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Tris(2,2'-bipyridine- $\kappa^2N:N'$)cobalt(III) trichloride tetrahydrate

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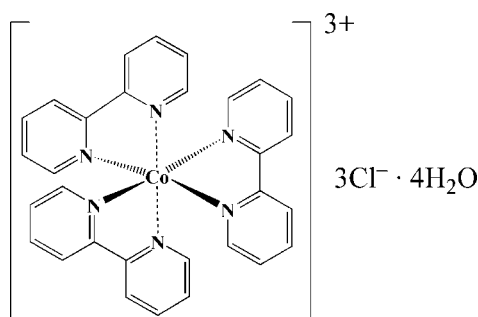
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.056; wR factor = 0.162; data-to-parameter ratio = 12.6.

The title compound, $[\text{Co}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$, contains discrete $[\text{Co}(\text{bpy})_3]^{3+}$ cations (bpy is 2,2'-bipyridine), Cl^- anions and water molecules. The $[\text{Co}(\text{bpy})_3]^{3+}$ complex cation exhibits C_2 symmetry with the twofold axis through the central Co atom and bisecting one bpy ligand and one of the Cl^- anions. The four solvent water molecules and the remaining two Cl^- anions lie on a mirror plane. Hydrogen-bond interactions define a two-dimensional layer structure parallel to (100), which consists of seven-membered $[\text{Cl}_2(\text{H}_2\text{O})_5]$, eight-membered $[\text{Cl}_4(\text{H}_2\text{O})_4]$ and ten-membered $[\text{Cl}_2(\text{H}_2\text{O})_8]$ rings.

Related literature

For general background, see: Liu *et al.* (1996); Nauta & Miller (2000); Ludwig (2001); Saha & Bernal (2005); Reger *et al.* (2006); Li *et al.* (2007); Mir & Vittal (2007). For related structures, see: Hernández-Molina *et al.* (1998).



Experimental

Crystal data

 $[\text{Co}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ $M_r = 705.90$ Orthorhombic, $Cmca$ $a = 20.171$ (4) Å $b = 23.170$ (5) Å $c = 13.316$ (3) Å $V = 6223$ (2) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.86$ mm⁻¹ $T = 295$ (2) K

0.12 × 0.10 × 0.08 mm

Data collection

Bruker P4 diffractometer
Absorption correction: ψ scan
(XSCANS; Siemens, 1996)
 $T_{\min} = 0.905$, $T_{\max} = 0.929$
3430 measured reflections
2824 independent reflections

1980 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.162$
 $S = 1.03$
2824 reflections
225 parameters
12 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 1.01$ e Å⁻³
 $\Delta\rho_{\min} = -0.66$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------------------------|----------|--------------|--------------|----------------|
| O1—H1W2 \cdots O2 | 0.85 (4) | 2.04 (5) | 2.885 (9) | 176 (9) |
| O1—H1W1 \cdots Cl1 ⁱ | 0.83 (4) | 2.30 (4) | 3.127 (7) | 180 (9) |
| O2—H2W1 \cdots Cl1 ⁱ | 0.84 (4) | 2.48 (4) | 3.317 (7) | 175 (6) |
| O2—H2W2 \cdots Cl2 ⁱⁱ | 0.84 (3) | 2.33 (3) | 3.165 (5) | 173 (7) |
| O3—H3W1 \cdots Cl1 ⁱⁱⁱ | 0.85 (6) | 2.33 (6) | 3.161 (5) | 166 (6) |
| O3—H3W2 \cdots Cl2 ⁱⁱⁱ | 0.84 (4) | 2.27 (5) | 3.095 (5) | 170 (7) |
| O4—H4W1 \cdots O1 | 0.79 (5) | 2.06 (5) | 2.841 (8) | 169 (5) |
| O4—H4W2 \cdots O3 | 0.81 (3) | 2.00 (3) | 2.795 (8) | 168 (7) |

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

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BG2219).

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supporting information

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Tris(2,2'-bipyridine- κ^2 N:N')cobalt(III) trichloride tetrahydrate

