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Crystal structure and Hirshfeld surface analysis of bis(2,6-diaminopyridinium) tetrachloridocobaltate(II)

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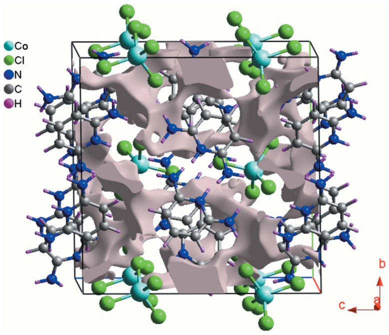
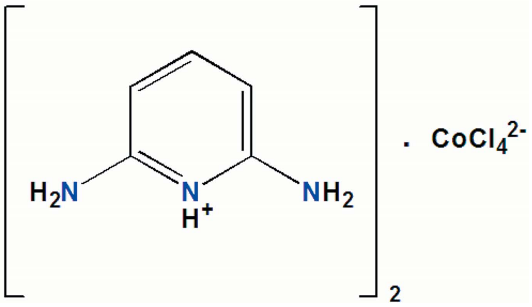
In the title molecular salt, $(C_5H_8N_3)_2[CoCl_4]$, the cations are protonated at their pyridine N atoms and the anion is an almost regular tetrahedron. The crystal structure consists of alternating inorganic layers, built from tetrachloridocobaltate anions, and organic layers formed by protonated cations of 2,6-diaminopyridinium. The crystal packing is governed by C/N—H···Cl hydrogen-bonding interactions between the organic and the inorganic ions and Cl···Cl interactions. Moreover, the cations show a *π*–*π* stacking interaction [inter-centroid distance = 3.763 (2) Å]. The prevalence of these interactions is illustrated by an analysis of the three-dimensional Hirshfeld surface and by two-dimensional fingerprint plots.



1. Chemical context

One of the best studied groups of organic–inorganic hybrid materials are the cobalt(II) halide compounds because of their important properties such as fluorescence and magnetism (Decaroli *et al.*, 2015; Kurmoo, 2009). The coordination sphere of Co^{II} is variable, leading to different geometries including octahedral, tetrahedral, square pyramidal, trigonal bipyramidal and square planar (Kurmoo, 2009). Pyridine as an organic heterocyclic molecule has various biological activities (Sellin, 1981; Davidson *et al.*, 1988). As part of our studies in this area, the title compound, $(C_5H_8N_3)_2[CoCl_4]$ (I), has been investigated.



2. Structural commentary

The asymmetric unit of (I) is made up of one tetrachloridocobaltate, $[CoCl_4]^{2-}$, anion and two protonated 2,6-diaminopyridinium, $(C_5H_8N_3)^+$, organic cations (Fig. 1). The geometry of the $CoCl_4$ anion is characterized by a range of Co—Cl bond

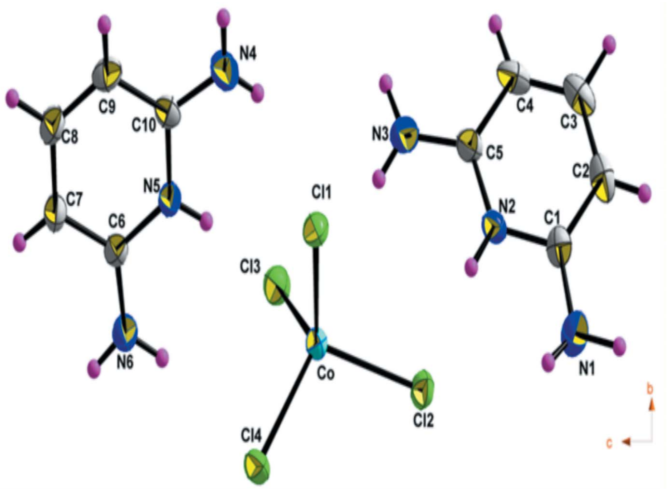


Figure 1
The asymmetric unit of (I), with displacement ellipsoids are drawn at the 30% probability level.

