)
Cl2...H1A <sup>i</sup>	3.1400	N3...C1	3.026 (4)
Cl2...H1A	3.1400	N4...N1 <sup>i</sup>	2.812 (4)
Cl2...H3	3.10 (5)	N4...O1	2.715 (3)
Cl2...H3	3.10 (5)	N4...O4 <sup>vii</sup>	2.987 (5)
O1...O2	2.255 (2)	N4...O1 <sup>i</sup>	2.715 (3)
O1...N3 <sup>iv</sup>	3.0478 (18)	N4...O5 <sup>xiv</sup>	3.145 (4)
O1...N3	2.743 (3)	N4...N1	2.812 (4)
O1...Co1 <sup>vi</sup>	3.7420 (17)	N4...C1	3.013 (5)
O1...N1	2.942 (2)	N4...O4 <sup>viii</sup>	2.987 (5)
O1...N4	2.715 (3)	N4...O5 <sup>xii</sup>	3.145 (4)
O1...O1 <sup>iv</sup>	3.028 (2)	N1...H5	2.66 (3)
O1...N3 <sup>vi</sup>	3.0478 (18)	N1...H3	2.85 (5)
O1...O1 <sup>i</sup>	2.158 (2)	N1...H4	2.86 (3)
O1...Co1 <sup>iv</sup>	3.7420 (17)	N1...H1B <sup>i</sup>	2.7800
O2...N1 <sup>vii</sup>	3.017 (3)	N1...H2	2.93 (3)
O2...N3 <sup>vii</sup>	3.020 (4)	N3...H1C <sup>i</sup>	2.8800
O2...Co1 <sup>viii</sup>	3.676 (2)	N3...H1B	2.6900
O2...O1 <sup>i</sup>	2.255 (2)	N3...H1C	2.8800
O2...N3 <sup>viii</sup>	3.020 (4)	N3...H1B <sup>i</sup>	2.6900
O2...Co1 <sup>vii</sup>	3.676 (2)	N4...H1A <sup>i</sup>	2.5900
O2...O1	2.255 (2)	N4...H1A	2.5900
O2...N1 <sup>viii</sup>	3.017 (3)	C1...O4 <sup>viii</sup>	3.231 (6)
O3...N1 <sup>ix</sup>	3.063 (3)	C1...N3	3.026 (4)
O3...N1 <sup>x</sup>	3.063 (3)	C1...N4	3.013 (5)
O4...N1 <sup>i</sup>	3.143 (5)	C1...O4 <sup>vii</sup>	3.231 (6)
O4...N4 <sup>ii</sup>	2.987 (5)	C1...H2	2.98 (3)
O4...C1 <sup>v</sup>	3.231 (6)	C1...H1C <sup>iv</sup>	2.7600
O4...C1 <sup>ii</sup>	3.231 (6)	C1...H4	3.03 (3)
O4...N4 <sup>v</sup>	2.987 (5)	C1...H1B <sup>viii</sup>	2.9400
O4...N1	3.143 (5)	C1...H4 <sup>i</sup>	3.03 (3)
O5...N4 <sup>xi</sup>	3.145 (4)	C1...H1C <sup>iii</sup>	2.7600
O5...N4 <sup>ix</sup>	3.145 (4)	C1...H1B <sup>vii</sup>	2.9400

