



Crystal structures of 1'-aminocobaltocenium-1-carboxylic acid chloride monohydrate and of its azo dye 1'-[2-(1-amino-2,6-dimethylphenyl)diazen-1-yl]cobaltocenium-1-carboxylic acid hexafluoridophosphate monohydrate

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1'-Aminocobaltocenium-1-carboxylic acid chloride, $[\text{Co}(\text{C}_5\text{H}_6\text{N})(\text{C}_6\text{H}_5\text{O}_2)]\text{Cl}\cdot\text{H}_2\text{O}$ (**3**), and its azo derivative 1'-[2-(1-amino-2,6-dimethylphenyl)diazen-1-yl]cobaltocenium-1-carboxylic acid hexafluoridophosphate, $[\text{Co}(\text{C}_{13}\text{H}_{14}\text{N}_3)(\text{C}_6\text{H}_5\text{O}_2)]\text{PF}_6\cdot\text{H}_2\text{O}$ (**5**) were obtained from cobaltocenium-1,1'-dicarboxylic acid hexafluoridophosphate by converting one carboxyl group to its chloro-carboxyl derivative followed by chloride/azide exchange, Curtius rearrangement, diazotiation and azo coupling with 2,6-dimethylaniline. Both title compounds crystallize as their monohydrates. In the crystal structure of **3**, both functional groups lie in the same direction, with the Cp rings being nearly eclipsed, and participate in an extended hydrogen-bonded supramolecular network including the counter-ion and the water molecule of crystallization. Although the functional groups in **5** are somewhat further apart, bearing a greater torsion angle with the Cp rings now staggered, a similar supramolecular network is observed with not only the carboxylic acid and azo groups, but also with the more remote amino group participating in a hydrogen-bonded network, again including the counter-ion and the water molecule. The hexafluoridophosphate ion shows positional disorder. Compound **3** was refined as an inversion twin. In **5**, each of the six F atoms is disordered over two sets of sites in a 1:1 ratio.

1. Chemical context

One of the title compounds, 1'-aminocobaltocenium-1-carboxylic acid chloride, **3**, is a new artificial organometallic amino acid. In comparison to its known iron analogue, 1'-aminoferrocene-1-carboxylic acid (Butler & Quayle, 1998; Barišić *et*

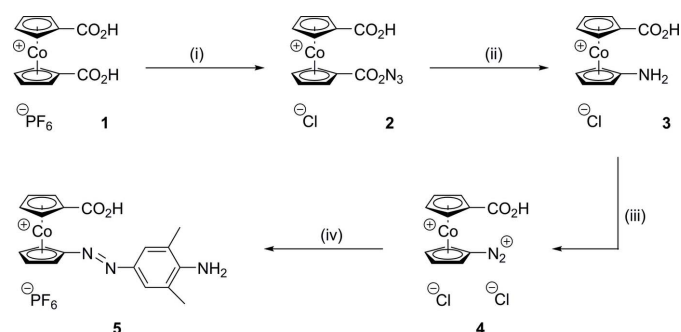
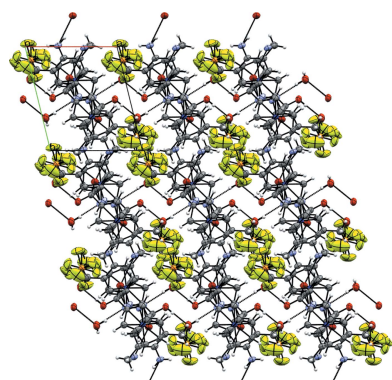
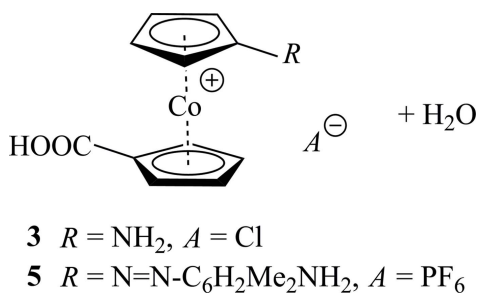


Figure 1
Synthetic scheme for obtaining the title compounds. (i) $\text{SOCl}_2/\text{NaN}_3$, (ii) H_2SO_4 , (iii) HCl/NaNO_2 , (iv) 2,6-dimethylaniline.

al., 2002; Erb *et al.*, 2018) and its frequently studied bioorganometallic chemistry (Heinze & Schlenker, 2004; Heinze & Beckmann, 2005, 2007; Barišić *et al.* 2004, 2006*a,b*, 2011, 2012; Mahmoud & Kraatz, 2007; Kovač *et al.*, 2009; Semencić *et al.*, 2009; Semencić *et al.*, 2010; Siebler *et al.*, 2010; Förster *et al.*, 2012; Kovačević *et al.*, 2014), 1'-aminocobaltocenium-1-carboxylic acid chloride is an intrinsically cationic amino acid of similar potential in bioorganometallic peptide chemistry. Synthetically (Fig. 1), compound **3** was obtained from cobaltocenium-1,1'-dicarboxylic acid hexafluoridophosphate, **1** (Sheats & Rausch, 1970) in varying yields *via* Curtius rearrangement of its cobaltocenium-1'-carboxylic acid azide-1-carboxylic acid chloride, **2**, in analogy to our recent work on aminocobaltocenium hexafluoridophosphate (Vanicek *et al.*, 2016). The amino group of **3** was diazotized *in situ* with nitrous acid to yield 1'-diazonio-cobaltocenium-1-carboxylic acid dichloride, **4**, and reacted with 2,6-dimethylaniline to afford the new diazo dye 1'-[(diazene-1-yl)-2-(2,6-dimethyl-1-aminophen-4-yl)]-cobaltocenium-1-carboxylic acid hexafluoridophosphate, **5**.



The molecular and crystal structures of compounds **3** and **5** are reported in this communication.

2. Structural commentary

Compounds **3** and **5** both crystallize as their monohydrates. Compound **3** forms crystals with one formula unit per asymmetric unit (Fig. 2). The cobalt atom is coordinated in a nearly eclipsed manner by the planar cyclopentadienide rings with a torsion angle of 15° between the substituents, but the bond lengths between Co and C are not equal. In the carboxyl-substituted ring, the shortest distance [2.028 (3) Å] is found between Co1 and C10, the atom bearing the carboxyl group, as is to be expected from the electron-poorest carbon atom. Bond lengths involving the other four carbon atoms in this ring are considerably longer [Co—C_{averaged} = 2.052 Å]. On the other hand, in the amino-substituted ring, the N-bonded carbon atom C1 shows a significantly longer bond length [2.153 (3) Å] to Co1 than the other four carbon atoms in this ring [Co—C_{averaged} = 2.031]. In addition, the formal C—N single bond [C1—N1 = 1.343 (4) Å] of the amino substituent is considerably shortened, as has also been observed in aminocobaltocenium tetraphenylborate [C—N = 1.340 (3) Å; Vanicek *et al.*, 2016] and aminopentamethylcobaltocenium hexafluoridophosphate [C—N = 1.351 (5) Å; Wolter-Stein-

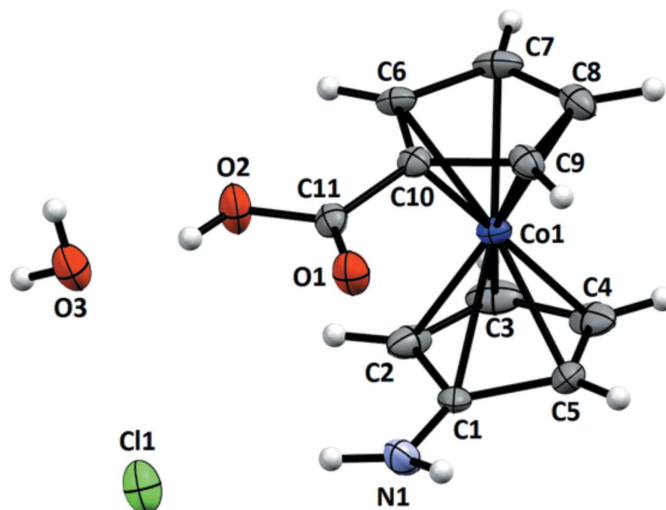


Figure 2
The molecular entities in the structure of **3** with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

grube *et al.*, 2014]. This is caused by the contribution of a mesomeric structure featuring an η^4 -bound cyclopentadiene with an iminium group, a general effect observed in donor-substituted cobaltocenium salts (Sheats, 1979). The bond lengths and angles of the carboxyl substituent are unexceptional and in line with expectations.

In the cobaltocenium cation of **5**, the cyclopentadienide rings are almost staggered with the substituents oriented in roughly the same direction and a torsion angle of 29 (**s.u.?**) $^\circ$ (Fig. 3). The Co—C_{ring} distances show no great variation, with the exception being the bond to C6, *i.e.* the carbon atom connected to the azo group [2.064 (2) Å]. This bond is slightly elongated but not as much as the corresponding bond to the amino group in the structure of **3**. The azo group features a *trans*-configuration with distances typical for asymmetric azo compounds.