length from 2.2595 (14) to 2.2795 (13) Å and Cl—Co—Cl angles varying from 106.44 (5) to 112.69 (5)°, building a slightly distorted tetrahedron. These data are in agreement with those found in related compounds (Mghandef & Boughzala, 2015). The calculated average values of the distortion indice as described by Baur (1974) corresponding to the different lengths and angles in the $CoCl_4$ tetrahedra [ΔI(Co—Cl) = 0.004 and ΔI(Cl—Co—Cl) = 0.0019] show a slight distortion of the tetrahedra. The interanionic Cl···Cl contact distances between the nearest neighbor tetrahedra are 3.986 (2) Å along the *a* axis and 3.889 (2) Å along the *c* axis (Fig. 2), compared to a van der Waals contact distance of 3.50 Å. These contacts are sometimes associated with weak antiferromagnetic interactions (Shapiro *et al.*, 2007), which decrease rapidly with increasing Cl···Cl separation.

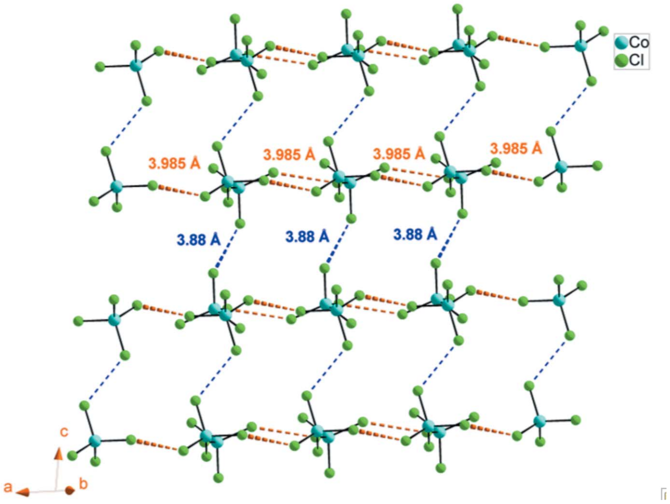


Figure 2
The interanionic Cl···Cl contact in the tetrachlorocobaltate anion of (I) along the *a* and *c* axis.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2*N*1···Cl2	0.84 (5)	2.69 (5)	3.432 (4)	147 (4)
N4—H2*N*4···Cl2^{i}	0.84 (5)	2.65 (5)	3.465 (5)	162 (4)
N6—H1*N*6···Cl4	0.85 (5)	2.58 (5)	3.406 (4)	165 (4)
N2—H1*N*2···Cl2	0.82 (4)	2.44 (4)	3.240 (3)	168 (4)
N5—H1*N*5···Cl1	0.82 (5)	2.43 (5)	3.191 (3)	156 (4)
N3—H1*N*3···Cl4^{ii}	0.88 (4)	2.53 (5)	3.390 (5)	166 (4)
N4—H1*N*4···Cl1	0.79 (4)	2.79 (4)	3.481 (5)	147 (4)
N6—H2*N*6···Cl3^{iii}	0.82 (5)	2.75 (5)	3.516 (4)	156 (4)
N3—H2*N*3···Cl3	0.83 (6)	2.61 (6)	3.420 (5)	166 (6)
N1—H1*N*1···Cl1^{iv}	0.94 (5)	2.69 (5)	3.326 (4)	126 (4)
C7—H7···Cl3^{iii}	0.91 (4)	2.89 (4)	3.669 (4)	145 (3)

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

Pyridinium cations always possess an expanded angle of C—N—C in comparison with the parent pyridine (Ben Nasr *et al.*, 2015). Thus, the observed angles in (I) of C1—N2—C5 and C6—N5—C10 are 124.2 (3) and 124.1 (3)°, respectively, are wider than that in neutral pyridine (116.6°), indicating that protonation takes place on the pyridine ring N2 and N5 atoms. Accordingly, within the cations, we note that the N—C and C—C distances range from 1.332 (5) to 1.393 (6) Å, while the C—C—C, N—C—N, C—C—N and N—C—C angles vary from 116.00 (4) to 126.50 (4)°. The 2,6-diaminopyridinium units are essentially planar, with an r.m.s. deviation from the mean plane of 0.002 and 0.006 Å for the N2 and N5 species, respectively.