Wen Liu, Wei Xu, Jian-Li Lin and Hong-Zhen Xie

S1. Comment

Due to the central role that water plays in biological and chemical processes, research on its structure, properties and functions has attracted the scientist's attention (Liu, *et al.*, 1996; Nauta & Miller, 2000; Ludwig, 2001; Mir & Vittal, 2007). However, there are only a few reports focused on the experimental identification and analysis of hydrogen-bond networks between water of crystallization and chloride counterions in crystalline materials. As a few examples we can mention [*cis*- α -(trine)CoCl₂]Cl₃·3H₂O (Saha & Bernal, 2005) where a two-dimensional layered structure containing [Cl₂(H₂O)₄] six-membered rings build up. In the crystal structure of {*p*-C₆H₄[CH₂OCH₂C(pz)₃]₂[Ru(*p*-cymene)]₂}Cl₄·14H₂O two-dimensional layers built from four-membered [Cl(H₂O)₃], five-membered [Cl(H₂O)₄], six-membered [Cl(H₂O)₅] and seven-membered [Cl₃(H₂O)₄] rings formed through hydrogen bond self-assembly (Reger, *et al.*, 2006). A hybrid water-chloride structure of 14 water molecules and 4 Cl⁻ anions connected into layers is formed in the crystal structure of an europium complex [Eu₃(BDC)₃(phen)₃Cl(H₂O)₆]Cl₂·4H₂O (Li, *et al.*, 2007). The references suggest that a great variety of mixed water-chloride supramolecular self-assemblies is possible. Herein, we describe a structure of a cobalt(III) complex containing discrete tris(2,2'-bipyridine)cobalt(III) cations and infinite layers of water and chloride anions, and where seven-membered (Cl₂(H₂O)₅), eight-membered (Cl₄(H₂O)₄) and ten-membered (Cl₂(H₂O)₈) rings can be found.

The crystal structure of the title compound is composed of [Co(bpy)₃]³⁺ complex cations, Cl⁻ anions and crystal H₂O molecules (Fig. 1). Within the trivalent complex cations, the Co atoms are each surrounded by six N atoms of three chelating bpy ligands to complete a distorted octahedral coordination with d(Co—N) = 1.928 (3)–1.939 (3) Å, the *cis* and *trans* N—Co—N bond angles in the range 83.50 (19)–93.82 (14) and 175.23 (14)–176.38 (19)°, respectively. Such distances are similar to those found in other related structures (Hernández-Molina, *et al.*, 1998). The complex cation exhibits C₂ symmetry with the twofold axis through the central Co atom and bisecting the C5—C5ⁱ bond of one bpy ligand (*i* = -*x* + 1/2, *y*, -*z* + 3/2), as well as one of the Cl⁻ anions (Cl3). Through a C—H⋯Cl weak hydrogen bond the [Co(phen)₃]³⁺ moieties are interlink into one-dimensional chains along the [001] direction (Fig.2). There are no π - π stacking interactions in the chains.

The most startling feature of the solid-state structure of 1 is the hydrogen-bonding interactions of the four water molecules and the remaining two Cl⁻ anions (Cl1 and Cl2), which lay on a mirror plane. The four crystal water molecules (O1, O2, O3, and O4) locate at the crystallographic 8f position and through intermolecular hydrogen bonds determine a linear water tetramer (H₂O)₄. The O⋯O distances span the range 2.795 (8)–2.885 (9) Å. Interestingly, such tetrameric water groups are further hydrogen-bond-interacting with the Cl⁻ anions to complete a two-dimensional water-chloride framework parallel to (100). As Shown in Fig. 3, the two-dimensional layers are composed by seven- (five water molecules and two Cl⁻ anions), eight- (four water molecules and four Cl⁻ anions) and ten-membered (eight water molecules and two Cl⁻ anions) rings through O—H⋯O and O—H⋯Cl interactions (Table 1). The O⋯Cl distances range from 3.095 (5) to 3.317 (7) Å and O—H⋯Cl angles span the range 166 (6) to 180 (9)°. The water-chloride layer can be

