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

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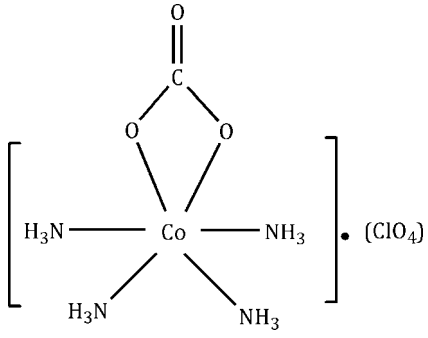
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(Cl–O) = 0.005 Å; $R$ factor = 0.042; $wR$ factor = 0.153; data-to-parameter ratio = 21.4.

In the title complex, $[Co(CO_3)(NH_3)_4]ClO_4$, both the cation and anion lie on a mirror plane. The $Co^{III}$ ion is coordinated by two $NH_3$ ligands and a chelating carbonato ligand in the equatorial sites and by two $NH_3$ groups in the axial sites, forming a distorted octahedral geometry. In the crystal, N—H···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 carbonatopentaammine-cobalt(III) and carboxylatopentamminecobalt(III) complexes, see: Busset *et al.* (2007); Palaniappan *et al.* (2001); Jothivenkatachalam *et al.* (2013). For related $Co^{III}$ complexes, see: Kim *et al.* (1998); Massoud *et al.* (2000); Sharma *et al.* (2004*a*,*b*, 2005*a*,*b*).




## Experimental

### Crystal data

$[Co(CO_3)(NH_3)_4]ClO_4$
$M_r$ = 286.53
Orthorhombic, *Pnma*
$a$ = 17.8961 (5) Å
$b$ = 8.0768 (2) Å
$c$ = 6.8871 (2) Å
$V$ = 995.48 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.01 mm$^{-1}$
$T$ = 296 K
0.09 × 0.08 × 0.07 mm

### Data collection

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

### Refinement

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

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1$A$···O5 | 0.89 | 2.52 | 3.371 (6) | 159 |
| N1—H1$B$···O2$^{i}$ | 0.89 | 2.18 | 3.017 (3) | 156 |
| N1—H1$C$···O3$^{ii}$ | 0.89 | 2.58 | 3.063 (3) | 115 |
| N1—H1$C$···O2$^{iii}$ | 0.89 | 2.58 | 3.313 (3) | 140 |
| N1—H1$C$···O1$^{iv}$ | 0.89 | 2.59 | 3.311 (3) | 139 |
| N4—H2···O5$^{ii}$ | 0.75 (3) | 2.44 (3) | 3.145 (4) | 158 (3) |
| N3—H4···O1$^{iv}$ | 0.78 (3) | 2.35 (2) | 3.0478 (18) | 151 (3) |
| N3—H5···O2$^{i}$ | 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).

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

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# supporting information

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

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

### S1. 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 carbanato 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 $[CoCO_3(NH_3)_4]^+$ cation and a $ClO_4^-$ 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 $Co^{III}$ ion is coordinated by two $NH_3$ ligands and a chelating carbanato ligand equatorially, by two $NH_3$ groups axially. Unlike other $d^6$ octahedral Co(II) complexes the title complex shows a distortion from ideal octahedral geometry. This can be noted by the deviation of O1—Co—$O1^i$ bond angle of 68.41 (7)° from the ideal octahedral bond angle of 90°. This is due to the steric restriction of the carbanato ligand in the formation of four membered chelate ring. The observed O—Co—O bond angle is similar to those observed in related $[Co(CO_3)(N)_4]$+ species (Kim *et al.*, 1998; Massoud *et al.*, 2000). The chelating $CO_3^{2-}$ has a slight influence on the N1—Co—$N1^i$ bond angle *trans* to the O1—Co—$O1^i$ angle. The N1—Co—$N1^i$ bond angle is 94.22 (8)°. The Co—N bond distances observed for the complex under investigation is similar to those reported earlier $[CoCO_3(L2)]ClO_4$, $[Co(NH_3)_2(NO_2)_4]^-$, $[Co(NH_3)_6]_3^+$, (Massoud *et al.*, 2000; Sharma *et al.*, 2004*a*,*b*; Sharma *et al.*, 2005*a*,*b*). In the crystal, N—H···O hydrogen bonds connect anions and cations to form a three-dimensional network (Fig. 2).

### S2. Experimental

Carbonatotetramminecobalt(III) perchlorate was synthesized by the treatment of sodium bicarbonate with aqua-pentaamminecobalt(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 carbonatotetramminecobalt(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

purple crystals of X-ray quality separated out after one week. These were filtered, washed with ethanol, acetone and air-dried.