O1...H1C <sup>iv</sup>	2.5900	C1...H2 <sup>i</sup>	2.98 (3)
O1...H2	2.52 (3)	H1A...H3	2.4300
O1...H4 <sup>iv</sup>	2.35 (2)	H1A...O3 <sup>xii</sup>	2.7300
O1...H4	2.58 (3)	H1A...O3 <sup>xiii</sup>	2.7300
O1...H1C	2.7900	H1A...O5	2.5200
O2...H1C <sup>iv</sup>	2.5800	H1A...C12	3.1400
O2...H5 <sup>viii</sup>	2.24 (4)	H1A...O4	2.7200
O2...H1B <sup>vii</sup>	2.1800	H1A...C12	3.1400
O2...H1C <sup>iii</sup>	2.5800	H1A...O4	2.7200
O2...H5 <sup>vii</sup>	2.24 (4)	H1B...O2 <sup>v</sup>	2.1800
O2...H1B <sup>viii</sup>	2.1800	H1B...C1 <sup>ii</sup>	2.9400
O3...H1A <sup>x</sup>	2.7300	H1B...H5	2.3600
O3...H1A <sup>ix</sup>	2.7300	H1B...O2 <sup>ii</sup>	2.1800
O3...H1C <sup>ix</sup>	2.5800	H1B...O4	2.8400
O3...H1C <sup>x</sup>	2.5800	H1B...O4	2.8400
O4...H1A	2.7200	H1B...C1 <sup>v</sup>	2.9400
O4...H2 <sup>ii</sup>	2.64 (3)	H1B...H1B <sup>i</sup>	2.4100
O4...H1B	2.8400	H1C...C1 <sup>vi</sup>	2.7600
O4...H2 <sup>v</sup>	2.64 (3)	H1C...O1 <sup>iv</sup>	2.5900
O4...H1A <sup>i</sup>	2.7200	H1C...O2 <sup>iv</sup>	2.5800
O4...H1B <sup>i</sup>	2.8400	H1C...O3 <sup>xii</sup>	2.5800
O5...H3	2.65 (5)	H1C...O2 <sup>vi</sup>	2.5800
O5...H1A	2.5200	H1C...C1 <sup>iv</sup>	2.7600
O5...H2 <sup>ix</sup>	2.44 (3)	H1C...O3 <sup>xiii</sup>	2.5800
O5...H3	2.65 (5)	H2...O4 <sup>viii</sup>	2.64 (3)
N1...O1	2.942 (2)	H2...O4 <sup>vii</sup>	2.64 (3)
N1...O4	3.143 (5)	H2...O5 <sup>xii</sup>	2.44 (3)
N1...N1 <sup>i</sup>	2.871 (2)	H3...C12	3.10 (5)
N1...N3	2.726 (3)	H3...O5	2.65 (5)
N1...O2 <sup>ii</sup>	3.017 (3)	H3...H1A	2.4300
N1...O4	3.143 (5)	H3...C12	3.10 (5)
N1...O3 <sup>xii</sup>	3.063 (3)	H3...O5 <sup>i</sup>	2.65 (5)
N1...N4	2.812 (4)	H3...H1A <sup>i</sup>	2.4300
N1...O2 <sup>v</sup>	3.017 (3)	H4...O1 <sup>iv</sup>	2.35 (2)
N1...O3 <sup>xiii</sup>	3.063 (3)	H5...O2 <sup>v</sup>	2.24 (4)
N3...O2 <sup>v</sup>	3.020 (4)	H5...H1B <sup>i</sup>	2.3600
N3...O1 <sup>iv</sup>	3.0478 (18)	H5...H1B	2.3600
N3...O1 <sup>i</sup>	2.743 (3)	H5...O2 <sup>ii</sup>	2.24 (4)
N3...O1 <sup>iii</sup>	3.0478 (18)		
O1—Co1—N1	98.67 (7)	Co1—O1—C1	89.86 (13)
O1—Co1—N3	90.39 (9)	Co1—N1—H1C	110.00
O1—Co1—N4	89.05 (10)	Co1—N1—H1B	109.00
O1—Co1—C1	34.21 (5)	H1A—N1—H1C	109.00
O1—Co1—O1 <sup>i</sup>	68.41 (7)	H1B—N1—H1C	110.00
O1—Co1—N1 <sup>i</sup>	167.04 (7)	H1A—N1—H1B	109.00
N1—Co1—N3	88.53 (8)	Co1—N1—H1A	110.00
N1—Co1—N4	91.94 (9)	H4—N3—H4 <sup>i</sup>	111 (3)
N1—Co1—C1	132.85 (6)	H4 <sup>i</sup> —N3—H5	109 (2)