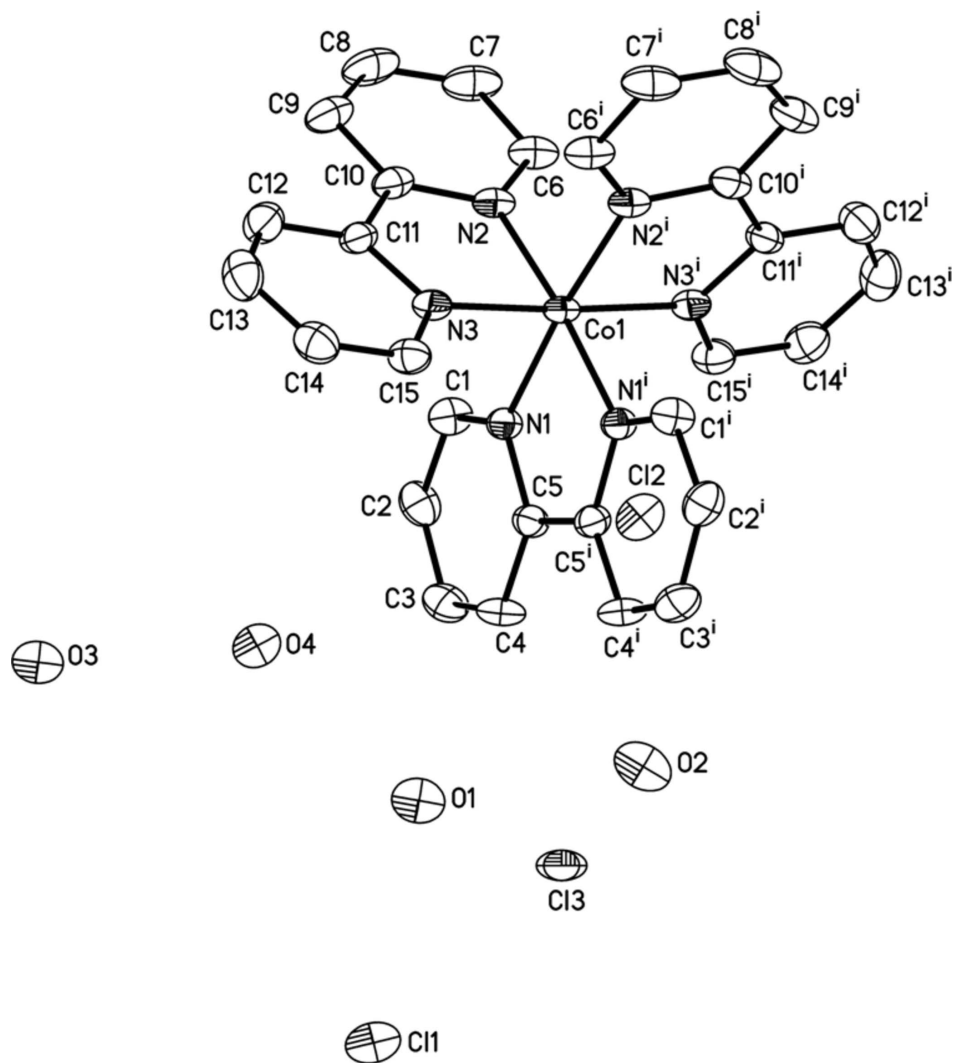
viewed as building blocks, which are pillared by $[\text{Co}(\text{bpy})_3]^{3+}$ spacers to produce an infinite three-dimensional supramolecular edifice. In this sense, the layer is different from already reported water clusters and other morphologies, which are situated within the host cavities or channels generated by organic and inorganic moieties (Fig. 4).

S2. Experimental

Addition of 10 ml CH_3OH containing 0.162 g (1.04 mmol) 2,2'-bipyridine (bpy) to an aqueous solution of 0.238 g (1.00 mmol) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 ml H_2O gave a yellow solution, then dropwise added 3 ml 30% H_2O_2 solution to the mixture, stirred for *ca* half an hour. The resulting light-yellow solution (PH = 6.48) was allowed to stand at room temperature. After 8 days, a small amount of yellow block crystals had grown.

S3. Refinement

H atoms bonded to C atoms were placed in geometrically calculated position and were refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. H atoms attached to O atoms were found in a difference Fourier synthesis and were refined using a riding model, with the O—H distances fixed as initially found and with $U_{\text{iso}}(\text{H})$ values set at $1.5 U_{\text{eq}}(\text{O})$.

**Figure 1**

ORTEP view of the title compound. The displacement ellipsoids are drawn at 40% probability level. [Symmetry code: (i) $-x + 1/2, y, -z + 3/2$]