3. Supramolecular features

Examination of the crystal structure of (I) reveals organic layers parallel to the *ab* plane made of 2,6-diaminopyridinium cations alternating with inorganic layers formed by tetrachloridocobaltate anions (Fig. 3), which is similar to those of

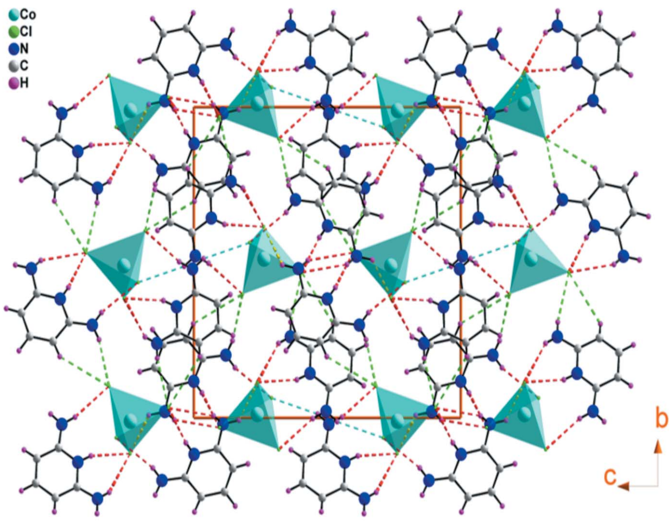


Figure 3
View of (I) towards the *bc* plane. The dotted lines indicate hydrogen bonds.

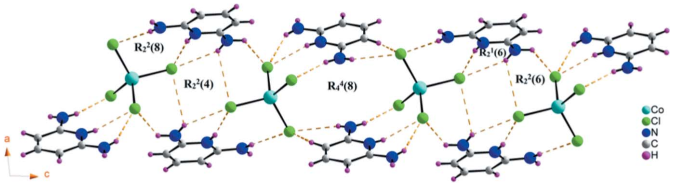


Figure 4
Projection of a part of the crystalline structure of the compound (I), showing the formation of the motifs $R_2^2(4)$, $R_2^2(6)$, $R_2^1(6)$, $R_4^4(8)$ and $R_2^2(8)$.

related materials: $(C_5H_6Br_2N_3)_2[MBr_4]$ (M = Cd, Mn) (Al-Far *et al.*, 2009) and $(C_5H_7N_2)_2[CoBr_4]$ (Mhadhbi *et al.*, 2016).

The construction of the three-dimensional architecture is consolidated by N—H⋯Cl and C—H⋯Cl hydrogen bonds (Table 1), generating $R_2^2(4)$, $R_2^2(6)$, $R_2^1(6)$, $R_4^4(8)$ and $R_2^2(8)$ graph-set motifs (Fig. 4).

As can be seen from Fig. 5, the two nearest neighboring anti-parallel organic cations, which are not connected by hydrogen bonding, are stacked in a face-to-face mode. The centroid–centroid distance is 3.762 (5) Å, slightly less than 3.8 Å, which is the maximum value accepted for π–π interactions (Ben Hassen *et al.*, 2017; Janiak, 2000).

4. Hirshfeld surface analysis

The Hirshfeld surface (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots were performed with *CrystalExplorer* (Wolff *et al.*, 2012). The Hirshfeld surface of the title compound mapped over $d_{\rm norm}$ is illustrated in Fig. 6. The red spots correspond to the H⋯Cl close contacts, which are due to the N—H⋯Cl hydrogen bonds. Similarly, the presence of H⋯Cl contacts (due to C—H⋯Cl hydrogen bonds) are indicated by a light-red color. The white areas correspond to the places where the distance separating neighboring atoms are close to the sum of the van der Waals radius of the considered atoms and indicate H⋯H interactions. The bluish areas illustrate areas where neighboring atoms are too far apart for there to be interactions between them. In the shape-index map (Fig. 7), the adjacent red and blue triangle-like patches show concave regions that indicate π–π stacking interactions (Bitzer *et al.*, 2017).

