Crystal structure and Hirshfeld surface analysis of 6,6′-dimethyl-2,2′-bipyridine-1,1′-diium tetrachloridocobaltate(II)

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In the title molecular salt, $(C_{12}H_{14}N_2)[CoCl_4]$, the dihedral angle between the pyridine rings of the cation is 52.46 (9)° and the N—C—C—N torsion angle is −128.78 (14)°, indicating that the ring nitrogen atoms are in *anti*-clinal conformation. The Cl—Co—Cl bond angles in the anion span the range 105.46 (3)–117.91 (2)°. In the extended structure, the cations and anions are linked by cation-to-anion N—H⋯Cl and C—H⋯Cl interactions, facilitating the formation of $R_4^4(18)$ and $R_4^4(20)$ ring motifs. Furthermore, the crystal structure features weak anion-to-cation Cl⋯π interactions [Cl⋯π = 3.4891 (12) and 3.5465 (12) Å]. Hirshfeld two-dimensional fingerprint plots revealed that the most significant interactions are Cl⋯H/H⋯Cl (45.5%), H⋯H (29.0%), Cl⋯C/C⋯Cl (7.8%), Cl⋯N/N⋯Cl (3.5%), Cl⋯Cl (1.4) and Co⋯H (1%) contacts.

1. Chemical context

In recent years, non-covalent interactions have played an important role in organic–inorganic hybrid materials that have attracted researchers because of their potential applications in catalysis, energy storage devices, luminescence, photography and drug delivery (Bringley *et al.*, 2005; Avila-Montiel *et al.*, 2020). Cobalt(II) halide compounds are used as metal catalysts in various organic transformations and possess important fluorescence and magnetic properties (Decaroli *et al.*, 2015). As part of our work in this area, we now describe the synthesis, structure and Hirshfeld surface analysis of the title salt, $C_{12}H_{14}N_2{}^{2+}\cdot[CoCl_4]^{2-}$, (**I**).
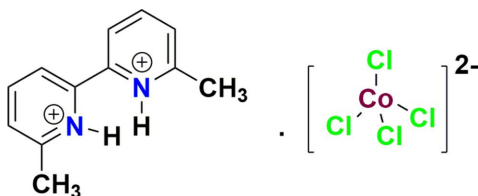
2. Structural commentary

The asymmetric unit of (**I**) contains one $C_{12}H_{14}N_2{}^{2+}$ (DMB²⁺) cation and one $[CoCl_4]^{2-}$ anion in the triclinic space group $P\bar{1}$ (Fig. 1). The pyridine ring nitrogen atoms are protonated, which is confirmed by the widening of the C2—N1—C6
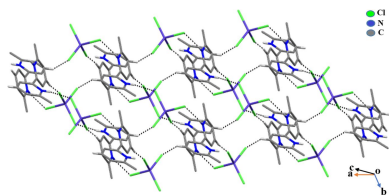
Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$\cdots$Cl1	0.93 (2)	2.32 (2)	3.2205 (16)	164.5 (18)
N2—H2$\cdots$Cl4^{i}	0.87 (2)	2.38 (2)	3.2436 (16)	171 (2)
C4—H4$\cdots$Cl3^{ii}	0.93	2.68	3.571 (2)	161
C9—H9$\cdots$Cl2^{iii}	0.93	2.79	3.565 (2)	141

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

[123.47 (14)°] and C8—C7—N2 [119.92 (14)°] bond angles compared to a value of 118.4° in the neutral compound (Sengül *et al.*, 1998). The dihedral angle between the pyridine rings in (**I**) is 52.46 (9)°, showing that they are substantially twisted with respect to each other. The values for the torsion angles C5—C6—C7—C8 [–127.95 (17)°] and N1—C6—C7—N2 [–128.78 (14)°] indicate that the nitrogen atoms of the pyridine rings exhibit a (–)*anti*-clinal conformation. The Co—Cl bond lengths in the $[CoCl_4]^{2-}$ anion range from 2.2600 (6)–2.2997 (7) Å, where Cl1 and Cl4 have a longer distance than Cl2 and Cl3. The average Co—Cl bond length of 2.280 Å is consistent with that of similar complexes (Zhang *et al.*, 2005; Jebas & Balasubramanian, 2006). The Cl—Co—Cl bond angles are in the range 105.46 (3)–117.91 (2)° with an average bond angle of 111.13 (2)° (Azadbakht *et al.*, 2012; Mghandef & Boughzala, 2015). The smallest bond angle (Cl2—Co1—Cl3) correlates with the shortest Co—Cl bond lengths but there is no obvious correlation between bond lengths and the largest angle.
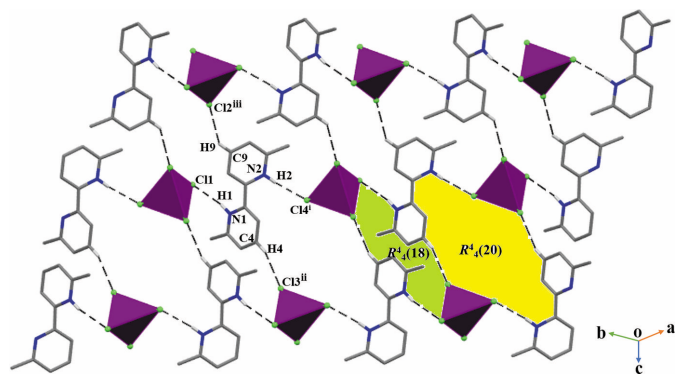
3. Supramolecular features