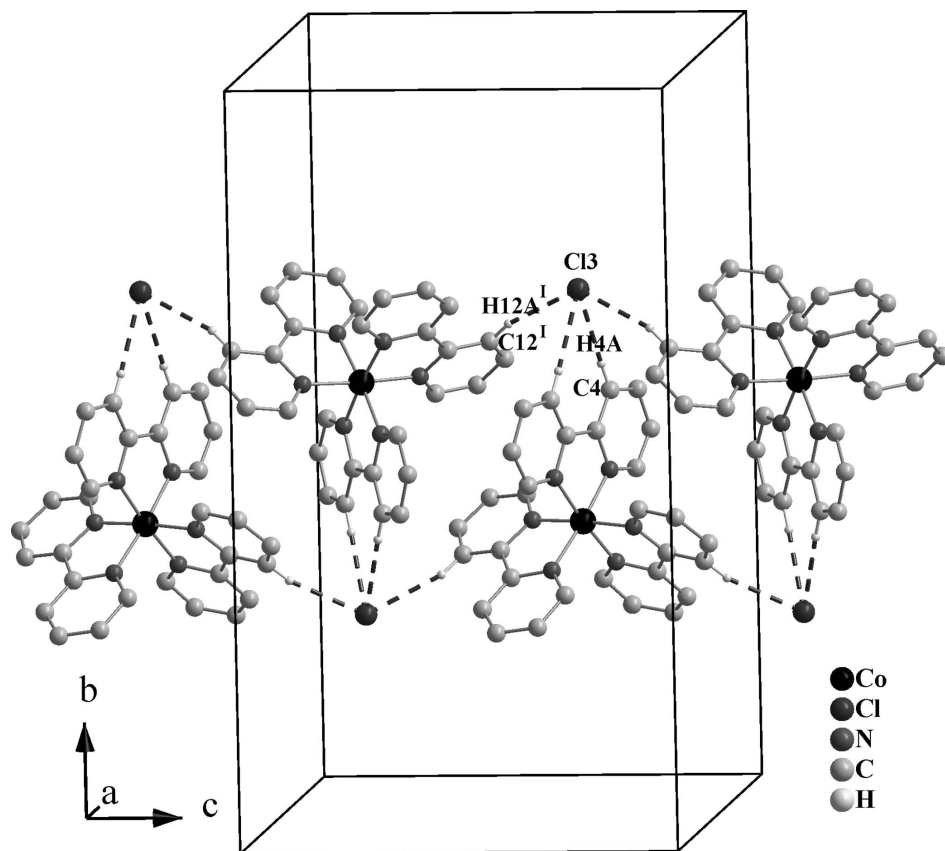
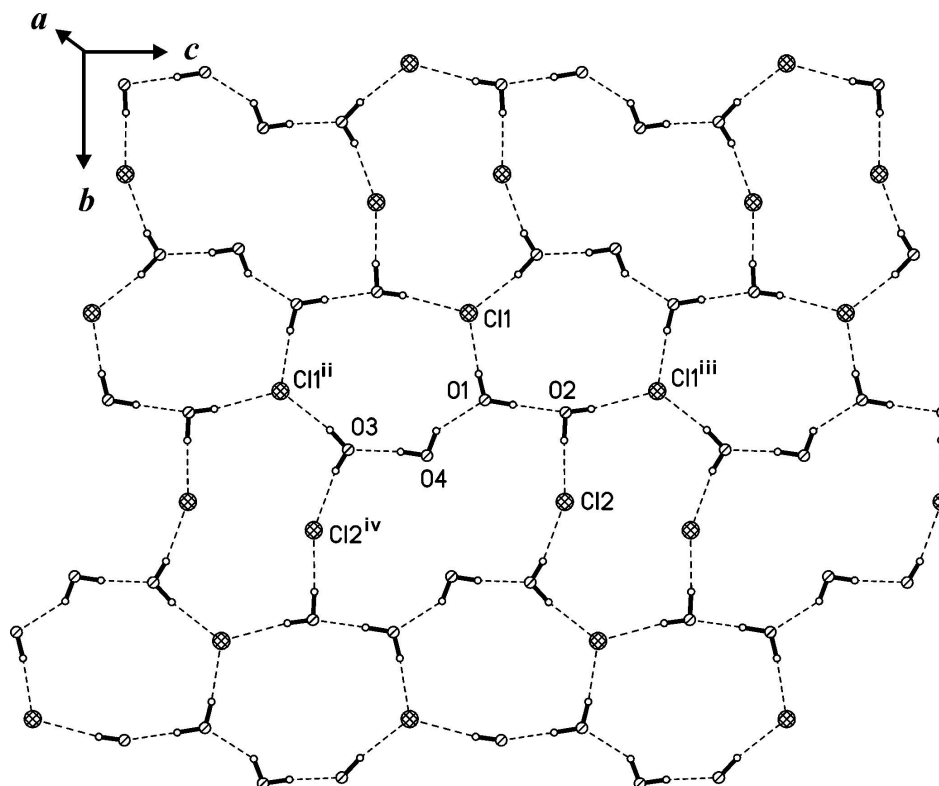
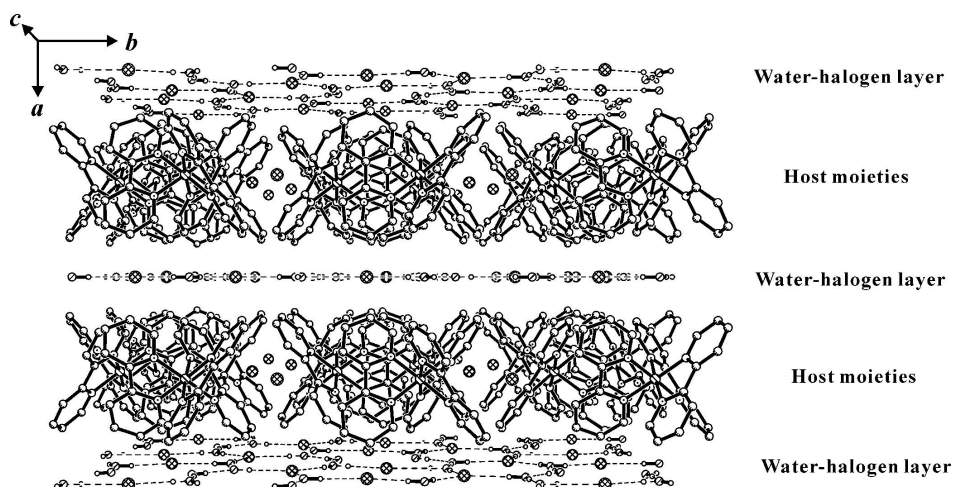


Figure 2

The one-dimensional chain of the $[\text{Co}(\text{phen})_3]^{3+}$ cations along with $[001]$ direction.