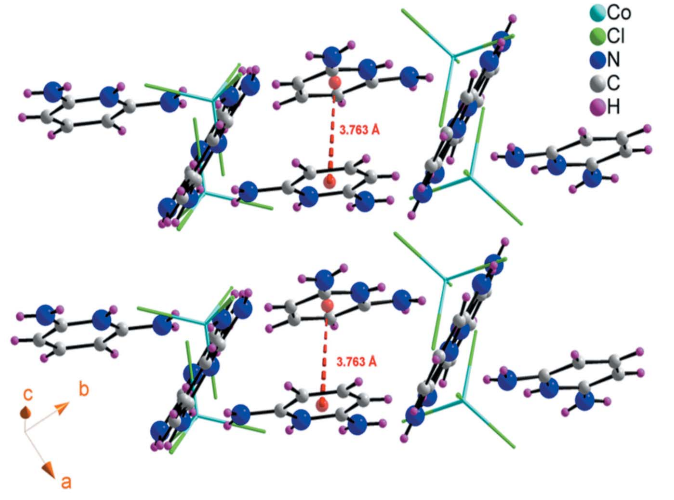


Figure 5
π–π stacking interactions between the neighboring aromatic organic cations in (I). The inorganic anions are shown as sticks for clarity.

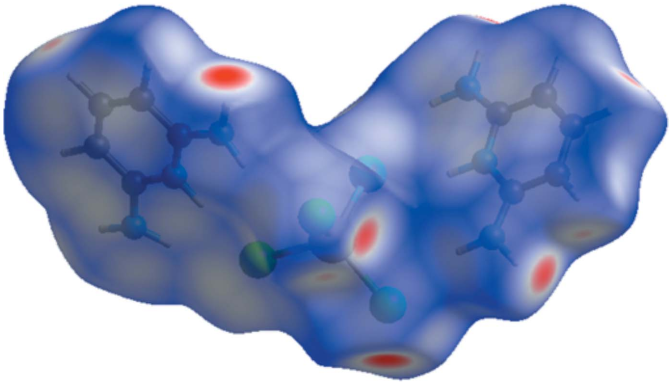


Figure 6
View of the Hirshfeld surface of (I) mapped over $d_{\rm norm}$.

The fingerprint plots of (I) (Fig. 8*a*) (Parkin *et al.*, 2007; Rohl *et al.*, 2008), reveal that the main intermolecular interactions with the highest percentage contributions are: H⋯Cl/Cl⋯H (41.6%, Fig. 8*b*), H⋯H (30.8%, Fig. 8*c*) and C⋯H/H⋯C (11.3%, Fig. 8*d*).

Fig. 9 shows the voids (Wolff *et al.*, 2012) in the crystal structure of (I). These are based on the sum of spherical atomic electron densities at the appropriate nuclear positions (procrystal electron density). The crystal voids calculation (results under 0.002 a.u. isovalue) shows the void volume of title compound to be of the order of 172 Å^3 and surface area in the order of 648 Å^2. With the porosity, the calculated void volume of (I) is 10%. There are no large cavities. We note that the electron-density isosurfaces are not completely closed around the components, but are open at those locations where interspecies approaches are found, *e.g.* N—H⋯Cl and C—H⋯Cl.

5. Synthesis and crystallization

2,6-diaminopyridine and $CoCl_2{\cdot}6H_2O$ (molar ratio 1:1) were dissolved in 10 ml of methanol; 3 ml of hydrochloric acid

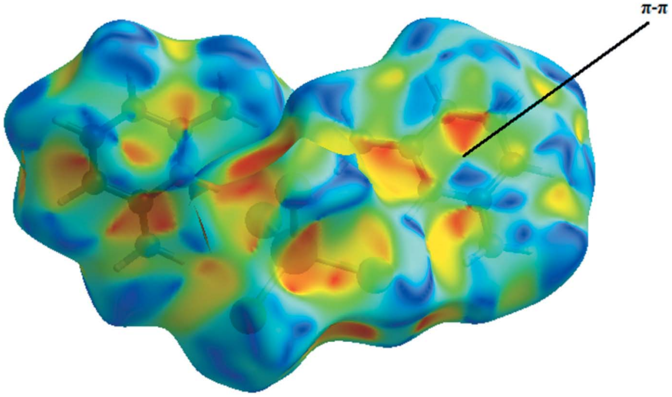


Figure 7
Hirshfeld surface mapped over shape-index, highlighting the regions involved in π–π stacking interactions.