In the extended structure of (**I**), the components are linked by N1—H1$\cdots$Cl1 and N2—H2$\cdots$Cl4 hydrogen bonds (Table 1), which generate infinite [1$\bar{1}$0] chains. Weak C4—H4$\cdots$Cl3 and C9—H9$\cdots$Cl2 hydrogen bonds also occur, so that each
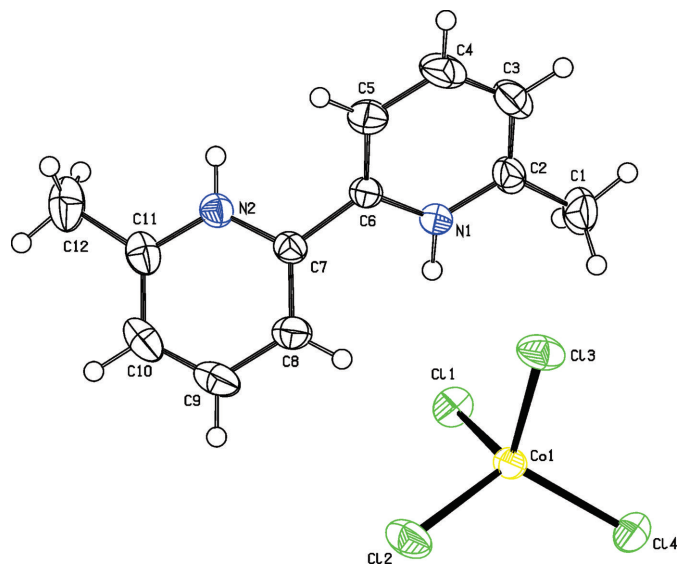
Figure 1
The molecular structure of (**I**), with displacement ellipsoids drawn at the 50% probability level.
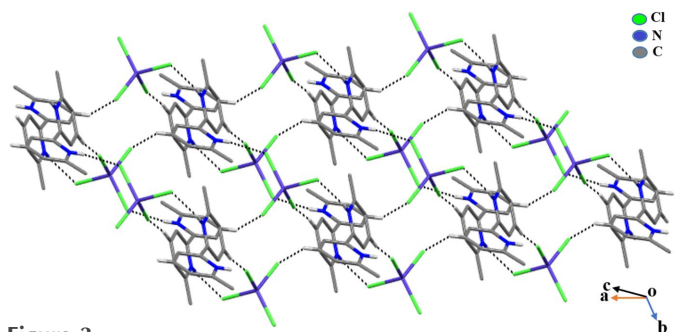

Figure 2
A view of the supramolecular architecture of (**I**), showing the $R_4^4(18)$ and $R_4^4(20)$ loops. [Symmetry code: (iv) $1 + x, y, z$.]

chlorine atom accepts one hydrogen bond. Together, the hydrogen bonds generate infinite sheets in which $R_4^4(18)$ and $R_4^4(20)$ loops are apparent (Fig. 2). A wavy sheet-like structure of the compound can be seen when the structure is viewed along the *ab*-axis direction (Fig. 3). The crystal structure also features weak anion$\cdots\pi$ interactions [Co1—Cl2$\cdots$Cg2^{iv} = 3.5465 (12) Å; Co1—Cl3$\cdots$Cg1^{iv} = 3.4891 (12) Å, where Cg1 is the centroid of the N1/C2–C6 ring and Cg2 is the centroid of the N2/C7–C11 ring; symmetry code: (iv) $1 + x, y, z$] (Degtyarenko & Domasevitch, 2014).