Figure 3

The two-dimensional water-chloride framework parallel to (100). [Symmetry codes: (ii) $-x, -y + 3/2, z - 1/2$; (iii) $-x, -y + 3/2, z + 1/2$; (iv): $x, -y + 1, -z + 1$]


Figure 4

Packing diagram of the supramolecular edifice viewed along the crystallographic c axis.

Tris(2,2'-bipyridine- $\kappa^2N:N'$)cobalt(III) trichloride tetrahydrate

Crystal data

[Co(C₁₀H₈N₂)₃]Cl₃·4H₂O $M_r = 705.90$ Orthorhombic, *Cmca*

Hall symbol: -C 2bc 2

 $a = 20.171$ (4) Å $b = 23.170$ (5) Å $c = 13.316$ (3) Å $V = 6223$ (2) Å³ $Z = 8$ $F(000) = 2912$ $D_x = 1.507$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 25 reflections

 $\theta = 5.0$ – 12.5° $\mu = 0.86$ mm⁻¹ $T = 295$ K

Block, yellow

 $0.12 \times 0.10 \times 0.08$ mm

Data collection

Bruker P4

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 $\theta/2\theta$ scansAbsorption correction: ψ scan

(XSCANS; Siemens, 1996)

 $T_{\min} = 0.905$, $T_{\max} = 0.929$

3430 measured reflections

2824 independent reflections

1980 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.049$ $\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.8^\circ$ $h = -23 \rightarrow 1$ $k = -1 \rightarrow 27$ $l = -1 \rightarrow 15$

3 standard reflections every 97 reflections

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.056$ $wR(F^2) = 0.162$ $S = 1.03$

2824 reflections

225 parameters

12 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

 $w = 1/[\sigma^2(F_o^2) + (0.1023P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 1.01$ e Å⁻³ $\Delta\rho_{\min} = -0.66$ e Å⁻³

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness 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 threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) 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 (Å²)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------|-------------|--------------|----------------------------------|
| Co1 | 0.2500 | 0.40805 (3) | 0.7500 | 0.0230 (2) |
| Cl1 | 0.0000 | 0.80958 (8) | 0.57842 (16) | 0.0580 (5) |
| Cl2 | 0.0000 | 0.52160 (8) | 0.83302 (13) | 0.0487 (5) |