### S3. Refinement

The H atoms attached to N3 and N4 were located from a difference Fourier map and were refined freely. The H atoms attached to N1 were placed in geometrically idealized positions and constrained to ride on their parent atom, with N—H distance of 0.89 Å, and with $U_{iso}$(H) set at 1.5$U_{eq}$(N).

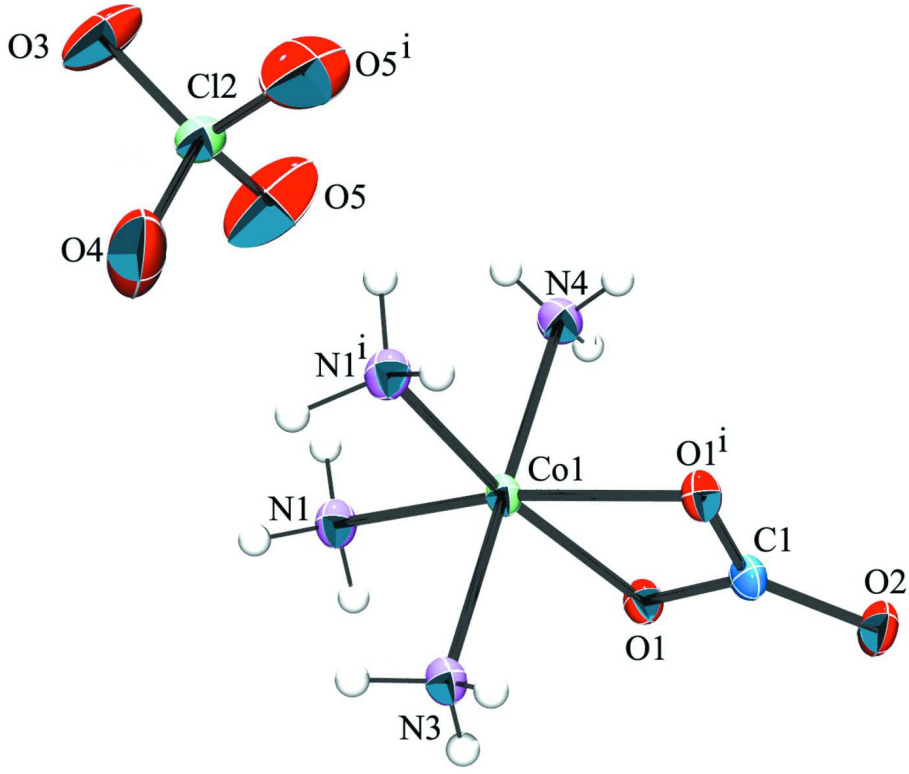


**Figure 1**

The molecular structure of the title compound, with anisotropic displacement ellipsoids drawn at 50% probability level [Symmetry code: (i) x, -y+1/2, z].