3. Supramolecular features

The water molecule of crystallization, carboxyl group, amino group and chloride anion of **3** are part of an extended hydrogen-bonding network in the crystal (Fig. 4, Table 1).

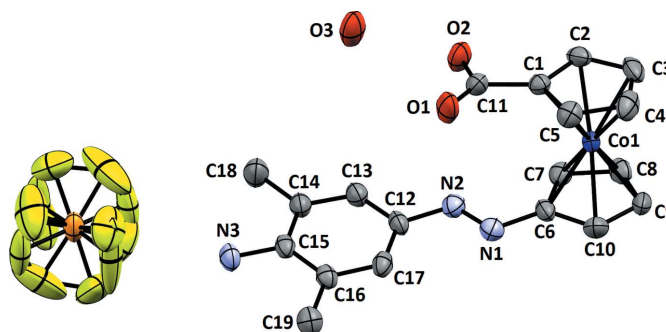


Figure 3
The molecular entities in the structure of **5** with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

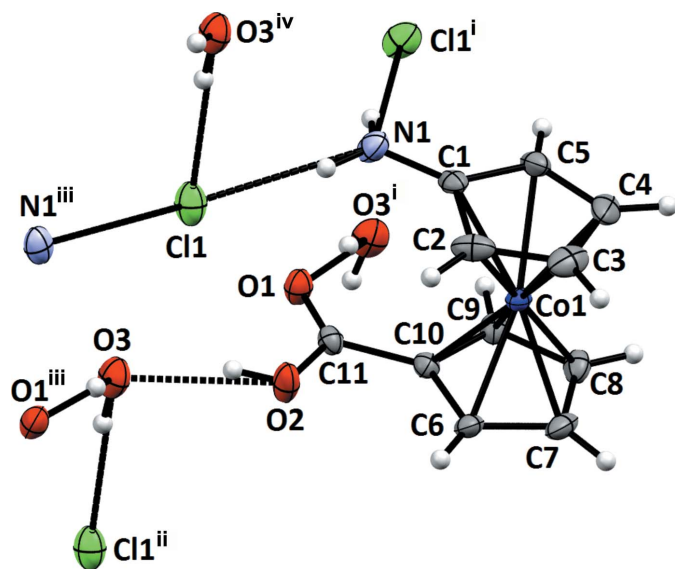


Figure 4
Hydrogen-bonding interactions between the amino group, the carboxyl group, the water molecule of crystallization and the counter-anion in the crystal structure of **3**. Displacement ellipsoids as in Fig. 2. [Symmetry codes: (i) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $-x + \frac{1}{2}, y, z - \frac{1}{2}$]

Zigzag chains are aligned parallel to the *c* axis (Fig. 5), in which every other molecule shows the same orientation. These chains are formed by an infinite hydrogen-bonding network, comprised of water molecules connecting the carboxyl groups of two neighboring cations and also forming a bond to the chloride anion. The chloride anions are also hydrogen-bonded to the NH₂ groups of two more cations, therefore forming a ladder-type network in which the ladders are connected to each other by the cobaltocenium moieties (Fig. 6). Overall, this arrangement results in an undulating layer structure extending parallel to (100) (Fig. 7).

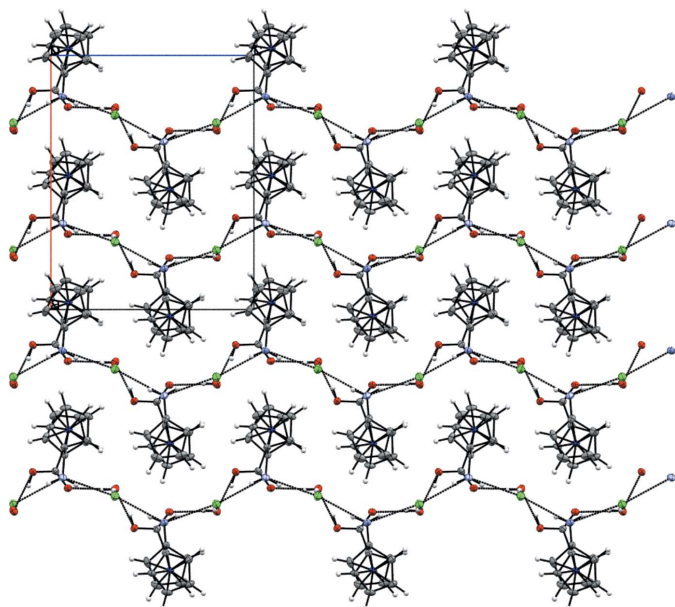


Figure 5
A view along the *b* axis of the crystal structure of **3** showing the formation of zigzag chains parallel to the *c* axis. Displacement ellipsoids as in Fig. 2.

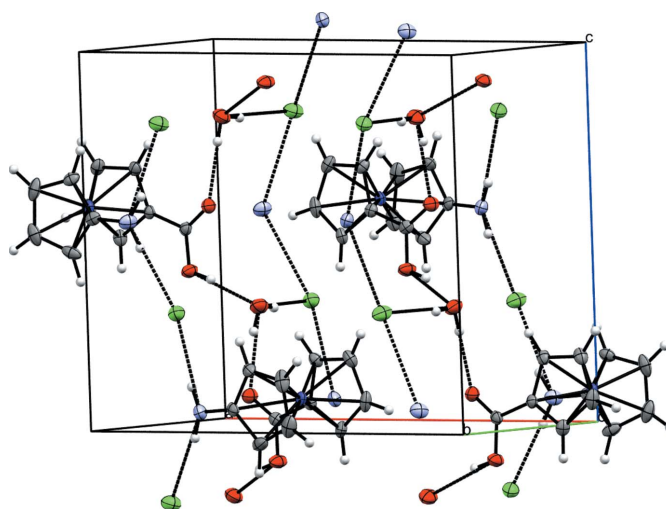


Figure 6
Ladder-type hydrogen-bonded network in the crystal structure of **3**. Displacement ellipsoids as in Fig. 2.

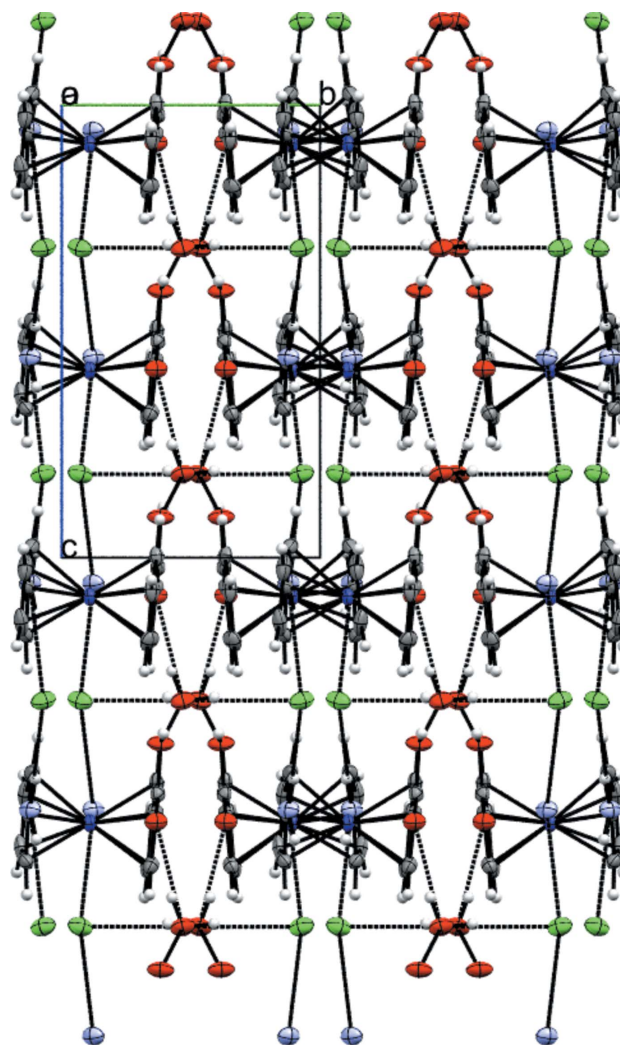


Figure 7
Formation of undulating layers parallel to (100) in the crystal structure of **3**. Displacement ellipsoids as in Fig. 2.