The Hirshfeld surface analysis and its related fingerprint plots were created with *Crystal Explorer 17.5* (Turner *et al.*, 2017). The Hirshfeld surface of the title salt (Fig. 4) mapped over d_{norm} within the range −0.43 to 1.17 a.u. shows bright red spots within the locales of $D\cdots A$ (D = donor, A = acceptor) interactions, as expected. The two-dimensional fingerprint plots (Fig. 5) show that the most significant contacts are Cl$\cdots$H/H$\cdots$Cl (45.5%), H$\cdots$H (29.0%), C$\cdots$H/H$\cdots$C (11.2%), Cl$\cdots$C/C$\cdots$Cl (7.8%), Cl$\cdots$N/N$\cdots$Cl (3.5%), Cl$\cdots$Cl (1.4%), Co$\cdots$H (1.0%) and C$\cdots$C (0.5%).
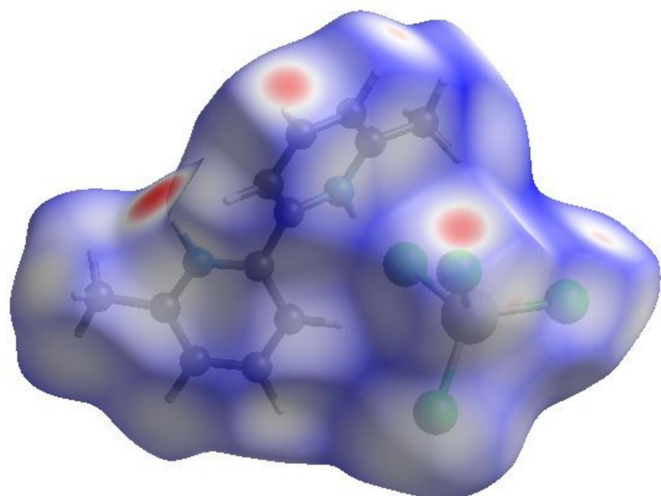
4. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.44. last update Jun 2023; Groom *et al.*, 2016) for the 6,6′-dimethyl-2,2′-bipyridinium ion yielded six entries, *viz.*

Figure 3
The wavy sheet-like two-dimensional supramolecular architecture of (**I**) viewed along the *ab* direction. The black dotted lines represent hydrogen bonds.

Figure 4
A view of the three-dimensional Hirshfeld surface of (I) mapped over d_{norm}.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_{12}H_{14}N_2)[CoCl_4]$
M_r	386.98
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	301
a, b, c (Å)	6.6419 (16), 7.6512 (19), 15.837 (4)
α, β, γ (°)	99.458 (6), 98.020 (6), 97.046 (6)
V (Å^3)	777.3 (3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.78
Crystal size (mm)	$0.21 \times 0.11 \times 0.04$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.625, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13285, 3890, 3661
R_{int}	0.041
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.673
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.081, 1.03
No. of reflections	3890
No. of parameters	180
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.41, −0.36

Computer programs: *APEX4* and *SAINT* (Bruker, 2021), *SHELXT2019/1* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

CSD refcodes IQUREU (Yoshikawa, 2021), IQUREU01 (Yoshikawa *et al.*, 2022), KARRAA (Jurowska *et al.*, 2021), QUJVUO (Thangavelu *et al.*, 2015), UWUKAZ02 (Kobayashi *et al.*, 2014) and YABGIS (Chan & Baird, 2004). The mean dihedral angle between the pyridine rings of the DMB^{2+} cations in these structures is 38.75 (10)°