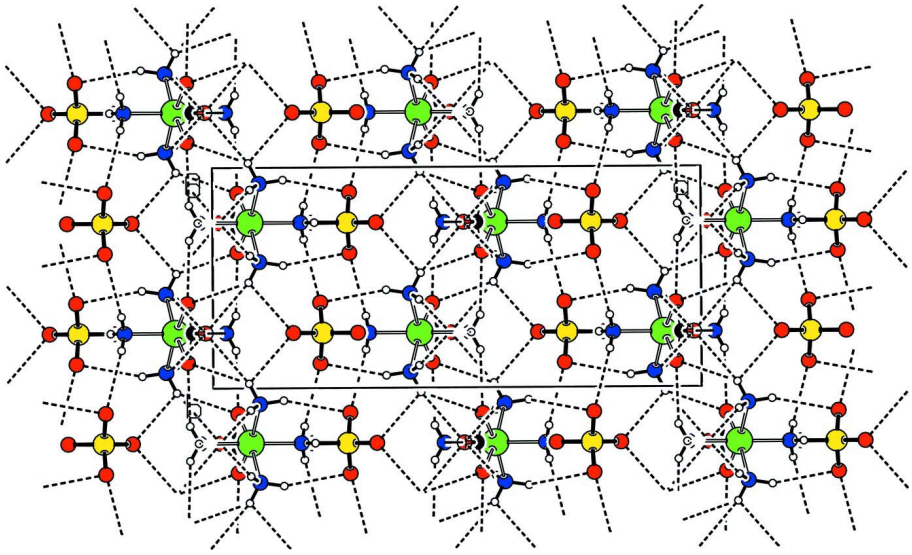

**Figure 2**

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

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*Crystal data*

$[Co(CO_3)(NH_3)_4]ClO_4$
$M_r = 286.53$
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
$a = 17.8961\ (5)$ Å
$b = 8.0768\ (2)$ Å
$c = 6.8871\ (2)$ Å
$V = 995.48\ (5)$ Å$^3$
$Z = 4$
$F(000) = 584$
$D_x = 1.912$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1947 reflections
$\theta = 2.3$–$33.0°$
$\mu = 2.01$ mm$^{-1}$
$T = 296$ K
Plate, purple
0.09 × 0.08 × 0.07 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 $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 33.0°$, $\theta_{min} = 2.3°$
$h = -27\rightarrow27$
$k = -11\rightarrow12$
$l = -10\rightarrow10$

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

$\Delta\rho_{max} = 1.06$ e Å$^{-3}$
$\Delta\rho_{min} = -0.75$ e Å$^{-3}$

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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 (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