| | | | | |
|------|--------------|--------------|------------|-------------|
| Cl3 | 0.2500 | 0.71245 (7) | 0.7500 | 0.0508 (5) |
| N1 | 0.19627 (15) | 0.47048 (14) | 0.6973 (2) | 0.0254 (7) |
| N2 | 0.19583 (15) | 0.34934 (14) | 0.6871 (3) | 0.0278 (8) |
| N3 | 0.29820 (15) | 0.40542 (14) | 0.6251 (2) | 0.0267 (8) |
| C1 | 0.13885 (18) | 0.46643 (19) | 0.6478 (3) | 0.0328 (10) |
| H1A | 0.1227 | 0.4300 | 0.6316 | 0.039* |
| C2 | 0.1025 (2) | 0.51433 (19) | 0.6198 (3) | 0.0367 (11) |
| H2A | 0.0628 | 0.5100 | 0.5852 | 0.044* |
| C3 | 0.1256 (2) | 0.5687 (2) | 0.6436 (3) | 0.0382 (11) |
| H3A | 0.1016 | 0.6014 | 0.6257 | 0.046* |
| C4 | 0.1849 (2) | 0.57363 (18) | 0.6944 (3) | 0.0370 (11) |
| H4A | 0.2019 | 0.6098 | 0.7102 | 0.044* |
| C5 | 0.21896 (19) | 0.52388 (17) | 0.7216 (3) | 0.0267 (9) |
| C6 | 0.1430 (2) | 0.32196 (18) | 0.7267 (4) | 0.0368 (11) |
| H6A | 0.1316 | 0.3286 | 0.7934 | 0.044* |
| C7 | 0.1052 (2) | 0.28387 (19) | 0.6695 (4) | 0.0453 (12) |
| H7A | 0.0695 | 0.2646 | 0.6983 | 0.054* |
| C8 | 0.1204 (2) | 0.27501 (19) | 0.5722 (4) | 0.0486 (13) |
| H8A | 0.0939 | 0.2512 | 0.5330 | 0.058* |
| C9 | 0.1750 (2) | 0.30103 (18) | 0.5309 (4) | 0.0407 (11) |
| H9A | 0.1867 | 0.2940 | 0.4645 | 0.049* |
| C10 | 0.2128 (2) | 0.33844 (17) | 0.5904 (3) | 0.0300 (9) |
| C11 | 0.27255 (19) | 0.36858 (17) | 0.5557 (3) | 0.0284 (9) |
| C12 | 0.3015 (2) | 0.3604 (2) | 0.4646 (3) | 0.0410 (11) |
| H12A | 0.2824 | 0.3358 | 0.4176 | 0.049* |
| C13 | 0.3601 (2) | 0.3892 (2) | 0.4427 (4) | 0.0452 (12) |
| H13A | 0.3813 | 0.3835 | 0.3815 | 0.054* |
| C14 | 0.3861 (2) | 0.4261 (2) | 0.5121 (3) | 0.0397 (11) |
| H14A | 0.4251 | 0.4459 | 0.4984 | 0.048* |
| C15 | 0.3545 (2) | 0.43360 (18) | 0.6017 (3) | 0.0329 (10) |
| H15A | 0.3725 | 0.4591 | 0.6482 | 0.039* |
| O1 | 0.0000 | 0.6769 (3) | 0.6215 (5) | 0.092 (2) |
| H1W1 | 0.0000 | 0.7122 (17) | 0.610 (8) | 0.138* |
| H1W2 | 0.0000 | 0.673 (5) | 0.685 (3) | 0.138* |
| O2 | 0.0000 | 0.6582 (2) | 0.8357 (5) | 0.0643 (15) |
| H2W1 | 0.0000 | 0.664 (3) | 0.898 (3) | 0.096* |
| H2W2 | 0.0000 | 0.6220 (14) | 0.829 (6) | 0.096* |
| O3 | 0.0000 | 0.6013 (2) | 0.2581 (4) | 0.0701 (17) |
| H3W1 | 0.0000 | 0.620 (3) | 0.203 (4) | 0.105* |
| H3W2 | 0.0000 | 0.5664 (14) | 0.241 (6) | 0.105* |
| O4 | 0.0000 | 0.5921 (2) | 0.4674 (4) | 0.0566 (13) |
| H4W1 | 0.0000 | 0.619 (2) | 0.504 (4) | 0.085* |
| H4W2 | 0.0000 | 0.600 (3) | 0.408 (2) | 0.085* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|----------|-------------|----------|
| Co1 | 0.0243 (4) | 0.0150 (4) | 0.0297 (4) | 0.000 | -0.0016 (3) | 0.000 |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C11 | 0.0727 (12) | 0.0362 (10) | 0.0651 (12) | 0.000 | 0.000 | -0.0075 (9) |
| C12 | 0.0512 (9) | 0.0463 (10) | 0.0486 (10) | 0.000 | 0.000 | -0.0087 (8) |
| C13 | 0.0791 (12) | 0.0197 (8) | 0.0537 (10) | 0.000 | 0.0244 (9) | 0.000 |
| N1 | 0.0284 (17) | 0.0208 (17) | 0.0269 (17) | -0.0004 (14) | 0.0009 (14) | 0.0003 (15) |
| N2 | 0.0262 (17) | 0.0184 (17) | 0.039 (2) | -0.0013 (14) | -0.0021 (14) | 0.0005 (15) |
| N3 | 0.0277 (17) | 0.0194 (16) | 0.0331 (18) | 0.0035 (14) | 0.0010 (14) | 0.0009 (15) |
| C1 | 0.026 (2) | 0.030 (2) | 0.042 (2) | 0.0006 (18) | -0.0036 (19) | -0.002 (2) |
| C2 | 0.031 (2) | 0.043 (3) | 0.037 (2) | 0.0062 (19) | -0.0053 (19) | 0.007 (2) |
| C3 | 0.037 (2) | 0.032 (2) | 0.046 (3) | 0.0104 (19) | -0.002 (2) | 0.007 (2) |
| C4 | 0.043 (3) | 0.016 (2) | 0.052 (3) | 0.0019 (18) | 0.000 (2) | 0.003 (2) |
| C5 | 0.0297 (19) | 0.022 (2) | 0.028 (2) | -0.0002 (18) | 0.0029 (17) | 0.0022 (17) |
| C6 | 0.034 (2) | 0.022 (2) | 0.054 (3) | -0.0020 (19) | -0.001 (2) | 0.001 (2) |
| C7 | 0.034 (2) | 0.026 (2) | 0.076 (4) | -0.0095 (19) | -0.005 (2) | -0.002 (2) |
| C8 | 0.045 (3) | 0.029 (3) | 0.072 (4) | -0.005 (2) | -0.018 (3) | -0.015 (3) |
| C9 | 0.044 (3) | 0.028 (2) | 0.051 (3) | 0.000 (2) | -0.008 (2) | -0.012 (2) |
| C10 | 0.031 (2) | 0.022 (2) | 0.038 (2) | 0.0031 (17) | -0.0054 (19) | -0.0041 (19) |
| C11 | 0.034 (2) | 0.021 (2) | 0.030 (2) | 0.0027 (17) | -0.0067 (18) | -0.0040 (18) |
| C12 | 0.049 (3) | 0.037 (2) | 0.037 (3) | 0.007 (2) | -0.005 (2) | -0.006 (2) |
| C13 | 0.044 (3) | 0.056 (3) | 0.036 (3) | 0.014 (2) | 0.008 (2) | 0.003 (2) |
| C14 | 0.038 (2) | 0.037 (2) | 0.044 (3) | 0.000 (2) | 0.006 (2) | 0.007 (2) |
| C15 | 0.033 (2) | 0.027 (2) | 0.040 (3) | -0.0023 (18) | 0.0043 (19) | 0.000 (2) |
| O1 | 0.168 (7) | 0.043 (3) | 0.064 (4) | 0.000 | 0.000 | 0.000 (3) |
| O2 | 0.069 (3) | 0.053 (3) | 0.071 (4) | 0.000 | 0.000 | 0.016 (3) |
| O3 | 0.112 (5) | 0.038 (3) | 0.060 (4) | 0.000 | 0.000 | 0.004 (3) |
| O4 | 0.078 (3) | 0.043 (3) | 0.048 (3) | 0.000 | 0.000 | -0.006 (3) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-----------|----------|-----------|
| Co1—N3 ⁱ | 1.928 (3) | C7—C8 | 1.347 (7) |
| Co1—N3 | 1.928 (3) | C7—H7A | 0.9300 |
| Co1—N2 ⁱ | 1.935 (3) | C8—C9 | 1.370 (7) |
| Co1—N2 | 1.935 (3) | C8—H8A | 0.9300 |
| Co1—N1 | 1.939 (3) | C9—C10 | 1.401 (6) |
| Co1—N1 ⁱ | 1.939 (3) | C9—H9A | 0.9300 |
| N1—C1 | 1.336 (5) | C10—C11 | 1.467 (6) |
| N1—C5 | 1.358 (5) | C11—C12 | 1.360 (6) |
| N2—C6 | 1.348 (5) | C12—C13 | 1.388 (7) |
| N2—C10 | 1.355 (5) | C12—H12A | 0.9300 |
| N3—C15 | 1.347 (5) | C13—C14 | 1.363 (7) |
| N3—C11 | 1.360 (5) | C13—H13A | 0.9300 |
| C1—C2 | 1.381 (6) | C14—C15 | 1.363 (6) |
| C1—H1A | 0.9300 | C14—H14A | 0.9300 |
| C2—C3 | 1.379 (6) | C15—H15A | 0.9300 |
| C2—H2A | 0.9300 | O1—H1W1 | 0.83 (3) |
| C3—C4 | 1.379 (6) | O1—H1W2 | 0.85 (3) |
| C3—H3A | 0.9300 | O2—H2W1 | 0.85 (3) |
| C4—C5 | 1.390 (6) | O2—H2W2 | 0.84 (3) |
| C4—H4A | 0.9300 | O3—H3W1 | 0.85 (3) |