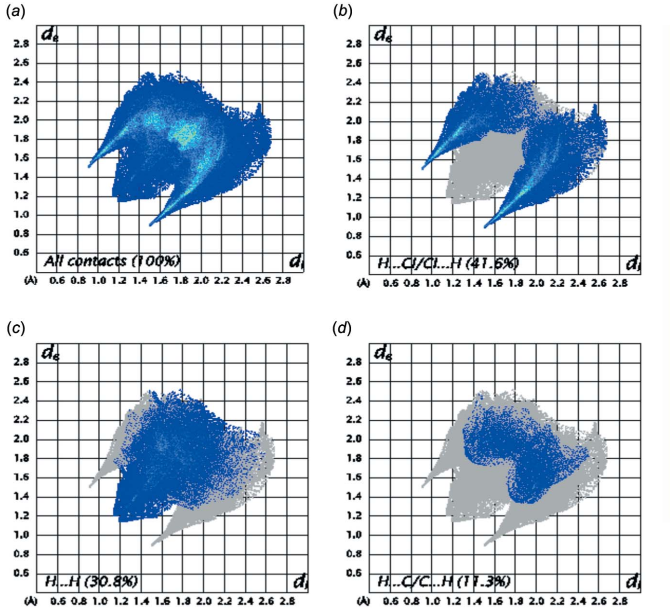


Figure 8
The two-dimensional fingerprint plots of (I), (*a*) showing all interactions and delineated into H···Cl/Cl···H (*b*), H···H (*c*) and C···H/H···C (*d*) interactions.

(37%) was added dropwise to the mixture and the resulting blue solution was put aside for crystallization at room temperature. After two weeks, blue crystals of (I) were recovered.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were found in a difference-Fourier map and refined isotropically.

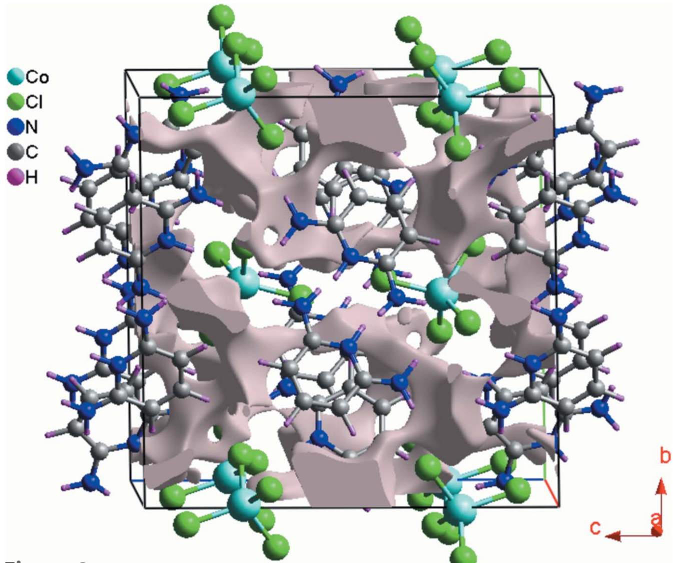


Figure 9
Void plot for (I).

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_5H_8N_3)_2[CoCl_4]$
M_r	421.02
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, b, c (Å)	7.390 (4), 15.373 (4), 15.387 (4)
β (°)	98.203 (4)
V (Å^3)	1730.1 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.61
Crystal size (mm)	0.4 × 0.3 × 0.1
Data collection	
Diffractometer	Enraf–Nonius CAD-4
Absorption correction	ψ scan (North *et al.*, 1968)
$T_{\min}$, $T_{\max}$	0.777, 0.998
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4367, 3770, 2396
$R_{\rm int}$	0.038
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.638
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.110, 1.01
No. of reflections	3770
No. of parameters	255
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.37, −0.42

Computer programs: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992), *XCAD4* (Harms & Wocadlo, 1995), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2006), *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

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supporting information

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Computing details

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

Bis(2,6-diaminopyridinium) tetrachloridocobaltate(II)