Table 1
Hydrogen-bond geometry (Å, °) for **3**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2O \cdots O3	0.82 (2)	1.78 (3)	2.577 (3)	163 (4)
N1—H1N \cdots Cl1 ⁱ	0.89 (2)	2.36 (3)	3.239 (3)	166 (4)
N1—H2N \cdots Cl1	0.89 (2)	2.37 (3)	3.253 (3)	172 (3)
O3—H3A \cdots Cl1 ⁱⁱ	0.82 (2)	2.30 (2)	3.106 (3)	172 (4)
O3—H3B \cdots O1 ⁱⁱⁱ	0.81 (2)	2.02 (3)	2.822 (4)	171 (3)

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

Table 2
Hydrogen-bond geometry (Å, °) for **5**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H2N \cdots O1 ⁱ	0.88 (2)	2.18 (2)	3.015 (3)	159 (3)
N3—H1N \cdots F5	0.88 (2)	2.29 (3)	2.994 (10)	137 (3)
N3—H1N \cdots F5A	0.88 (2)	2.24 (3)	2.896 (8)	131 (3)
O2—H2O \cdots O3	0.84 (2)	1.80 (2)	2.625 (3)	170 (4)
O3—H3A \cdots N1 ⁱⁱ	0.86 (2)	2.06 (2)	2.907 (3)	171 (4)
O3—H3B \cdots F5 ⁱⁱⁱ	0.84 (2)	2.22 (3)	2.988 (8)	153 (4)
O3—H3B \cdots F2A ⁱⁱⁱ	0.84 (2)	2.34 (3)	3.112 (8)	154 (4)

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

In the crystal structure of **5**, the azo, carboxyl, amino groups and the water molecule of crystallization are part of a hydrogen-bonded network (Table 2). Dimers result from hydrogen bonds between the amino function (N3—H) of one molecule and the carboxylic acid group (O1) of a neighbouring molecule. Additionally, these dimers are connected to one another by water molecules (O3), forming hydrogen bonds involving the carboxylic acid group (O1) and the azo group (N1). In addition, the disordered hexafluoridophosphate ions interact with the otherwise unbound second hydrogen atom of the water molecule and the second hydrogen atom of the amino functionality (Fig. 8), thereby forming layers parallel the bc plane that separate layers of cations (Fig. 9).

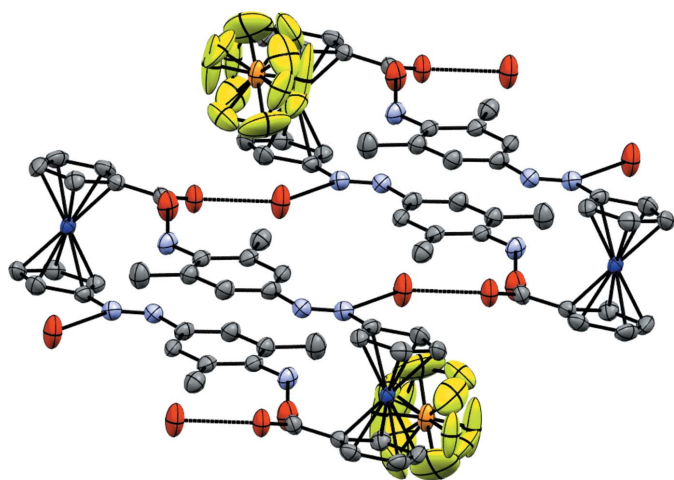


Figure 8
Formation of hydrogen-bonded dimers in the crystal structure of **5**. Displacement ellipsoids as in Fig. 3; hydrogen atoms were omitted for clarity.

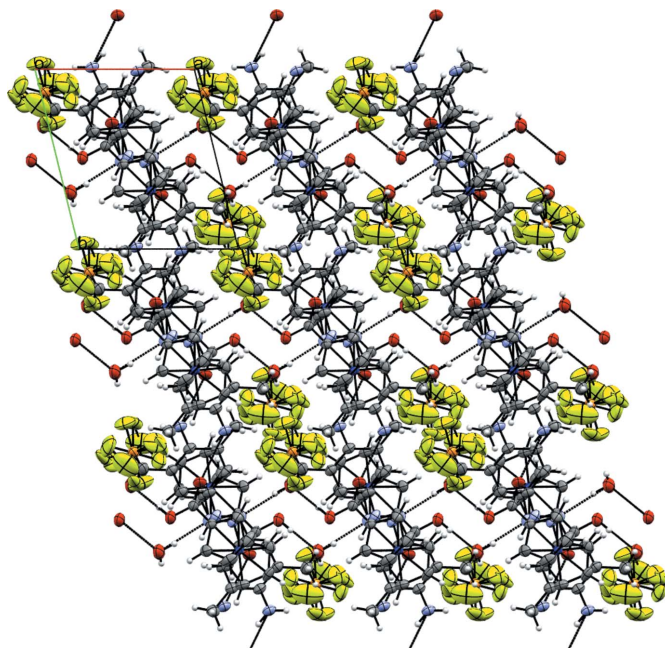


Figure 9
Molecular packing of the crystal structure of **5** in a view along the c axis, showing the alternating anionic and cationic layers parallel to the bc plane. Displacement ellipsoids as in Fig. 3.

4. Synthesis and crystallization

Compound 3: 1'-Aminocobaltocenium-1-carboxylic acid chloride hydrate, **3**, was obtained in varying yields starting from cobaltocenium-1,1'-bis carboxylic acid hexafluoridophosphate by converting it first to its mono carboxylic azide followed by Curtius rearrangement, in a variant analogous to monosubstituted cobaltocenium carboxylic acid hexafluoridophosphate (Vanicek *et al.*, 2016). Column chromatography on alumina using methanol/water as eluent, separated it from 1,1'-diaminocobaltocenium, which was eluted before with acetonitrile. After addition of hydrochloric acid to hydrolyze the methoxyaluminum species, the volatiles were evaporated, the residue extracted with ethanol, filtered and dried first on a rotary evaporator and then *in vacuo*. Single crystals were obtained *via* slow concentration of a solution in methanol. ^1H NMR (CD_3OD), ppm: δ = 5.16 (pseudo- t , J = 2.1 Hz), 5.48 (pseudo- t , J = 2.1 Hz), 5.51 (pseudo- t , J = 2.1 Hz), 5.97 (pseudo- t , J = 2.1 Hz). ESI-MS showed a signal at 248.0139 m/z in accordance to the molecular cation.

Compound 5: 1'-Aminocobaltocenium-1-carboxylic acid chloride hydrate (**3**) (100.9 mg, 0.3345 mmol, 1 equivalent) was dissolved in 5 ml of concentrated HCl and the mixture was cooled to 273 K. Then NaNO_2 (26.6 mg, 0.3850 mmol, 1.15 equivalent) was added and the yellow solution was stirred for 15 min. After addition of 2,6-dimethylaniline (63.5 μl , 0.5134 mmol, 1.5 equivalents), the solution immediately turned red and was stirred for a further 30 min. When neutralized with saturated Na_2CO_3 solution, the reaction mixture again changed color to a darker red. The mixture was concentrated on a rotary evaporator and the salts were precipitated with ethanol. The solution was filtered, evapo-

Table 3
Experimental details.

	3	5
Crystal data		
Chemical formula	[Co(C ₆ H ₅ N)(C ₆ H ₅ O ₂)]Cl·H ₂ O	[Co(C ₆ H ₅ O ₂)]PF ₆ ·H ₂ O
<i>M_r</i>	301.60	543.29
Crystal system, space group	Orthorhombic, <i>Pca</i> 2 ₁	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	193	191
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.7269 (5), 6.7024 (3), 11.7607 (4)	7.9891 (4), 9.4310 (5), 15.5425 (8)
α , β , γ (°)	90, 90, 90	74.415 (3), 78.183 (2), 73.798 (2)
<i>V</i> (Å ³)	1160.85 (8)	1072.48 (10)
<i>Z</i>	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	1.70	0.95
Crystal size (mm)	0.13 × 0.11 × 0.03	0.16 × 0.16 × 0.03
Data collection		
Diffractometer	Bruker D8 QUEST PHOTON 100	Bruker D8 QUEST PHOTON 100
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.858, 0.942	0.826, 0.901
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	14289, 2163, 2099	20686, 3945, 3290
<i>R</i> _{int}	0.031	0.043
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.020, 0.046, 1.08	0.035, 0.086, 1.04
No. of reflections	2163	3945
No. of parameters	175	372
No. of restraints	6	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.50, -0.31	0.54, -0.31
Absolute structure	Refined as an inversion twin	–
Absolute structure parameter	0.067 (17)	–

Computer programs: *APEX3* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *CHEM3D* (Cambridge Soft, 2001), *ORTEP-3 for Windows* (Farrugia, 2012) and *publCIF* (Westrip, 2010).