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

| | | | |
|---|---|---|---|
| O4···N4$^{v}$ | 2.987 (5) | C1···H1B$^{viii}$ | 2.9400 |
| O4···N1 | 3.143 (5) | C1···H4$^{i}$ | 3.03 (3) |
| O5···N4$^{xi}$ | 3.145 (4) | C1···H1C$^{iii}$ | 2.7600 |
| O5···N4$^{ix}$ | 3.145 (4) | C1···H1B$^{vii}$ | 2.9400 |
| O1···H1C$^{iv}$ | 2.5900 | C1···H2$^{i}$ | 2.98 (3) |
| O1···H2 | 2.52 (3) | H1A···H3 | 2.4300 |
| O1···H4$^{iv}$ | 2.35 (2) | H1A···O3$^{xii}$ | 2.7300 |
| O1···H4 | 2.58 (3) | H1A···O3$^{xiii}$ | 2.7300 |
| O1···H1C | 2.7900 | H1A···O5 | 2.5200 |
| O2···H1C$^{iv}$ | 2.5800 | H1A···Cl2 | 3.1400 |
| O2···H5$^{viii}$ | 2.24 (4) | H1A···O4 | 2.7200 |
| O2···H1B$^{vii}$ | 2.1800 | H1A···Cl2 | 3.1400 |
| O2···H1C$^{iii}$ | 2.5800 | H1A···O4 | 2.7200 |
| O2···H5$^{vii}$ | 2.24 (4) | H1B···O2$^{v}$ | 2.1800 |
| O2···H1B$^{viii}$ | 2.1800 | H1B···C1$^{ii}$ | 2.9400 |
| O3···H1A$^{x}$ | 2.7300 | H1B···H5 | 2.3600 |
| O3···H1A$^{ix}$ | 2.7300 | H1B···O2$^{ii}$ | 2.1800 |
| O3···H1C$^{ix}$ | 2.5800 | H1B···O4 | 2.8400 |
| O3···H1C$^{x}$ | 2.5800 | H1B···O4 | 2.8400 |
| O4···H1A | 2.7200 | H1B···C1$^{v}$ | 2.9400 |
| O4···H2$^{ii}$ | 2.64 (3) | H1B···H1B$^{i}$ | 2.4100 |
| O4···H1B | 2.8400 | H1C···C1$^{vi}$ | 2.7600 |
| O4···H2$^{v}$ | 2.64 (3) | H1C···O1$^{iv}$ | 2.5900 |
| O4···H1A$^{i}$ | 2.7200 | H1C···O2$^{iv}$ | 2.5800 |
| O4···H1B$^{i}$ | 2.8400 | H1C···O3$^{xii}$ | 2.5800 |
| O5···H3 | 2.65 (5) | H1C···O2$^{vi}$ | 2.5800 |
| O5···H1A | 2.5200 | H1C···C1$^{iv}$ | 2.7600 |
| O5···H2$^{ix}$ | 2.44 (3) | H1C···O3$^{xiii}$ | 2.5800 |
| O5···H3 | 2.65 (5) | H2···O4$^{viii}$ | 2.64 (3) |
| N1···O1 | 2.942 (2) | H2···O4$^{vii}$ | 2.64 (3) |
| N1···O4 | 3.143 (5) | H2···O5$^{xii}$ | 2.44 (3) |
| N1···N1$^{i}$ | 2.871 (2) | H3···Cl2 | 3.10 (5) |
| N1···N3 | 2.726 (3) | H3···O5 | 2.65 (5) |
| N1···O2$^{ii}$ | 3.017 (3) | H3···H1A | 2.4300 |
| N1···O4 | 3.143 (5) | H3···Cl2 | 3.10 (5) |
| N1···O3$^{xii}$ | 3.063 (3) | H3···O5$^{i}$ | 2.65 (5) |
| N1···N4 | 2.812 (4) | H3···H1A$^{i}$ | 2.4300 |
| N1···O2$^{v}$ | 3.017 (3) | H4···O1$^{iv}$ | 2.35 (2) |
| N1···O3$^{xiii}$ | 3.063 (3) | H5···O2$^{v}$ | 2.24 (4) |
| N3···O2$^{v}$ | 3.020 (4) | H5···H1B$^{i}$ | 2.3600 |
| N3···O1$^{iv}$ | 3.0478 (18) | H5···H1B | 2.3600 |
| N3···O1$^{i}$ | 2.743 (3) | H5···O2$^{ii}$ | 2.24 (4) |
| N3···O1$^{iii}$ | 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$^{i}$ | 68.41 (7) | H1B—N1—H1C | 110.00 |
| O1—Co1—N1$^{i}$ | 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$^{i}$ | 111 (3) |
| N1—Co1—C1 | 132.85 (6) | H4$^{i}$—N3—H5 | 109 (2) |
| O1$^{i}$—Co1—N1 | 167.04 (7) | H4—N3—H5 | 109 (2) |
| N1—Co1—N1$^{i}$ | 94.22 (8) | Co1—N3—H4$^{i}$ | 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$^{i}$—Co1—N3 | 90.39 (9) | H2$^{i}$—N4—H3 | 106 (3) |
| N1$^{i}$—Co1—N3 | 88.53 (8) | Co1—N4—H2$^{i}$ | 108 (2) |
| N4—Co1—C1 | 89.33 (13) | Co1—N4—H2 | 108 (2) |
| O1$^{i}$—Co1—N4 | 89.05 (10) | Co1—N4—H3 | 118 (4) |
| N1$^{i}$—Co1—N4 | 91.94 (9) | H2—N4—H2$^{i}$ | 110 (4) |
| O1$^{i}$—Co1—C1 | 34.21 (5) | H2—N4—H3 | 106 (3) |
| N1$^{i}$—Co1—C1 | 132.85 (6) | Co1—C1—O2 | 176.8 (3) |
| O1$^{i}$—Co1—N1$^{i}$ | 98.67 (7) | Co1—C1—O1$^{i}$ | 55.93 (12) |
| O5—Cl2—O5$^{i}$ | 106.9 (3) | O1—C1—O1$^{i}$ | 111.9 (2) |
| O3—Cl2—O5 | 110.4 (2) | O1$^{i}$—C1—O2 | 124.05 (12) |
| O3—Cl2—O5$^{i}$ | 110.4 (2) | O1—C1—O2 | 124.05 (12) |
| O3—Cl2—O4 | 114.9 (3) | Co1—C1—O1 | 55.93 (12) |
| O4—Cl2—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$^{i}$—Co1—C1—O1 | −178.6 (3) |
| O1$^{i}$—Co1—O1—C1 | 0.87 (16) | N1$^{i}$—Co1—C1—O1 | 178.69 (14) |
| O1—Co1—C1—O1$^{i}$ | 178.6 (3) | O1—Co1—O1$^{i}$—C1 | −0.87 (16) |
| N1—Co1—C1—O1 | 2.7 (2) | Co1—O1—C1—O2 | 176.1 (3) |
| N1—Co1—C1—O1$^{i}$ | −178.69 (14) | Co1—O1—C1—O1$^{i}$ | −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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···O5 | 0.89 | 2.52 | 3.371 (6) | 159 |
| N1—H1*B*···O2$^{ii}$ | 0.89 | 2.18 | 3.017 (3) | 156 |
| N1—H1*C*···O3$^{xii}$ | 0.89 | 2.58 | 3.063 (3) | 115 |
| N1—H1*C*···O2$^{vi}$ | 0.89 | 2.58 | 3.313 (3) | 140 |
| N1—H1*C*···O1$^{iv}$ | 0.89 | 2.59 | 3.311 (3) | 139 |
| N4—H2···O5$^{xii}$ | 0.75 (3) | 2.44 (3) | 3.145 (4) | 158 (3) |
| N3—H4···O1$^{iv}$ | 0.78 (3) | 2.35 (2) | 3.0478 (18) | 151 (3) |
| N3—H5···O2$^{ii}$ | 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.