Crystal data

$(C_5H_8N_3)_2[CoCl_4]$
$M_r = 421.02$
Monoclinic, $P2_1/n$
$a = 7.390\ (4)$ Å
$b = 15.373\ (4)$ Å
$c = 15.387\ (4)$ Å
$\beta = 98.203\ (4)°$
$V = 1730.1\ (11)$ Å^3
$Z = 4$
$F(000) = 852$
$D_x = 1.616$ Mg m^{-3}
$D_m = 1.616$ Mg m^{-3}
D_m measured by ?
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.1–14.9°$
$\mu = 1.61$ mm^{-1}
$T = 293$ K
Parallelepiped, blue
0.4 × 0.3 × 0.1 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.777$, $T_{max} = 0.998$
4367 measured reflections
3770 independent reflections
2396 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.0°$, $\theta_{min} = 2.7°$
$h = -9 \rightarrow 1$
$k = -1 \rightarrow 19$
$l = -19 \rightarrow 19$
2 standard reflections every 120 reflections
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.110$
$S = 1.01$
3770 reflections
255 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.37$ e Å^{-3}
$\Delta\rho_{\min} = -0.42$ e Å^{-3}

Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^{*}=kFc[1+0.001xFc^{2}\lambda^{3}/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0049 (8)

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 (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
Co1	0.44824 (7)	0.51081 (3)	0.73764 (3)	0.03878 (16)
Cl1	0.66787 (14)	0.61509 (6)	0.73884 (6)	0.0497 (2)
Cl2	0.36703 (14)	0.46854 (6)	0.59572 (6)	0.0500 (3)
Cl3	0.20113 (14)	0.56398 (7)	0.79102 (6)	0.0547 (3)
Cl4	0.58007 (17)	0.39816 (6)	0.81784 (7)	0.0627 (3)
N2	0.1002 (5)	0.6175 (2)	0.4994 (2)	0.0451 (7)
N5	0.8682 (4)	0.6428 (2)	0.9347 (2)	0.0425 (7)
N4	0.9624 (6)	0.7606 (3)	0.8611 (3)	0.0623 (10)
N1	0.1431 (6)	0.5199 (3)	0.3912 (3)	0.0646 (10)
N6	0.7523 (6)	0.5209 (2)	0.9947 (3)	0.0678 (12)
N3	0.0650 (7)	0.7017 (3)	0.6196 (3)	0.0759 (13)
C6	0.8422 (5)	0.5964 (2)	1.0067 (2)	0.0444 (8)
C10	0.9484 (5)	0.7226 (2)	0.9377 (2)	0.0434 (8)
C1	0.0856 (5)	0.5995 (3)	0.4122 (2)	0.0483 (9)
C7	0.9051 (6)	0.6309 (3)	1.0881 (2)	0.0571 (11)
C5	0.0425 (6)	0.6919 (2)	0.5325 (3)	0.0489 (9)
C9	1.0121 (6)	0.7571 (3)	1.0189 (3)	0.0532 (10)
C8	0.9889 (6)	0.7105 (3)	1.0922 (3)	0.0581 (11)
C2	0.0069 (6)	0.6621 (4)	0.3543 (3)	0.0630 (12)
C3	−0.0514 (6)	0.7378 (3)	0.3851 (3)	0.0651 (13)
C4	−0.0359 (6)	0.7541 (3)	0.4729 (4)	0.0606 (12)
H7	0.874 (6)	0.603 (3)	1.136 (3)	0.066 (13)*
H2	0.000 (6)	0.648 (3)	0.298 (3)	0.074 (14)*
H4	−0.066 (5)	0.803 (3)	0.498 (2)	0.047 (11)*
H9	1.071 (6)	0.802 (3)	1.022 (3)	0.075 (15)*
H8	1.035 (6)	0.735 (3)	1.146 (3)	0.062 (12)*
H3	−0.108 (7)	0.784 (3)	0.345 (3)	0.094 (16)*
H2N1	0.222 (6)	0.493 (3)	0.427 (3)	0.061 (14)*
H2N4	1.020 (6)	0.808 (3)	0.863 (3)	0.067 (14)*
H1N6	0.720 (7)	0.498 (3)	0.945 (3)	0.074 (15)*
H1N2	0.157 (6)	0.581 (3)	0.530 (3)	0.058 (13)*
H1N5	0.839 (6)	0.623 (3)	0.886 (3)	0.079 (16)*
H1N3	0.026 (6)	0.748 (3)	0.645 (3)	0.062 (13)*
H1N4	0.913 (6)	0.740 (3)	0.817 (3)	0.047 (13)*
H2N6	0.747 (7)	0.488 (3)	1.036 (3)	0.082 (17)*