rated to dryness, the residue taken up in acetonitrile and after filtering and evaporating to dryness the product was dissolved in small amounts of water, and a few drops of aqueous HPF₆ (60%) were added. The solution was extracted three times with dichloromethane, the combined dark-violet-colored organic phases were evaporated to dryness and the product (**5**) was dried *in vacuo*. Yield: 92.1 mg (52.2%) as a dark orange–red powder. Slow concentration of a solution in ethanol yielded single crystals suitable for X-ray analysis. ¹H NMR (CD₃OD), ppm: δ = 2.3 (2,6-Me, *t*, *J* = 0.6 Hz), 5.80 (pseudo-*t*, *J* = 2.1 Hz), 5.89 (pseudo-*t*, *J* = 2.1 Hz), 6.15 (pseudo-*t*, *J* = 2.1 Hz), 6.29 (pseudo-*t*, *J* = 2.1 Hz), 7.52 (3,5-CH, *t*, *J* = 0.6 Hz). ESI-MS showed a signal at 380.0836 *m/z* in accordance with the molecular cation.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. In both compounds, C-bound H atoms were positioned geometrically (C–H = 0.95–0.98) and refined as riding with *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(Cmethyl). For the refinement of **3**, H atoms bound to N1, O2 and O3 were found in difference-Fourier maps and were treated with restraints on bond lengths (*d* = 0.89 Å for N and *d* = 0.83 Å for O) and refined with isotropic displacement parameters. The crystal studied was refined as an inversion twin. For **5**, H atoms

bound to N3 and O2 were treated in the same way as for **3** while the H atoms of the water molecule (also found from a difference-Fourier map and treated with restraints on the bond length) were refined with *U*_{iso}(H) = 1.2*U*_{eq}(O3). The hexafluoridophosphate ion shows positional disorder. Each of the six F atoms was refined with two sets of sites in a 1:1 ratio.

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supporting information

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Crystal structures of 1'-aminocobaltocenium-1-carboxylic acid chloride monohydrate and of its azo dye 1'-[2-(1-amino-2,6-dimethylphenyl)diazen-1-yl]cobaltocenium-1-carboxylic acid hexafluoridophosphate monohydrate

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Computing details

For both structures, data collection: *APEX3* (Bruker, 2013); cell refinement: *S SAINT* (Bruker, 2013); data reduction: *S SAINT* (Bruker, 2013); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *CHEM DRAW* (Cambridge Soft, 2001) and *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

1'-Aminocobaltocenium-1-carboxylic acid chloride monohydrate (3)

Crystal data

[Co(C₅H₆N)(C₆H₅O₂)]Cl·H₂O

M_r = 301.60

Orthorhombic, *Pca*2₁

a = 14.7269 (5) Å

b = 6.7024 (3) Å

c = 11.7607 (4) Å

V = 1160.85 (8) Å³

Z = 4

F(000) = 616

D_x = 1.726 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 9295 reflections

θ = 2.7–50.7°

μ = 1.70 mm⁻¹

T = 193 K

Plate, orange

0.13 × 0.11 × 0.03 mm

Data collection

Bruker D8 QUEST PHOTON 100
diffractometer

Radiation source: Incoatec Microfocus
Multi layered optics monochromator

Detector resolution: 10.4 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Krause *et al.*, 2015)

T_{min} = 0.858, *T_{max}* = 0.942

14289 measured reflections

2163 independent reflections

2099 reflections with *I* > 2σ(*I*)

R_{int} = 0.031

θ_{max} = 25.7°, θ_{min} = 2.8°

h = -17→17

k = -8→8

l = -14→13

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.020

wR(*F*²) = 0.046

S = 1.08

2163 reflections

175 parameters

6 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0262*P*)² + 0.115*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

$$\Delta\rho_{\max} = 0.50 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$$

Absolute structure: Refined as an inversion twin
 Absolute structure parameter: 0.067 (17)

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.

Refinement. Refined as a two-component inversion twin. Hydrogens at N1, O2 and O3 were found and refined isotropically with bond restraints ($d = 89 \text{ pm}$ for N and $d = 83 \text{ pm}$ for O).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.52686 (2)	0.10826 (4)	0.58678 (3)	0.01564 (11)
C11	0.23429 (5)	-0.07147 (13)	0.31541 (7)	0.0317 (2)
O1	0.29710 (11)	0.3651 (3)	0.5834 (2)	0.0246 (4)
O2	0.36058 (15)	0.3830 (4)	0.41056 (19)	0.0286 (5)
H2O	0.3077 (19)	0.393 (6)	0.389 (4)	0.037 (12)*
N1	0.33888 (18)	-0.1222 (4)	0.5573 (2)	0.0256 (6)
H1N	0.310 (3)	-0.099 (5)	0.623 (2)	0.041 (12)*
H2N	0.315 (2)	-0.102 (5)	0.489 (2)	0.035 (10)*
C1	0.42978 (19)	-0.1291 (4)	0.5660 (2)	0.0180 (6)
C2	0.4952 (3)	-0.1153 (5)	0.4754 (3)	0.0262 (8)
H2	0.4817	-0.0925	0.3975	0.031*
C3	0.5837 (3)	-0.1416 (6)	0.5224 (4)	0.0307 (9)
H3	0.6390	-0.1480	0.4810	0.037*
C4	0.5743 (2)	-0.1564 (5)	0.6425 (3)	0.0301 (8)
H4	0.6225	-0.1746	0.6953	0.036*
C5	0.4807 (2)	-0.1393 (5)	0.6701 (3)	0.0212 (8)
H5	0.4560	-0.1352	0.7447	0.025*
C6	0.5386 (2)	0.3681 (4)	0.4969 (3)	0.0191 (6)
H6	0.5413	0.3791	0.4164	0.023*
C7	0.61365 (18)	0.3494 (4)	0.5717 (3)	0.0249 (7)
H7	0.6757	0.3472	0.5499	0.030*
C8	0.5806 (2)	0.3345 (5)	0.6843 (3)	0.0228 (6)
H8	0.6166	0.3198	0.7509	0.027*
C9	0.4845 (2)	0.3453 (5)	0.6807 (3)	0.0194 (6)
H9	0.4449	0.3391	0.7443	0.023*
C10	0.45771 (18)	0.3671 (4)	0.5654 (2)	0.0161 (7)
C11	0.3632 (2)	0.3719 (4)	0.5221 (2)	0.0176 (6)
O3	0.20765 (15)	0.4689 (4)	0.3159 (2)	0.0312 (5)
H3A	0.212 (3)	0.590 (4)	0.309 (4)	0.036 (12)*
H3B	0.210 (2)	0.428 (5)	0.251 (2)	0.024 (10)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.01400 (17)	0.01243 (17)	0.02049 (19)	-0.00030 (13)	0.00119 (18)	0.0009 (2)

C11	0.0290 (5)	0.0424 (4)	0.0238 (4)	0.0066 (3)	-0.0033 (3)	-0.0045 (3)
O1	0.0177 (8)	0.0342 (10)	0.0219 (9)	0.0028 (8)	0.0008 (12)	-0.0004 (11)
O2	0.0193 (11)	0.0487 (15)	0.0177 (11)	0.0029 (10)	-0.0022 (9)	0.0023 (9)
N1	0.0211 (13)	0.0325 (15)	0.0231 (16)	-0.0081 (11)	-0.0023 (10)	-0.0003 (10)
C1	0.0234 (14)	0.0120 (12)	0.0187 (18)	-0.0042 (10)	-0.0029 (12)	0.0002 (11)
C2	0.0400 (18)	0.0180 (17)	0.0205 (17)	-0.0060 (14)	0.0091 (16)	-0.0037 (13)
C3	0.0271 (19)	0.0152 (18)	0.050 (2)	0.0015 (14)	0.0104 (16)	-0.0045 (15)
C4	0.0236 (18)	0.0145 (17)	0.052 (2)	0.0019 (15)	-0.0080 (16)	0.0072 (16)
C5	0.0260 (18)	0.0177 (17)	0.0197 (18)	-0.0040 (12)	-0.0021 (13)	0.0044 (12)
C6	0.0158 (15)	0.0155 (16)	0.0259 (16)	-0.0028 (12)	0.0032 (12)	0.0020 (12)
C7	0.0152 (12)	0.0158 (12)	0.044 (2)	-0.0029 (10)	0.0041 (15)	0.0010 (15)
C8	0.0207 (15)	0.0180 (14)	0.0296 (16)	0.0001 (13)	-0.0077 (12)	-0.0042 (12)
C9	0.0195 (16)	0.0169 (14)	0.0218 (16)	0.0020 (12)	-0.0032 (12)	-0.0038 (12)
C10	0.0168 (12)	0.0128 (12)	0.019 (2)	0.0016 (10)	0.0002 (12)	-0.0009 (11)
C11	0.0195 (14)	0.0149 (14)	0.0186 (15)	0.0029 (11)	-0.0021 (11)	0.0001 (10)
O3	0.0283 (12)	0.0415 (16)	0.0237 (12)	-0.0009 (11)	-0.0054 (11)	-0.0047 (12)

Geometric parameters (Å, °)