5. Synthesis and crystallization

The compound of interest was synthesized by a literature method (Jagadeesan *et al.*, 2013) by dissolving 2.00 mmol (0.3682 g) of the ligand in methanol and adding directly 1.00 mmol (0.1289 g) of anhydrous cobaltous chloride. The whole mixture was refluxed for about an hour. A dark-brown solution was obtained. Afterwards, a sufficient amount of chlorine gas was passed through the solution until precipitation occurred. The precipitate was dissolved in aqueous HCl (0.001 M) by warming to 333 K for 30 min and the resulting mixture was kept undisturbed overnight. The resulting precipitate was discarded and the filtrate was kept for a few weeks until dark-blue crystals of (**I**) appeared (0.067 g).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were positioned geometrically (C—H = 0.93–0.96 Å) and were refined using a riding model with $U_{iso}(H) = 1.2U_{eq}(C)$.
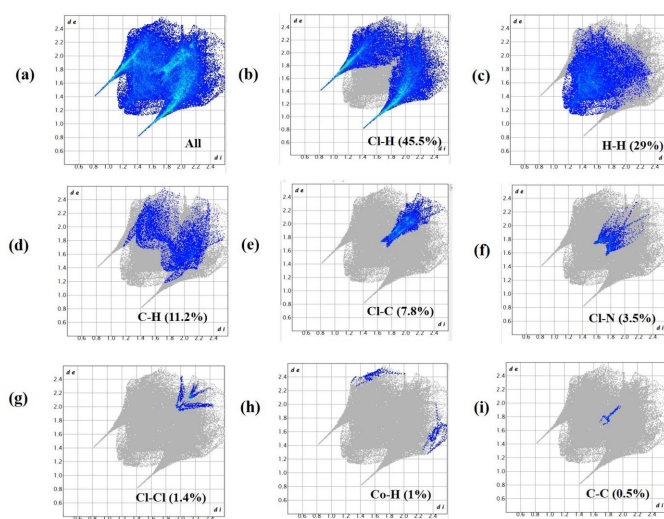
Figure 5
The two-dimensional fingerprint plot for (**I**) showing all intermolecular interactions and delineated into Cl···H/H···Cl, H···H, C···H/H···C, Cl···C/C···Cl, Cl···N/N···Cl, Cl···Cl, Co···H and C··· contacts.

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Computing details

6,6′-Dimethyl-2,2′-bipyridine-1,1′-diium tetrachloridocobaltate(II)

Crystal data

$(C_{12}H_{14}N_2)[CoCl_4]$	$Z = 2$
$M_r = 386.98$	$F(000) = 390$
Triclinic, $P\overline{1}$	$D_x = 1.653$ Mg m^{-3}
$a = 6.6419 (16)$ Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.6512 (19)$ Å	Cell parameters from 9272 reflections
$c = 15.837 (4)$ Å	$\theta = 2.7–28.6°$
$\alpha = 99.458 (6)°$	$\mu = 1.78$ mm^{-1}
$\beta = 98.020 (6)°$	$T = 301$ K
$\gamma = 97.046 (6)°$	Block, blue
$V = 777.3 (3)$ Å^3	$0.21 \times 0.11 \times 0.04$ mm

Data collection

Bruker APEXII CCD diffractometer	3890 independent reflections
φ and ω scans	3661 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$R_{int} = 0.041$
	$\theta_{max} = 28.6°$, $\theta_{min} = 2.7°$
$T_{min} = 0.625$, $T_{max} = 0.746$	$h = -8 \rightarrow 8$
13285 measured reflections	$k = -10 \rightarrow 10$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.029$	
$wR(F^2) = 0.081$	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.2392P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
3890 reflections	$(\Delta/\sigma)_{max} = 0.002$
180 parameters	$\Delta\rho_{max} = 0.41$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.36$ 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	0.83193 (3)	0.11776 (3)	0.75825 (2)	0.02835 (8)
Cl1	0.50544 (6)	0.08040 (5)	0.79190 (3)	0.03681 (10)
Cl2	1.04301 (7)	0.30332 (6)	0.87001 (3)	0.04763 (12)
Cl3	0.82188 (7)	0.26717 (7)	0.64540 (3)	0.04459 (11)
Cl4	0.91033 (8)	−0.16382 (6)	0.71718 (3)	0.04905 (12)
N1	0.34377 (19)	0.34550 (17)	0.66800 (8)	0.0288 (2)
H1	0.371 (3)	0.276 (3)	0.7098 (14)	0.043*
N2	0.2849 (2)	0.69414 (16)	0.82797 (8)	0.0295 (2)
H2	0.178 (3)	0.719 (3)	0.7963 (14)	0.044*
C1	0.2787 (3)	0.0670 (3)	0.56372 (13)	0.0511 (5)
H1A	0.235167	0.025817	0.502509	0.077*
H1B	0.181069	0.013236	0.594770	0.077*
H1C	0.411174	0.033861	0.580711	0.077*
C2	0.2923 (2)	0.2659 (2)	0.58417 (10)	0.0351 (3)
C3	0.2537 (3)	0.3744 (3)	0.52323 (11)	0.0432 (4)
H3	0.220294	0.323926	0.464580	0.052*
C4	0.2648 (3)	0.5561 (3)	0.54950 (11)	0.0465 (4)
H4	0.239832	0.628226	0.508449	0.056*
C5	0.3130 (3)	0.6328 (2)	0.63697 (11)	0.0386 (3)
H5	0.317851	0.755367	0.655242	0.046*
C6	0.3535 (2)	0.52315 (19)	0.69586 (9)	0.0276 (3)
C7	0.4097 (2)	0.58981 (18)	0.79017 (9)	0.0276 (3)
C8	0.5805 (3)	0.5515 (2)	0.83936 (11)	0.0360 (3)
H8	0.669290	0.481996	0.814006	0.043*
C9	0.6170 (3)	0.6193 (2)	0.92811 (11)	0.0440 (4)
H9	0.731908	0.595592	0.962668	0.053*
C10	0.4840 (3)	0.7213 (2)	0.96494 (10)	0.0441 (4)
H10	0.507794	0.764127	1.024450	0.053*
C11	0.3147 (3)	0.7606 (2)	0.91364 (10)	0.0368 (3)
C12	0.1623 (4)	0.8715 (3)	0.94657 (14)	0.0555 (5)
H12A	0.186823	0.894239	1.008855	0.083*
H12B	0.025769	0.808301	0.925793	0.083*
H12C	0.176477	0.983126	0.926248	0.083*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02780 (12)	0.03196 (12)	0.02530 (12)	0.00566 (8)	0.00268 (8)	0.00579 (8)
Cl1	0.03370 (19)	0.03675 (19)	0.0430 (2)	0.00376 (14)	0.01266 (15)	0.01194 (15)