O1 <sup>i</sup> —Co1—N1	167.04 (7)	H4—N3—H5	109 (2)
N1—Co1—N1 <sup>i</sup>	94.22 (8)	Co1—N3—H4 <sup>i</sup>	110 (2)
N3—Co1—N4	179.32 (13)	Co1—N3—H4	110 (2)
N3—Co1—C1	89.99 (11)	Co1—N3—H5	109 (3)
O1 <sup>i</sup> —Co1—N3	90.39 (9)	H2 <sup>i</sup> —N4—H3	106 (3)
N1 <sup>i</sup> —Co1—N3	88.53 (8)	Co1—N4—H2 <sup>i</sup>	108 (2)
N4—Co1—C1	89.33 (13)	Co1—N4—H2	108 (2)
O1 <sup>i</sup> —Co1—N4	89.05 (10)	Co1—N4—H3	118 (4)
N1 <sup>i</sup> —Co1—N4	91.94 (9)	H2—N4—H2 <sup>i</sup>	110 (4)
O1 <sup>i</sup> —Co1—C1	34.21 (5)	H2—N4—H3	106 (3)
N1 <sup>i</sup> —Co1—C1	132.85 (6)	Co1—C1—O2	176.8 (3)
O1 <sup>i</sup> —Co1—N1 <sup>i</sup>	98.67 (7)	Co1—C1—O1 <sup>i</sup>	55.93 (12)
O5—C12—O5 <sup>i</sup>	106.9 (3)	O1—C1—O1 <sup>i</sup>	111.9 (2)
O3—C12—O5	110.4 (2)	O1 <sup>i</sup> —C1—O2	124.05 (12)
O3—C12—O5 <sup>i</sup>	110.4 (2)	O1—C1—O2	124.05 (12)
O3—C12—O4	114.9 (3)	Co1—C1—O1	55.93 (12)
O4—C12—O5	107.0 (2)		
N1—Co1—O1—C1	-177.97 (17)	N3—Co1—C1—O1	90.72 (15)
N3—Co1—O1—C1	-89.40 (17)	N4—Co1—C1—O1	-89.29 (15)
N4—Co1—O1—C1	90.22 (17)	O1 <sup>i</sup> —Co1—C1—O1	-178.6 (3)
O1 <sup>i</sup> —Co1—O1—C1	0.87 (16)	N1 <sup>i</sup> —Co1—C1—O1	178.69 (14)
O1—Co1—C1—O1 <sup>i</sup>	178.6 (3)	O1—Co1—O1 <sup>i</sup> —C1	-0.87 (16)
N1—Co1—C1—O1	2.7 (2)	Co1—O1—C1—O2	176.1 (3)
N1—Co1—C1—O1 <sup>i</sup>	-178.69 (14)	Co1—O1—C1—O1 <sup>i</sup>	-1.3 (2)

Symmetry codes: (i)  $x, -y+1/2, z$ ; (ii)  $x, y, z-1$ ; (iii)  $-x, y+1/2, -z+2$ ; (iv)  $-x, -y, -z+2$ ; (v)  $x, -y+1/2, z-1$ ; (vi)  $-x, y-1/2, -z+2$ ; (vii)  $x, -y+1/2, z+1$ ; (viii)  $x, y, z+1$ ; (ix)  $-x+1/2, -y, z-1/2$ ; (x)  $-x+1/2, y+1/2, z-1/2$ ; (xi)  $-x+1/2, y-1/2, z-1/2$ ; (xii)  $-x+1/2, -y, z+1/2$ ; (xiii)  $-x+1/2, y-1/2, z+1/2$ ; (xiv)  $-x+1/2, y+1/2, z+1/2$ .

Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ O5	0.89	2.52	3.371 (6)	159
N1—H1B $\cdots$ O2 <sup>ii</sup>	0.89	2.18	3.017 (3)	156
N1—H1C $\cdots$ O3 <sup>xii</sup>	0.89	2.58	3.063 (3)	115
N1—H1C $\cdots$ O2 <sup>vi</sup>	0.89	2.58	3.313 (3)	140
N1—H1C $\cdots$ O1 <sup>iv</sup>	0.89	2.59	3.311 (3)	139
N4—H2 $\cdots$ O5 <sup>xii</sup>	0.75 (3)	2.44 (3)	3.145 (4)	158 (3)
N3—H4 $\cdots$ O1 <sup>iv</sup>	0.78 (3)	2.35 (2)	3.0478 (18)	151 (3)
N3—H5 $\cdots$ O2 <sup>ii</sup>	0.82 (4)	2.24 (4)	3.020 (4)	158 (3)

Symmetry codes: (ii)  $x, y, z-1$ ; (iv)  $-x, -y, -z+2$ ; (vi)  $-x, y-1/2, -z+2$ ; (xii)  $-x+1/2, -y, z+1/2$ .