Co1—C4	2.016 (4)	C2—H2	0.9500
Co1—C3	2.019 (4)	C3—C4	1.423 (5)
Co1—C10	2.028 (3)	C3—H3	0.9500
Co1—C9	2.033 (3)	C4—C5	1.421 (5)
Co1—C5	2.043 (3)	C4—H4	0.9500
Co1—C2	2.044 (4)	C5—H5	0.9500
Co1—C6	2.044 (3)	C6—C7	1.418 (4)
Co1—C8	2.060 (3)	C6—C10	1.439 (4)
Co1—C7	2.068 (3)	C6—H6	0.9500
Co1—C1	2.153 (3)	C7—C8	1.414 (5)
O1—C11	1.213 (4)	C7—H7	0.9500
O2—C11	1.314 (4)	C8—C9	1.419 (4)
O2—H2O	0.82 (2)	C8—H8	0.9500
N1—C1	1.343 (4)	C9—C10	1.419 (4)
N1—H1N	0.89 (2)	C9—H9	0.9500
N1—H2N	0.89 (2)	C10—C11	1.482 (4)
C1—C5	1.437 (4)	O3—H3A	0.82 (2)
C1—C2	1.439 (5)	O3—H3B	0.81 (2)
C2—C3	1.427 (6)		
C4—Co1—C3	41.29 (13)	C1—C2—Co1	74.07 (18)
C4—Co1—C10	165.32 (14)	C3—C2—H2	125.8
C3—Co1—C10	150.63 (14)	C1—C2—H2	125.8
C4—Co1—C9	128.13 (14)	Co1—C2—H2	123.2
C3—Co1—C9	168.22 (15)	C4—C3—C2	107.7 (4)
C10—Co1—C9	40.91 (12)	C4—C3—Co1	69.2 (2)
C4—Co1—C5	40.98 (16)	C2—C3—Co1	70.4 (2)
C3—Co1—C5	69.17 (14)	C4—C3—H3	126.1
C10—Co1—C5	125.96 (13)	C2—C3—H3	126.1

C9—Co1—C5	105.78 (15)	Co1—C3—H3	125.8
C4—Co1—C2	69.06 (16)	C5—C4—C3	108.4 (4)
C3—Co1—C2	41.12 (17)	C5—C4—Co1	70.53 (19)
C10—Co1—C2	115.67 (14)	C3—C4—Co1	69.5 (2)
C9—Co1—C2	148.29 (15)	C5—C4—H4	125.8
C5—Co1—C2	68.66 (15)	C3—C4—H4	125.8
C4—Co1—C6	152.63 (14)	Co1—C4—H4	125.8
C3—Co1—C6	118.50 (14)	C4—C5—C1	108.4 (3)
C10—Co1—C6	41.38 (11)	C4—C5—Co1	68.49 (18)
C9—Co1—C6	68.98 (12)	C1—C5—Co1	74.15 (18)
C5—Co1—C6	165.42 (13)	C4—C5—H5	125.8
C2—Co1—C6	108.20 (14)	C1—C5—H5	125.8
C4—Co1—C8	109.46 (15)	Co1—C5—H5	123.2
C3—Co1—C8	131.28 (15)	C7—C6—C10	107.3 (3)
C10—Co1—C8	68.42 (12)	C7—C6—Co1	70.72 (17)
C9—Co1—C8	40.56 (12)	C10—C6—Co1	68.68 (16)
C5—Co1—C8	117.29 (15)	C7—C6—H6	126.4
C2—Co1—C8	169.83 (14)	C10—C6—H6	126.4
C6—Co1—C8	68.19 (12)	Co1—C6—H6	125.8
C4—Co1—C7	120.07 (14)	C8—C7—C6	108.7 (3)
C3—Co1—C7	111.08 (14)	C8—C7—Co1	69.65 (17)
C10—Co1—C7	68.35 (11)	C6—C7—Co1	68.94 (16)
C9—Co1—C7	68.01 (13)	C8—C7—H7	125.7
C5—Co1—C7	151.79 (13)	C6—C7—H7	125.7
C2—Co1—C7	131.23 (15)	Co1—C7—H7	127.3
C6—Co1—C7	40.34 (13)	C7—C8—C9	108.1 (3)
C8—Co1—C7	40.07 (14)	C7—C8—Co1	70.27 (17)
C4—Co1—C1	67.48 (13)	C9—C8—Co1	68.71 (17)
C3—Co1—C1	67.67 (13)	C7—C8—H8	125.9
C10—Co1—C1	106.55 (11)	C9—C8—H8	125.9
C9—Co1—C1	115.79 (11)	Co1—C8—H8	126.6
C5—Co1—C1	39.94 (12)	C8—C9—C10	108.1 (3)
C2—Co1—C1	40.01 (13)	C8—C9—Co1	70.73 (17)
C6—Co1—C1	128.84 (12)	C10—C9—Co1	69.34 (17)
C8—Co1—C1	149.60 (12)	C8—C9—H9	125.9
C7—Co1—C1	168.03 (13)	C10—C9—H9	125.9
C11—O2—H2O	110 (3)	Co1—C9—H9	125.6
C1—N1—H1N	114 (3)	C9—C10—C6	107.8 (2)
C1—N1—H2N	118 (2)	C9—C10—C11	126.3 (3)
H1N—N1—H2N	125 (4)	C6—C10—C11	125.8 (3)
N1—C1—C5	125.9 (3)	C9—C10—Co1	69.76 (16)
N1—C1—C2	127.4 (3)	C6—C10—Co1	69.94 (16)
C5—C1—C2	106.5 (3)	C11—C10—Co1	122.18 (18)
N1—C1—Co1	130.2 (2)	O1—C11—O2	124.9 (3)
C5—C1—Co1	65.91 (16)	O1—C11—C10	123.3 (3)
C2—C1—Co1	65.92 (18)	O2—C11—C10	111.8 (3)
C3—C2—C1	108.5 (3)	H3A—O3—H3B	104 (4)
C3—C2—Co1	68.5 (2)		

N1—C1—C2—C3	-176.6 (3)	C6—C7—C8—C9	-0.4 (3)
C5—C1—C2—C3	7.0 (3)	Co1—C7—C8—C9	-58.5 (2)
Co1—C1—C2—C3	60.2 (2)	C6—C7—C8—Co1	58.0 (2)
N1—C1—C2—Co1	123.2 (3)	C7—C8—C9—C10	0.0 (3)
C5—C1—C2—Co1	-53.2 (2)	Co1—C8—C9—C10	-59.5 (2)
C1—C2—C3—C4	-4.4 (4)	C7—C8—C9—Co1	59.4 (2)
Co1—C2—C3—C4	59.4 (3)	C8—C9—C10—C6	0.5 (3)
C1—C2—C3—Co1	-63.7 (2)	Co1—C9—C10—C6	-59.84 (19)
C2—C3—C4—C5	-0.1 (5)	C8—C9—C10—C11	176.0 (2)
Co1—C3—C4—C5	60.0 (3)	Co1—C9—C10—C11	115.7 (3)
C2—C3—C4—Co1	-60.1 (3)	C8—C9—C10—Co1	60.3 (2)
C3—C4—C5—C1	4.5 (4)	C7—C6—C10—C9	-0.8 (3)
Co1—C4—C5—C1	63.9 (2)	Co1—C6—C10—C9	59.7 (2)
C3—C4—C5—Co1	-59.4 (3)	C7—C6—C10—C11	-176.3 (2)
N1—C1—C5—C4	176.5 (3)	Co1—C6—C10—C11	-115.8 (3)
C2—C1—C5—C4	-7.0 (3)	C7—C6—C10—Co1	-60.49 (19)
Co1—C1—C5—C4	-60.2 (2)	C9—C10—C11—O1	3.0 (4)
N1—C1—C5—Co1	-123.3 (3)	C6—C10—C11—O1	177.8 (3)
C2—C1—C5—Co1	53.22 (19)	Co1—C10—C11—O1	90.4 (3)
C10—C6—C7—C8	0.7 (3)	C9—C10—C11—O2	-176.6 (3)
Co1—C6—C7—C8	-58.5 (2)	C6—C10—C11—O2	-1.8 (4)
C10—C6—C7—Co1	59.19 (19)	Co1—C10—C11—O2	-89.2 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2O...O3	0.82 (2)	1.78 (3)	2.577 (3)	163 (4)
N1—H1N...C11 ⁱ	0.89 (2)	2.36 (3)	3.239 (3)	166 (4)
N1—H2N...C11	0.89 (2)	2.37 (3)	3.253 (3)	172 (3)
O3—H3A...C11 ⁱⁱ	0.82 (2)	2.30 (2)	3.106 (3)	172 (4)
O3—H3B...O1 ⁱⁱⁱ	0.81 (2)	2.02 (3)	2.822 (4)	171 (3)

Symmetry codes: (i) $-x+1/2, y, z+1/2$; (ii) $x, y+1, z$; (iii) $-x+1/2, y, z-1/2$.**1'-[2-(1-Amino-2,6-dimethylphenyl)diazen-1-yl]cobaltocenium-1-carboxylic acid hexafluoridophosphate monohydrate (5)***Crystal data*[Co(C₁₃H₁₄N₃)(C₆H₅O₂)]PF₆·H₂O $M_r = 543.29$ Triclinic, $P\bar{1}$ $a = 7.9891$ (4) Å $b = 9.4310$ (5) Å $c = 15.5425$ (8) Å $\alpha = 74.415$ (3)° $\beta = 78.183$ (2)° $\gamma = 73.798$ (2)° $V = 1072.48$ (10) Å³ $Z = 2$ $F(000) = 552$ $D_x = 1.682$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8266 reflections

 $\theta = 2.3$ – 25.3 ° $\mu = 0.95$ mm⁻¹ $T = 191$ K

Plate, brown

 $0.16 \times 0.16 \times 0.03$ mm

Data collection

Bruker D8 QUEST PHOTON 100
diffractometer
Radiation source: Incoatec Microfocus
Multi layered optics monochromator
Detector resolution: 10.4 pixels mm⁻¹
 φ and ω scans
Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.826$, $T_{\max} = 0.901$

20686 measured reflections
3945 independent reflections
3290 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$
 $\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 2.3^\circ$
 $h = -9 \rightarrow 9$
 $k = -11 \rightarrow 11$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.086$
 $S = 1.04$
3945 reflections
372 parameters
5 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0353P)^2 + 0.9559P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.54 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

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.