H2N3	0.095 (9)	0.661 (4)	0.654 (4)	0.12 (2)*
H1N1	0.139 (7)	0.508 (3)	0.331 (3)	0.089 (17)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0442 (3)	0.0358 (3)	0.0350 (2)	0.0012 (2)	0.00079 (19)	0.00112 (19)
Cl1	0.0558 (6)	0.0446 (5)	0.0472 (5)	−0.0080 (4)	0.0022 (4)	−0.0022 (4)
Cl2	0.0553 (6)	0.0531 (5)	0.0382 (5)	0.0072 (4)	−0.0049 (4)	−0.0042 (4)
Cl3	0.0573 (6)	0.0547 (6)	0.0547 (5)	0.0058 (5)	0.0170 (5)	0.0013 (5)
Cl4	0.0892 (8)	0.0407 (5)	0.0511 (6)	0.0053 (5)	−0.0141 (5)	0.0073 (4)
N2	0.0487 (19)	0.0386 (16)	0.0468 (17)	0.0056 (15)	0.0027 (15)	0.0068 (14)
N5	0.0458 (18)	0.0446 (17)	0.0360 (16)	−0.0034 (14)	0.0023 (13)	−0.0017 (14)
N4	0.068 (3)	0.059 (2)	0.059 (2)	−0.015 (2)	0.006 (2)	0.010 (2)
N1	0.061 (2)	0.077 (3)	0.054 (2)	0.011 (2)	0.0023 (19)	−0.011 (2)
N6	0.103 (3)	0.053 (2)	0.045 (2)	−0.028 (2)	0.001 (2)	−0.0006 (18)
N3	0.122 (4)	0.047 (2)	0.063 (3)	0.011 (2)	0.030 (3)	−0.001 (2)
C6	0.051 (2)	0.0416 (19)	0.0397 (19)	−0.0056 (17)	0.0037 (16)	−0.0002 (15)
C10	0.040 (2)	0.041 (2)	0.049 (2)	0.0030 (16)	0.0073 (16)	0.0048 (16)
C1	0.039 (2)	0.057 (2)	0.048 (2)	−0.0024 (18)	0.0032 (16)	0.0011 (18)
C7	0.078 (3)	0.057 (3)	0.035 (2)	−0.015 (2)	0.004 (2)	−0.0021 (18)
C5	0.054 (2)	0.041 (2)	0.053 (2)	0.0032 (18)	0.0151 (18)	0.0070 (18)
C9	0.050 (2)	0.046 (2)	0.062 (3)	−0.013 (2)	0.002 (2)	−0.0082 (19)
C8	0.070 (3)	0.058 (3)	0.044 (2)	−0.014 (2)	−0.002 (2)	−0.0083 (19)
C2	0.054 (3)	0.085 (3)	0.047 (2)	−0.006 (2)	0.000 (2)	0.016 (2)
C3	0.060 (3)	0.061 (3)	0.073 (3)	0.001 (2)	0.005 (2)	0.029 (2)
C4	0.059 (3)	0.040 (2)	0.085 (3)	0.009 (2)	0.019 (2)	0.015 (2)

Geometric parameters (Å, º)

Co1—Cl3	2.2595 (14)	N6—H2N6	0.82 (5)
Co1—Cl4	2.2645 (11)	N3—C5	1.335 (6)
Co1—Cl2	2.2754 (11)	N3—H1N3	0.88 (4)
Co1—Cl1	2.2795 (13)	N3—H2N3	0.83 (6)
N2—C5	1.346 (5)	C6—C7	1.379 (5)
N2—C1	1.359 (5)	C10—C9	1.378 (5)
N2—H1N2	0.82 (4)	C1—C2	1.382 (6)
N5—C6	1.355 (4)	C7—C8	1.369 (6)
N5—C10	1.360 (5)	C7—H7	0.91 (4)
N5—H1N5	0.82 (5)	C5—C4	1.393 (6)
N4—C10	1.332 (5)	C9—C8	1.367 (6)
N4—H2N4	0.84 (5)	C9—H9	0.82 (5)
N4—H1N4	0.79 (4)	C8—H8	0.93 (4)
N1—C1	1.349 (5)	C2—C3	1.350 (7)
N1—H2N1	0.84 (5)	C2—H2	0.89 (4)
N1—H1N1	0.94 (5)	C3—C4	1.362 (7)
N6—C6	1.337 (5)	C3—H3	0.99 (5)
N6—H1N6	0.85 (5)	C4—H4	0.89 (4)