Cl2	0.0492 (2)	0.0456 (2)	0.0389 (2)	−0.00486 (18)	−0.01213 (18)	0.00607 (17)
Cl3	0.0398 (2)	0.0659 (3)	0.0347 (2)	0.00992 (19)	0.00815 (16)	0.02524 (19)
Cl4	0.0507 (3)	0.0430 (2)	0.0507 (3)	0.02070 (19)	0.00004 (19)	−0.00242 (18)
N1	0.0270 (6)	0.0315 (6)	0.0266 (6)	0.0068 (5)	0.0002 (4)	0.0032 (5)
N2	0.0350 (6)	0.0275 (6)	0.0265 (6)	0.0043 (5)	0.0051 (5)	0.0068 (4)
C1	0.0499 (10)	0.0451 (10)	0.0481 (10)	0.0075 (8)	0.0000 (8)	−0.0142 (8)
C2	0.0264 (7)	0.0447 (8)	0.0298 (7)	0.0061 (6)	0.0014 (5)	−0.0034 (6)
C3	0.0377 (8)	0.0659 (11)	0.0241 (7)	0.0080 (8)	0.0028 (6)	0.0040 (7)
C4	0.0482 (10)	0.0668 (12)	0.0301 (8)	0.0134 (9)	0.0054 (7)	0.0224 (8)
C5	0.0462 (9)	0.0390 (8)	0.0343 (8)	0.0109 (7)	0.0058 (7)	0.0149 (6)
C6	0.0266 (6)	0.0315 (7)	0.0253 (6)	0.0063 (5)	0.0031 (5)	0.0062 (5)
C7	0.0312 (7)	0.0250 (6)	0.0257 (6)	0.0018 (5)	0.0020 (5)	0.0061 (5)
C8	0.0353 (8)	0.0330 (7)	0.0371 (8)	0.0045 (6)	−0.0039 (6)	0.0078 (6)
C9	0.0470 (9)	0.0429 (9)	0.0355 (8)	−0.0034 (7)	−0.0117 (7)	0.0117 (7)
C10	0.0619 (11)	0.0393 (8)	0.0247 (7)	−0.0076 (8)	0.0003 (7)	0.0045 (6)
C11	0.0511 (9)	0.0294 (7)	0.0298 (7)	−0.0015 (6)	0.0123 (7)	0.0058 (6)
C12	0.0712 (14)	0.0506 (11)	0.0466 (10)	0.0094 (10)	0.0273 (10)	−0.0002 (8)

Geometric parameters (Å, º)