Refinement. Hydrogen atoms at N3 and O2 were found and refined isotropically with bond restraints ($d=89\text{pm}$ for N and $d=83\text{pm}$ for). Also the hydrogens at water molecule were found, refined with bond restraints but with isotropic displacement parameter of 1.2 higher than $U(\text{iso})$ of O3. The fluorine of the anion PF6⁻ show a nearly 1:1 positional disorder F1-F1: F1A-F6A.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.45960 (4)	0.32404 (4)	0.84877 (2)	0.02519 (11)	
O1	0.6004 (3)	0.7001 (2)	0.75554 (15)	0.0513 (6)	
O2	0.8374 (3)	0.5069 (2)	0.75963 (15)	0.0469 (5)	
H2O	0.895 (5)	0.564 (4)	0.722 (2)	0.091 (14)*	
N1	0.3994 (3)	0.5104 (3)	0.65242 (15)	0.0361 (5)	
N2	0.5502 (3)	0.5139 (3)	0.60815 (14)	0.0352 (5)	
N3	0.6392 (4)	1.0108 (3)	0.33140 (16)	0.0381 (5)	
H1N	0.746 (3)	1.013 (4)	0.303 (2)	0.057 (10)*	
H2N	0.549 (3)	1.087 (3)	0.317 (2)	0.057 (10)*	
C1	0.5893 (3)	0.4716 (3)	0.86280 (16)	0.0280 (5)	
C2	0.6649 (4)	0.3213 (3)	0.90866 (18)	0.0350 (6)	
H2	0.7831	0.2661	0.8968	0.042*	
C3	0.5322 (4)	0.2695 (3)	0.97471 (18)	0.0449 (7)	
H3	0.5459	0.1732	1.0155	0.054*	
C4	0.3756 (4)	0.3851 (4)	0.96977 (18)	0.0462 (8)	
H4	0.2657	0.3796	1.0064	0.055*	
C5	0.4106 (4)	0.5106 (3)	0.90090 (18)	0.0366 (6)	

H5	0.3287	0.6042	0.8834	0.044*	
C6	0.4099 (4)	0.3705 (3)	0.71763 (16)	0.0327 (6)	
C7	0.5527 (4)	0.2416 (3)	0.73550 (17)	0.0339 (6)	
H7	0.6701	0.2312	0.7053	0.041*	
C8	0.4880 (4)	0.1317 (3)	0.80667 (18)	0.0379 (6)	
H8	0.5542	0.0336	0.8314	0.046*	
C9	0.3095 (4)	0.1925 (3)	0.83431 (18)	0.0403 (7)	
H9	0.2345	0.1427	0.8811	0.048*	
C10	0.2603 (4)	0.3404 (3)	0.78064 (18)	0.0390 (6)	
H10	0.1473	0.4078	0.7857	0.047*	
C11	0.6753 (3)	0.5731 (3)	0.78691 (18)	0.0330 (6)	
C12	0.5566 (4)	0.6439 (3)	0.53849 (16)	0.0326 (6)	
C13	0.7250 (4)	0.6491 (3)	0.49348 (17)	0.0351 (6)	
H13	0.8212	0.5671	0.5109	0.042*	
C14	0.7569 (4)	0.7695 (3)	0.42443 (17)	0.0350 (6)	
C15	0.6122 (3)	0.8902 (3)	0.39860 (16)	0.0310 (6)	
C16	0.4380 (3)	0.8863 (3)	0.44206 (16)	0.0316 (6)	
C17	0.4144 (4)	0.7632 (3)	0.51119 (16)	0.0345 (6)	
H17	0.2988	0.7593	0.5410	0.041*	
C18	0.9404 (4)	0.7752 (4)	0.3787 (2)	0.0503 (8)	
H18A	1.0240	0.6850	0.4065	0.076*	
H18B	0.9683	0.8662	0.3854	0.076*	
H18C	0.9486	0.7782	0.3145	0.076*	
C19	0.2862 (4)	1.0137 (3)	0.41259 (19)	0.0406 (7)	
H19A	0.1771	0.9950	0.4507	0.061*	
H19B	0.2775	1.0203	0.3496	0.061*	
H19C	0.3046	1.1091	0.4182	0.061*	
P1	1.02857 (10)	1.13338 (9)	0.12566 (5)	0.0440 (2)	
F1	0.8815 (9)	1.0964 (8)	0.0890 (6)	0.108 (2)	0.5
F2	1.1759 (6)	1.1734 (6)	0.1606 (5)	0.0803 (14)	0.5
F3	0.9908 (6)	1.2937 (6)	0.0619 (6)	0.090 (2)	0.5
F4	1.0704 (9)	0.9680 (7)	0.1867 (4)	0.088 (3)	0.5
F5	0.8818 (13)	1.1883 (11)	0.2032 (6)	0.083 (3)	0.5
F6	1.1786 (15)	1.0780 (13)	0.0534 (6)	0.105 (4)	0.5
F1A	0.9618 (12)	1.1992 (12)	0.0352 (5)	0.142 (3)	0.5
F2A	1.0947 (12)	1.0805 (10)	0.2208 (4)	0.141 (3)	0.5
F3A	1.0275 (11)	1.3037 (7)	0.1226 (5)	0.113 (3)	0.5
F4A	1.0215 (11)	0.9684 (8)	0.1367 (7)	0.118 (3)	0.5
F5A	0.8398 (14)	1.1641 (10)	0.1748 (9)	0.179 (7)	0.5
F6A	1.2124 (13)	1.0946 (12)	0.0709 (8)	0.138 (6)	0.5
O3	1.0363 (3)	0.6853 (3)	0.65768 (18)	0.0613 (7)	
H3A	1.145 (3)	0.639 (4)	0.650 (2)	0.074*	
H3B	1.037 (5)	0.747 (4)	0.687 (2)	0.074*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.02688 (19)	0.02523 (18)	0.02200 (18)	-0.00943 (13)	-0.00294 (12)	0.00010 (13)