| | | | |
|--------------------------------------|-------------|-----------------------|-----------|
| C5—C5 ⁱ | 1.462 (8) | O3—H3W2 | 0.84 (3) |
| C6—C7 | 1.394 (6) | O4—H4W1 | 0.80 (3) |
| C6—H6A | 0.9300 | O4—H4W2 | 0.81 (3) |
| N3 ⁱ —Co1—N3 | 176.38 (19) | N1—C5—C5 ⁱ | 114.3 (2) |
| N3 ⁱ —Co1—N2 ⁱ | 83.63 (14) | C4—C5—C5 ⁱ | 123.9 (3) |
| N3—Co1—N2 ⁱ | 93.82 (14) | N2—C6—C7 | 121.1 (4) |
| N3 ⁱ —Co1—N2 | 93.82 (14) | N2—C6—H6A | 119.4 |
| N3—Co1—N2 | 83.63 (14) | C7—C6—H6A | 119.4 |
| N2 ⁱ —Co1—N2 | 90.69 (19) | C8—C7—C6 | 119.8 (4) |
| N3 ⁱ —Co1—N1 | 93.09 (13) | C8—C7—H7A | 120.1 |
| N3—Co1—N1 | 89.61 (13) | C6—C7—H7A | 120.1 |
| N2 ⁱ —Co1—N1 | 175.23 (14) | C7—C8—C9 | 120.2 (4) |
| N2—Co1—N1 | 92.99 (13) | C7—C8—H8A | 119.9 |
| N3 ⁱ —Co1—N1 ⁱ | 89.61 (13) | C9—C8—H8A | 119.9 |
| N3—Co1—N1 ⁱ | 93.09 (13) | C8—C9—C10 | 118.9 (5) |
| N2 ⁱ —Co1—N1 ⁱ | 92.99 (13) | C8—C9—H9A | 120.6 |
| N2—Co1—N1 ⁱ | 175.23 (14) | C10—C9—H9A | 120.6 |
| N1—Co1—N1 ⁱ | 83.50 (19) | N2—C10—C9 | 121.0 (4) |
| C1—N1—C5 | 118.3 (3) | N2—C10—C11 | 114.7 (3) |
| C1—N1—Co1 | 127.6 (3) | C9—C10—C11 | 124.3 (4) |
| C5—N1—Co1 | 113.9 (2) | N3—C11—C12 | 122.0 (4) |
| C6—N2—C10 | 119.0 (4) | N3—C11—C10 | 113.4 (3) |
| C6—N2—Co1 | 127.4 (3) | C12—C11—C10 | 124.6 (4) |
| C10—N2—Co1 | 113.5 (3) | C11—C12—C13 | 119.1 (4) |
| C15—N3—C11 | 117.9 (4) | C11—C12—H12A | 120.5 |
| C15—N3—Co1 | 127.6 (3) | C13—C12—H12A | 120.5 |
| C11—N3—Co1 | 114.5 (3) | C14—C13—C12 | 119.1 (4) |
| N1—C1—C2 | 122.5 (4) | C14—C13—H13A | 120.5 |
| N1—C1—H1A | 118.8 | C12—C13—H13A | 120.5 |
| C2—C1—H1A | 118.8 | C13—C14—C15 | 119.6 (4) |
| C3—C2—C1 | 119.5 (4) | C13—C14—H14A | 120.2 |
| C3—C2—H2A | 120.3 | C15—C14—H14A | 120.2 |
| C1—C2—H2A | 120.3 | N3—C15—C14 | 122.3 (4) |
| C2—C3—C4 | 118.8 (4) | N3—C15—H15A | 118.9 |
| C2—C3—H3A | 120.6 | C14—C15—H15A | 118.9 |
| C4—C3—H3A | 120.6 | H1W1—O1—H1W2 | 107 (7) |
| C3—C4—C5 | 119.2 (4) | H2W1—O2—H2W2 | 106 (5) |
| C3—C4—H4A | 120.4 | H3W1—O3—H3W2 | 106 (5) |
| C5—C4—H4A | 120.4 | H4W1—O4—H4W2 | 114 (5) |
| N1—C5—C4 | 121.8 (4) | | |