Cl3—Co1—Cl4	112.69 (5)	N4—C10—N5	117.1 (4)
Cl3—Co1—Cl2	109.64 (5)	N4—C10—C9	125.0 (4)
Cl4—Co1—Cl2	109.80 (4)	N5—C10—C9	117.9 (3)
Cl3—Co1—Cl1	110.73 (5)	N1—C1—N2	116.0 (4)
Cl4—Co1—Cl1	106.44 (5)	N1—C1—C2	126.5 (4)
Cl2—Co1—Cl1	107.37 (4)	N2—C1—C2	117.4 (4)
C5—N2—C1	124.2 (3)	C8—C7—C6	118.5 (4)
C5—N2—H1N2	123 (3)	C8—C7—H7	123 (3)
C1—N2—H1N2	113 (3)	C6—C7—H7	118 (3)
C6—N5—C10	124.1 (3)	N3—C5—N2	118.3 (4)
C6—N5—H1N5	120 (3)	N3—C5—C4	124.4 (4)
C10—N5—H1N5	116 (3)	N2—C5—C4	117.3 (4)
C10—N4—H2N4	117 (3)	C8—C9—C10	118.7 (4)
C10—N4—H1N4	120 (3)	C8—C9—H9	121 (3)
H2N4—N4—H1N4	123 (4)	C10—C9—H9	120 (3)
C1—N1—H2N1	119 (3)	C9—C8—C7	122.7 (4)
C1—N1—H1N1	117 (3)	C9—C8—H8	117 (3)
H2N1—N1—H1N1	118 (4)	C7—C8—H8	121 (3)
C6—N6—H1N6	124 (3)	C3—C2—C1	120.0 (4)
C6—N6—H2N6	121 (4)	C3—C2—H2	125 (3)
H1N6—N6—H2N6	114 (4)	C1—C2—H2	115 (3)
C5—N3—H1N3	122 (3)	C2—C3—C4	121.4 (4)
C5—N3—H2N3	123 (4)	C2—C3—H3	122 (3)
H1N3—N3—H2N3	114 (5)	C4—C3—H3	117 (3)
N6—C6—N5	118.1 (3)	C3—C4—C5	119.7 (4)
N6—C6—C7	123.7 (4)	C3—C4—H4	127 (2)
N5—C6—C7	118.1 (3)	C5—C4—H4	114 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2*N*1···Cl2	0.84 (5)	2.69 (5)	3.432 (4)	147 (4)
N4—H2*N*4···Cl2^{i}	0.84 (5)	2.65 (5)	3.465 (5)	162 (4)
N6—H1*N*6···Cl4	0.85 (5)	2.58 (5)	3.406 (4)	165 (4)
N2—H1*N*2···Cl2	0.82 (4)	2.44 (4)	3.240 (3)	168 (4)
N5—H1*N*5···Cl1	0.82 (5)	2.43 (5)	3.191 (3)	156 (4)
N3—H1*N*3···Cl4^{ii}	0.88 (4)	2.53 (5)	3.390 (5)	166 (4)
N4—H1*N*4···Cl1	0.79 (4)	2.79 (4)	3.481 (5)	147 (4)
N6—H2*N*6···Cl3^{iii}	0.82 (5)	2.75 (5)	3.516 (4)	156 (4)
N3—H2*N*3···Cl3	0.83 (6)	2.61 (6)	3.420 (5)	166 (6)
N1—H1*N*1···Cl1^{iv}	0.94 (5)	2.69 (5)	3.326 (4)	126 (4)
C7—H7···Cl3^{iii}	0.91 (4)	2.89 (4)	3.669 (4)	145 (3)

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