O1	0.0437 (12)	0.0342 (12)	0.0620 (14)	-0.0097 (9)	-0.0085 (10)	0.0136 (10)
O2	0.0301 (11)	0.0478 (12)	0.0540 (13)	-0.0124 (9)	0.0035 (9)	-0.0004 (10)
N1	0.0384 (13)	0.0396 (13)	0.0323 (12)	-0.0122 (10)	-0.0057 (10)	-0.0077 (10)
N2	0.0373 (13)	0.0398 (13)	0.0321 (12)	-0.0150 (10)	-0.0042 (10)	-0.0083 (10)
N3	0.0470 (16)	0.0303 (13)	0.0344 (13)	-0.0147 (11)	-0.0037 (11)	0.0015 (10)
C1	0.0291 (13)	0.0281 (13)	0.0287 (13)	-0.0080 (10)	-0.0059 (10)	-0.0067 (10)
C2	0.0380 (15)	0.0338 (14)	0.0363 (15)	-0.0084 (11)	-0.0174 (12)	-0.0037 (11)
C3	0.072 (2)	0.0444 (17)	0.0244 (14)	-0.0280 (16)	-0.0155 (13)	0.0040 (12)
C4	0.0558 (19)	0.063 (2)	0.0282 (14)	-0.0323 (16)	0.0116 (13)	-0.0178 (14)
C5	0.0375 (15)	0.0362 (15)	0.0373 (15)	-0.0087 (12)	0.0005 (12)	-0.0145 (12)
C6	0.0462 (16)	0.0307 (14)	0.0247 (13)	-0.0169 (12)	-0.0096 (11)	-0.0004 (10)
C7	0.0374 (15)	0.0374 (15)	0.0305 (14)	-0.0143 (12)	-0.0001 (11)	-0.0116 (11)
C8	0.0528 (18)	0.0266 (14)	0.0368 (15)	-0.0132 (12)	-0.0126 (13)	-0.0024 (11)
C9	0.0482 (17)	0.0484 (17)	0.0306 (14)	-0.0320 (14)	-0.0096 (12)	0.0051 (12)
C10	0.0321 (15)	0.0485 (17)	0.0370 (15)	-0.0121 (12)	-0.0116 (12)	-0.0030 (13)
C11	0.0298 (14)	0.0337 (15)	0.0360 (14)	-0.0116 (11)	-0.0057 (11)	-0.0035 (12)
C12	0.0466 (16)	0.0268 (13)	0.0241 (13)	-0.0124 (11)	-0.0073 (11)	0.0002 (10)
C13	0.0408 (15)	0.0322 (14)	0.0308 (14)	-0.0107 (12)	-0.0073 (11)	-0.0008 (11)
C14	0.0407 (15)	0.0342 (14)	0.0304 (14)	-0.0137 (12)	-0.0044 (11)	-0.0030 (11)
C15	0.0435 (15)	0.0291 (13)	0.0236 (12)	-0.0157 (11)	-0.0035 (11)	-0.0048 (10)
C16	0.0418 (15)	0.0300 (13)	0.0244 (13)	-0.0110 (11)	-0.0031 (11)	-0.0070 (10)
C17	0.0427 (16)	0.0402 (15)	0.0256 (13)	-0.0212 (12)	0.0033 (11)	-0.0096 (11)
C18	0.0426 (17)	0.0498 (18)	0.0515 (18)	-0.0149 (14)	-0.0056 (14)	0.0038 (15)
C19	0.0439 (17)	0.0366 (15)	0.0388 (16)	-0.0082 (12)	-0.0016 (12)	-0.0089 (12)
P1	0.0332 (4)	0.0384 (4)	0.0465 (4)	-0.0085 (3)	0.0011 (3)	0.0085 (3)
F1	0.076 (4)	0.119 (5)	0.139 (6)	-0.058 (4)	-0.049 (4)	0.015 (5)
F2	0.058 (3)	0.085 (4)	0.114 (4)	-0.017 (3)	-0.029 (3)	-0.036 (4)
F3	0.039 (2)	0.050 (3)	0.122 (6)	0.002 (2)	0.019 (3)	0.043 (3)
F4	0.086 (5)	0.048 (3)	0.075 (4)	0.005 (3)	0.024 (3)	0.028 (3)
F5	0.088 (6)	0.090 (5)	0.067 (3)	-0.024 (4)	0.030 (3)	-0.036 (3)
F6	0.128 (9)	0.098 (6)	0.056 (3)	-0.013 (5)	0.049 (4)	-0.026 (4)
F1A	0.155 (7)	0.152 (8)	0.096 (5)	0.018 (6)	-0.083 (5)	0.002 (5)
F2A	0.240 (9)	0.110 (6)	0.063 (4)	-0.009 (6)	-0.071 (5)	-0.002 (4)
F3A	0.185 (8)	0.060 (4)	0.099 (5)	-0.057 (4)	0.013 (5)	-0.019 (4)
F4A	0.116 (6)	0.049 (4)	0.194 (9)	-0.035 (4)	-0.003 (6)	-0.031 (6)
F5A	0.064 (5)	0.073 (6)	0.249 (14)	0.029 (4)	0.091 (7)	0.081 (7)
F6A	0.034 (3)	0.095 (7)	0.178 (11)	0.016 (3)	0.024 (5)	0.083 (7)
O3	0.0341 (12)	0.0587 (16)	0.0721 (17)	-0.0104 (11)	0.0085 (11)	0.0039 (12)

Geometric parameters (Å, °)

Co1—C8	2.029 (3)	C8—H8	0.9500
Co1—C1	2.029 (2)	C9—C10	1.414 (4)
Co1—C9	2.030 (3)	C9—H9	0.9500
Co1—C7	2.033 (3)	C10—H10	0.9500
Co1—C2	2.036 (3)	C12—C13	1.391 (4)
Co1—C10	2.036 (3)	C12—C17	1.402 (4)
Co1—C5	2.039 (3)	C13—C14	1.379 (3)

Co1—C4	2.041 (3)	C13—H13	0.9500
Co1—C3	2.047 (3)	C14—C15	1.415 (4)
Co1—C6	2.064 (2)	C14—C18	1.501 (4)
O1—C11	1.199 (3)	C15—C16	1.422 (4)
O2—C11	1.309 (3)	C16—C17	1.381 (3)
O2—H2O	0.837 (19)	C16—C19	1.498 (4)
N1—N2	1.263 (3)	C17—H17	0.9500
N1—C6	1.424 (3)	C18—H18A	0.9800
N2—C12	1.407 (3)	C18—H18B	0.9800
N3—C15	1.356 (3)	C18—H18C	0.9800
N3—H1N	0.878 (18)	C19—H19A	0.9800
N3—H2N	0.881 (18)	C19—H19B	0.9800
C1—C5	1.415 (4)	C19—H19C	0.9800
C1—C2	1.428 (3)	P1—F1A	1.517 (6)
C1—C11	1.486 (3)	P1—F5A	1.531 (8)
C2—C3	1.411 (4)	P1—F4A	1.534 (7)
C2—H2	0.9500	P1—F6A	1.540 (9)
C3—C4	1.411 (4)	P1—F6	1.544 (7)
C3—H3	0.9500	P1—F3	1.556 (4)
C4—C5	1.417 (4)	P1—F1	1.561 (5)
C4—H4	0.9500	P1—F2	1.562 (4)
C5—H5	0.9500	P1—F4	1.577 (5)
C6—C10	1.424 (4)	P1—F2A	1.579 (5)
C6—C7	1.425 (4)	P1—F5	1.585 (8)
C7—C8	1.419 (4)	P1—F3A	1.592 (6)
C7—H7	0.9500	O3—H3A	0.856 (19)
C8—C9	1.404 (4)	O3—H3B	0.835 (19)
C8—Co1—C1	144.40 (11)	C8—C7—Co1	69.40 (15)
C8—Co1—C9	40.48 (12)	C6—C7—Co1	70.80 (15)
C1—Co1—C9	174.67 (11)	C8—C7—H7	126.2
C8—Co1—C7	40.90 (10)	C6—C7—H7	126.2
C1—Co1—C7	113.95 (10)	Co1—C7—H7	125.2
C9—Co1—C7	68.65 (11)	C9—C8—C7	108.5 (2)
C8—Co1—C2	113.50 (11)	C9—C8—Co1	69.78 (16)
C1—Co1—C2	41.12 (10)	C7—C8—Co1	69.70 (15)
C9—Co1—C2	143.37 (11)	C9—C8—H8	125.8
C7—Co1—C2	109.64 (11)	C7—C8—H8	125.8
C8—Co1—C10	68.40 (12)	Co1—C8—H8	126.3
C1—Co1—C10	135.01 (11)	C8—C9—C10	108.4 (2)
C9—Co1—C10	40.70 (11)	C8—C9—Co1	69.74 (15)
C7—Co1—C10	68.79 (11)	C10—C9—Co1	69.90 (15)
C2—Co1—C10	175.35 (11)	C8—C9—H9	125.8
C8—Co1—C5	174.07 (11)	C10—C9—H9	125.8
C1—Co1—C5	40.70 (10)	Co1—C9—H9	126.1
C9—Co1—C5	134.61 (12)	C9—C10—C6	108.0 (2)
C7—Co1—C5	144.43 (11)	C9—C10—Co1	69.39 (15)
C2—Co1—C5	68.73 (11)	C6—C10—Co1	70.71 (14)