Symmetry code: (i) $-x+1/2, y, -z+3/2$.

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------|----------|-------------|-------------|---------------|
| O1—H1W2 \cdots O2 | 0.85 (4) | 2.04 (5) | 2.885 (9) | 176 (9) |

| | | | | |
|---------------------------------------|----------|----------|-----------|---------|
| O1—H1 <i>W</i> 1...C11 | 0.83 (4) | 2.30 (4) | 3.127 (7) | 180 (9) |
| O2—H2 <i>W</i> 1...C11 ⁱⁱ | 0.84 (4) | 2.48 (4) | 3.317 (7) | 175 (6) |
| O2—H2 <i>W</i> 2...C12 | 0.84 (3) | 2.33 (3) | 3.165 (5) | 173 (7) |
| O3—H3 <i>W</i> 1...C11 ⁱⁱⁱ | 0.85 (6) | 2.33 (6) | 3.161 (5) | 166 (6) |
| O3—H3 <i>W</i> 2...C12 ^{iv} | 0.84 (4) | 2.27 (5) | 3.095 (5) | 170 (7) |
| O4—H4 <i>W</i> 1...O1 | 0.79 (5) | 2.06 (5) | 2.841 (8) | 169 (5) |
| O4—H4 <i>W</i> 2...O3 | 0.81 (3) | 2.00 (3) | 2.795 (8) | 168 (7) |
| C1—H1 <i>A</i> ...N2 | 0.93 | 2.49 | 2.993 (5) | 114 |
| C4—H4 <i>A</i> ...C13 | 0.93 | 2.62 | 3.552 (4) | 179 |
| C6—H6 <i>A</i> ...N3 ⁱ | 0.93 | 2.52 | 3.007 (6) | 113 |
| C8—H8 <i>A</i> ...C11 ^{iv} | 0.93 | 2.79 | 3.710 (5) | 172 |
| C12—H12 <i>A</i> ...C13 ^v | 0.93 | 2.58 | 3.477 (4) | 162 |
| C14—H14 <i>A</i> ...C12 ^v | 0.93 | 2.77 | 3.526 (4) | 139 |
| C15—H15 <i>A</i> ...N1 ⁱ | 0.93 | 2.49 | 2.991 (5) | 114 |

Symmetry codes: (i) $-x+1/2, y, -z+3/2$; (ii) $-x, -y+3/2, z+1/2$; (iii) $-x, -y+3/2, z-1/2$; (iv) $x, -y+1, -z+1$; (v) $-x+1/2, -y+1, z-1/2$.