Co1—Cl2	2.2600 (6)	C4—C5	1.389 (2)
Co1—Cl3	2.2720 (6)	C4—H4	0.9300
Co1—Cl4	2.2901 (7)	C5—C6	1.374 (2)
Co1—Cl1	2.2997 (7)	C5—H5	0.9300
N1—C2	1.3441 (19)	C6—C7	1.4758 (19)
N1—C6	1.3490 (19)	C7—C8	1.375 (2)
N1—H1	0.93 (2)	C8—C9	1.392 (2)
N2—C11	1.346 (2)	C8—H8	0.9300
N2—C7	1.3511 (19)	C9—C10	1.376 (3)
N2—H2	0.87 (2)	C9—H9	0.9300
C1—C2	1.492 (3)	C10—C11	1.387 (3)
C1—H1A	0.9600	C10—H10	0.9300
C1—H1B	0.9600	C11—C12	1.492 (3)
C1—H1C	0.9600	C12—H12A	0.9600
C2—C3	1.390 (3)	C12—H12B	0.9600
C3—C4	1.374 (3)	C12—H12C	0.9600
C3—H3	0.9300		
Cl2—Co1—Cl3	105.46 (3)	C6—C5—C4	118.36 (16)
Cl2—Co1—Cl4	117.91 (2)	C6—C5—H5	120.8
Cl3—Co1—Cl4	110.39 (2)	C4—C5—H5	120.8
Cl2—Co1—Cl1	108.93 (2)	N1—C6—C5	119.83 (14)
Cl3—Co1—Cl1	107.287 (19)	N1—C6—C7	116.98 (12)
Cl4—Co1—Cl1	106.46 (2)	C5—C6—C7	123.19 (14)
C2—N1—C6	123.47 (14)	N2—C7—C8	119.92 (14)
C2—N1—H1	119.4 (14)	N2—C7—C6	116.93 (13)
C6—N1—H1	117.1 (14)	C8—C7—C6	123.15 (14)
C11—N2—C7	123.32 (14)	C7—C8—C9	118.30 (16)

C11—N2—H2	117.4 (14)	C7—C8—H8	120.9
C7—N2—H2	119.2 (14)	C9—C8—H8	120.9
C2—C1—H1A	109.5	C10—C9—C8	120.32 (16)
C2—C1—H1B	109.5	C10—C9—H9	119.8
H1A—C1—H1B	109.5	C8—C9—H9	119.8
C2—C1—H1C	109.5	C9—C10—C11	120.25 (15)
H1A—C1—H1C	109.5	C9—C10—H10	119.9
H1B—C1—H1C	109.5	C11—C10—H10	119.9
N1—C2—C3	117.74 (15)	N2—C11—C10	117.86 (16)
N1—C2—C1	117.33 (16)	N2—C11—C12	117.45 (17)
C3—C2—C1	124.93 (16)	C10—C11—C12	124.69 (17)
C4—C3—C2	120.12 (15)	C11—C12—H12A	109.5
C4—C3—H3	119.9	C11—C12—H12B	109.5
C2—C3—H3	119.9	H12A—C12—H12B	109.5
C3—C4—C5	120.43 (16)	C11—C12—H12C	109.5
C3—C4—H4	119.8	H12A—C12—H12C	109.5
C5—C4—H4	119.8	H12B—C12—H12C	109.5
C6—N1—C2—C3	2.1 (2)	N1—C6—C7—N2	−128.78 (14)
C6—N1—C2—C1	−177.24 (15)	C5—C6—C7—N2	51.6 (2)
N1—C2—C3—C4	−1.2 (3)	N1—C6—C7—C8	51.7 (2)
C1—C2—C3—C4	178.05 (18)	C5—C6—C7—C8	−127.95 (17)
C2—C3—C4—C5	−0.5 (3)	N2—C7—C8—C9	1.4 (2)
C3—C4—C5—C6	1.4 (3)	C6—C7—C8—C9	−179.06 (15)
C2—N1—C6—C5	−1.2 (2)	C7—C8—C9—C10	0.3 (3)
C2—N1—C6—C7	179.19 (14)	C8—C9—C10—C11	−1.4 (3)
C4—C5—C6—N1	−0.6 (2)	C7—N2—C11—C10	1.0 (2)
C4—C5—C6—C7	178.99 (15)	C7—N2—C11—C12	−179.01 (15)
C11—N2—C7—C8	−2.1 (2)	C9—C10—C11—N2	0.8 (2)
C11—N2—C7—C6	178.36 (14)	C9—C10—C11—C12	−179.26 (18)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1	0.93 (2)	2.32 (2)	3.2205 (16)	164.5 (18)
N2—H2···Cl4[i]	0.87 (2)	2.38 (2)	3.2436 (16)	171 (2)
C4—H4···Cl3[ii]	0.93	2.68	3.571 (2)	161
C9—H9···Cl2[iii]	0.93	2.79	3.565 (2)	141

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