C10—Co1—C5	109.82 (12)	C9—C10—H10	126.0
C8—Co1—C4	134.27 (11)	C6—C10—H10	126.0
C1—Co1—C4	68.36 (10)	Co1—C10—H10	125.5
C9—Co1—C4	109.53 (11)	O1—C11—O2	125.5 (2)
C7—Co1—C4	174.18 (12)	O1—C11—C1	122.3 (2)
C2—Co1—C4	68.28 (12)	O2—C11—C1	112.2 (2)
C10—Co1—C4	113.72 (12)	C13—C12—C17	118.9 (2)
C5—Co1—C4	40.63 (11)	C13—C12—N2	114.1 (2)
C8—Co1—C3	109.59 (11)	C17—C12—N2	127.1 (2)
C1—Co1—C3	68.37 (10)	C14—C13—C12	122.1 (3)
C9—Co1—C3	113.47 (11)	C14—C13—H13	119.0
C7—Co1—C3	134.63 (12)	C12—C13—H13	119.0
C2—Co1—C3	40.43 (11)	C13—C14—C15	118.3 (2)
C10—Co1—C3	143.69 (12)	C13—C14—C18	121.2 (3)
C5—Co1—C3	68.24 (12)	C15—C14—C18	120.4 (2)
C4—Co1—C3	40.39 (13)	N3—C15—C14	119.8 (2)
C8—Co1—C6	68.24 (11)	N3—C15—C16	119.4 (2)
C1—Co1—C6	110.41 (10)	C14—C15—C16	120.8 (2)
C9—Co1—C6	68.23 (10)	C17—C16—C15	118.3 (2)
C7—Co1—C6	40.71 (11)	C17—C16—C19	121.7 (2)
C2—Co1—C6	135.43 (11)	C15—C16—C19	120.0 (2)
C10—Co1—C6	40.65 (10)	C16—C17—C12	121.6 (2)
C5—Co1—C6	114.40 (11)	C16—C17—H17	119.2
C4—Co1—C6	144.43 (13)	C12—C17—H17	119.2
C3—Co1—C6	174.79 (12)	C14—C18—H18A	109.5
C11—O2—H2O	115 (3)	C14—C18—H18B	109.5
N2—N1—C6	109.2 (2)	H18A—C18—H18B	109.5
N1—N2—C12	114.9 (2)	C14—C18—H18C	109.5
C15—N3—H1N	120 (2)	H18A—C18—H18C	109.5
C15—N3—H2N	119 (2)	H18B—C18—H18C	109.5
H1N—N3—H2N	121 (3)	C16—C19—H19A	109.5
C5—C1—C2	108.0 (2)	C16—C19—H19B	109.5
C5—C1—C11	123.9 (2)	H19A—C19—H19B	109.5
C2—C1—C11	128.0 (2)	C16—C19—H19C	109.5
C5—C1—Co1	70.02 (14)	H19A—C19—H19C	109.5
C2—C1—Co1	69.69 (14)	H19B—C19—H19C	109.5
C11—C1—Co1	124.91 (18)	F1A—P1—F5A	90.6 (6)
C3—C2—C1	107.6 (2)	F1A—P1—F4A	98.4 (6)
C3—C2—Co1	70.20 (15)	F5A—P1—F4A	88.8 (6)
C1—C2—Co1	69.19 (14)	F1A—P1—F6A	86.0 (6)
C3—C2—H2	126.2	F5A—P1—F6A	174.5 (9)
C1—C2—H2	126.2	F4A—P1—F6A	87.4 (6)
Co1—C2—H2	126.0	F6—P1—F3	89.5 (5)
C2—C3—C4	108.4 (2)	F6—P1—F1	95.1 (6)
C2—C3—Co1	69.37 (15)	F3—P1—F1	88.6 (4)
C4—C3—Co1	69.60 (16)	F6—P1—F2	84.5 (5)
C2—C3—H3	125.8	F3—P1—F2	90.2 (4)
C4—C3—H3	125.8	F1—P1—F2	178.8 (3)

Co1—C3—H3	126.8	F6—P1—F4	88.3 (5)
C3—C4—C5	108.3 (2)	F3—P1—F4	177.6 (5)
C3—C4—Co1	70.01 (16)	F1—P1—F4	90.6 (4)
C5—C4—Co1	69.60 (15)	F2—P1—F4	90.5 (4)
C3—C4—H4	125.9	F1A—P1—F2A	174.7 (5)
C5—C4—H4	125.9	F5A—P1—F2A	88.1 (7)
Co1—C4—H4	126.1	F4A—P1—F2A	86.7 (4)
C1—C5—C4	107.7 (2)	F6A—P1—F2A	95.6 (6)
C1—C5—Co1	69.27 (14)	F6—P1—F5	177.1 (6)
C4—C5—Co1	69.78 (16)	F3—P1—F5	91.9 (5)
C1—C5—H5	126.1	F1—P1—F5	87.5 (5)
C4—C5—H5	126.1	F2—P1—F5	92.9 (4)
Co1—C5—H5	126.4	F4—P1—F5	90.4 (4)
C10—C6—N1	121.0 (2)	F1A—P1—F3A	84.8 (4)
C10—C6—C7	107.5 (2)	F5A—P1—F3A	87.5 (6)
N1—C6—C7	131.5 (2)	F4A—P1—F3A	175.2 (4)
C10—C6—Co1	68.64 (14)	F6A—P1—F3A	96.4 (5)
N1—C6—Co1	127.67 (18)	F2A—P1—F3A	90.0 (5)
C7—C6—Co1	68.48 (14)	H3A—O3—H3B	103 (4)
C8—C7—C6	107.6 (2)		
C6—N1—N2—C12	177.3 (2)	C7—C8—C9—Co1	-59.15 (18)
C5—C1—C2—C3	-0.2 (3)	C8—C9—C10—C6	1.1 (3)
C11—C1—C2—C3	-179.0 (2)	Co1—C9—C10—C6	60.46 (18)
Co1—C1—C2—C3	-59.96 (18)	C8—C9—C10—Co1	-59.34 (19)
C5—C1—C2—Co1	59.76 (18)	N1—C6—C10—C9	178.3 (2)
C11—C1—C2—Co1	-119.0 (3)	C7—C6—C10—C9	-2.1 (3)
C1—C2—C3—C4	0.5 (3)	Co1—C6—C10—C9	-59.63 (19)
Co1—C2—C3—C4	-58.8 (2)	N1—C6—C10—Co1	-122.0 (2)
C1—C2—C3—Co1	59.32 (18)	C7—C6—C10—Co1	57.55 (18)
C2—C3—C4—C5	-0.6 (3)	C5—C1—C11—O1	4.2 (4)
Co1—C3—C4—C5	-59.28 (19)	C2—C1—C11—O1	-177.2 (3)
C2—C3—C4—Co1	58.70 (19)	Co1—C1—C11—O1	92.3 (3)
C2—C1—C5—C4	-0.2 (3)	C5—C1—C11—O2	-175.4 (2)
C11—C1—C5—C4	178.7 (2)	C2—C1—C11—O2	3.3 (4)
Co1—C1—C5—C4	59.40 (19)	Co1—C1—C11—O2	-87.2 (3)
C2—C1—C5—Co1	-59.55 (17)	N1—N2—C12—C13	177.0 (2)
C11—C1—C5—Co1	119.3 (2)	N1—N2—C12—C17	-3.4 (4)
C3—C4—C5—C1	0.5 (3)	C17—C12—C13—C14	1.6 (4)
Co1—C4—C5—C1	-59.08 (18)	N2—C12—C13—C14	-178.7 (2)
C3—C4—C5—Co1	59.5 (2)	C12—C13—C14—C15	-0.7 (4)
N2—N1—C6—C10	176.2 (2)	C12—C13—C14—C18	178.0 (3)
N2—N1—C6—C7	-3.3 (4)	C13—C14—C15—N3	179.5 (2)
N2—N1—C6—Co1	90.4 (3)	C18—C14—C15—N3	0.8 (4)
C10—C6—C7—C8	2.3 (3)	C13—C14—C15—C16	-0.8 (4)
N1—C6—C7—C8	-178.2 (3)	C18—C14—C15—C16	-179.5 (3)
Co1—C6—C7—C8	59.90 (18)	N3—C15—C16—C17	-179.0 (2)
C10—C6—C7—Co1	-57.65 (18)	C14—C15—C16—C17	1.3 (4)

N1—C6—C7—Co1	121.9 (3)	N3—C15—C16—C19	0.9 (4)
C6—C7—C8—C9	-1.6 (3)	C14—C15—C16—C19	-178.8 (2)
Co1—C7—C8—C9	59.20 (19)	C15—C16—C17—C12	-0.3 (4)
C6—C7—C8—Co1	-60.79 (18)	C19—C16—C17—C12	179.8 (2)
C7—C8—C9—C10	0.3 (3)	C13—C12—C17—C16	-1.1 (4)
Co1—C8—C9—C10	59.45 (19)	N2—C12—C17—C16	179.3 (2)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H2 <i>N</i> ...O1 ⁱ	0.88 (2)	2.18 (2)	3.015 (3)	159 (3)
N3—H1 <i>N</i> ...F5	0.88 (2)	2.29 (3)	2.994 (10)	137 (3)
N3—H1 <i>N</i> ...F5 <i>A</i>	0.88 (2)	2.24 (3)	2.896 (8)	131 (3)
O2—H2 <i>O</i> ...O3	0.84 (2)	1.80 (2)	2.625 (3)	170 (4)
O3—H3 <i>A</i> ...N1 ⁱⁱ	0.86 (2)	2.06 (2)	2.907 (3)	171 (4)
O3—H3 <i>B</i> ...F5 ⁱⁱⁱ	0.84 (2)	2.22 (3)	2.988 (8)	153 (4)
O3—H3 <i>B</i> ...F2 <i>A</i> ⁱⁱⁱ	0.84 (2)	2.34 (3)	3.112 (8)	154 (4)

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