metal-organic compounds

Hexakis(1*H*-imidazole-κN^3)cobalt(III) tris(hexafluoridophosphate) hexahydrate

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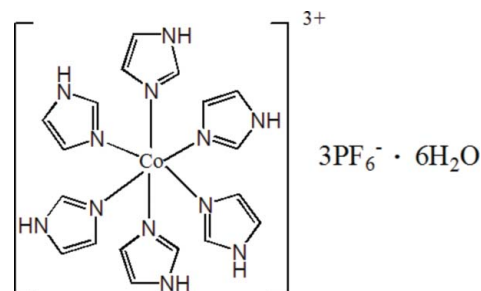Correspondence e-mail: lianger@sun.ac.za

In the crystal structure of the title compound, $[Co(C_3H_4N_2)_6]$-$(PF_6)_3 \cdot 6H_2O$, the Co^{III} atom lies on a special position with site-symmetry $\bar{3}$ and the P atom is located on a special position with site symmetry $\bar{1}$. The Co^{III} atom has an almost ideal octahedral coordination formed by the N atoms of six imidazole ligands. The water molecules form hydrogen-bonded helical chains propagating in [001] by O—H···O interactions with a distance of 2.913 (2) Å. They simulta-neously interact as hydrogen-bond acceptors and donors with the cations and anions, respectively, resulting in the formation of a three-dimensional assembly. Weak C—H···F interactions further stabilize the crystal structure.

Related literature

For Co^{III} complexes with heterocycles, see: Wojtczak *et al.* (1990); Pazderski *et al.* (2008). For the hexakis(imidazole)-cobalt(III) ion in solution, see: Navon & Panigel (1989); Wiśniewska & Kita (2006). For Co—N bond distances in hexakis(imidazole)-cobalt(II) complexes, see: Tong *et al.* (2002). For Co^{III}—N and Co^{II}—N bond lengths in hexa-ammine–cobalt complexes, see: Kime & Ibers (1969). The water molecules present in the crystal structure form helical chains similar to those observed in a trichlorophloroglucinol structure, see: Saha & Nangia (2005).

Experimental

Crystal data

$[Co(C_3H_4N_2)_6](PF_6)_3 \cdot 6H_2O$	$Z = 3$
$M_r = 1010.43$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}$	$\mu = 0.77$ mm^{-1}
$a = 20.9911$ (13) Å	$T = 100$ K
$c = 7.0156$ (9) Å	$0.25 \times 0.25 \times 0.21$ mm
$V = 2677.1$ (4) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	4893 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	1373 independent reflections
$T_{min} = 0.832$, $T_{max} = 0.856$	1288 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.083$	
$S = 1.08$	
1373 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
98 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
3 restraints	

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H6···O1^i	0.96 (3)	1.98 (3)	2.913 (2)	163 (3)
N3—H3···O1	0.88	1.98	2.834 (2)	165
O1—H7···F3^{ii}	0.96 (3)	2.10 (3)	2.945 (2)	146 (2)
C2—H2···F3^{iii}	0.95	2.34	3.042 (2)	131
C4—H4···F1^{iv}	0.95	2.40	3.303 (2)	158

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour 2001); software used to prepare material for publication: *SHELXL97*.

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supporting information

Hexakis(1*H*-imidazole-*κN*³)cobalt(III) tris(hexafluoridophosphate) hexahydrate

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S1. Comment

During the course of ongoing studies on Co^{III} complexes with heterocycles (Wojtczak *et al.*, 1990; Pazderski *et al.*, 2008) the title compound (I) was isolated. The crystal structure of (I) is built of mononuclear [Co(imidazole)$_6$]$^{3+}$ trications with the Co1 atom lying on Wyckoff position 3a (site symmetry $\bar{3}$), PF$_6^-$ anions with P atom lying on Wyckoff position 9 d (site symmetry $\bar{1}$) and lattice water molecules (Fig.1). It is worth mentioning that this is the first structure consisting of a hexakis(imidazole)-cobalt(III) cationic complex, whereas more than 15 structures consisting of a hexakis(imidazole)-cobalt(II) complex ion were reported. Furthermore, there are only two papers on the hexakis(imidazole)-cobalt(III) ion in solution, describing spectroscopic (Navon & Panigel, 1989) and kinetic properties (Wiśniewska & Kita, 2006) respectively. The Co^{III} ion has an almost ideal octahedral environment formed by six imidazole N atoms, with *cis*-N—Co—N angles of 88.68 (7)° and 91.32 (7)°. The planes of neighbouring imidazole rings are twisted from their usual perpendicular positions. This is the result of the extensive net of hydrogen bonds in the structure in which imidazole rings are involved (dihedral angle = 72.4 (6)°). The Co—N bond distance is equal to 1.961 (1) Å and as expected is slightly shorter than those reported for hexakis(imidazole)-cobalt(II) complexes with distances of 2.140±2.188 Å (Tong *et al.*, 2002). A similar relation of bond lengths was reported for Co^{III}—N and Co(II)—N in hexaamminecobalt complexes (Kime & Ibers, 1969) with differences between those distances of 0.18 Å. The water molecules present in the crystal structure form helical chains (helix pitch = 7.016 (2) Å, *c* axis) similar to those observed in a trichlorophloroglucinol structure (Saha & Nangia, 2005). They are propagated in [001] directions by O1—H6···O1^i interactions (symmetry operation: -*y* + 2/3, *x*-*y* + 1/3, *z* + 1/3) with a distance of 2.913 (2) Å), which are stabilized by hydrogen bonding with the remaining molecular units (Table 1) giving in turn a three-dimensional assembly. The weak C—H···F interactions (Table 1) further stabilize the packing arrangement (Fig. 2).

S2. Experimental

A mixture of 11.84 g (174 mmol) of imidazole and 2.02 g (5 mmol) of Co(pyridine)$_3$Cl$_3$ was grinded for several minutes until the color changed from green to red. The mixture was subsequently dissolved in 100 ml of distilled water and the pH was adjusted to 2–3 by adding 3 *M* HCl. Then the mixture was diluted with water to a final volume of 2 l and passed through a Sephadex SP C-25 column starting with an aqueous 0.05 *M* HCl solution as eluent. The fraction obtained by using 0.2 *M* HCl was evaporated in a stream of cold air and the product [Co(imidazole)$_6$]Cl$_3$ was filtrated and washed with ethanol. 10 mg of this compound was placed in a 50 ml beaker and 20 ml of a saturated aqueous solution of NH$_4$PF$_6$ was added. Red crystals suitable for single-crystal X-ray analysis were obtained by slow evaporation.

S3. Refinement

Water H atoms were located in a difference map and refined with a restrained O—H distance of 0.96 (3) Å, whereas U_{iso}(H) values were allowed to refine independently. The remaining H atoms were positioned geometrically, with C—H =

0.95 Å and N—H = 0.88 Å, and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C,N)$.
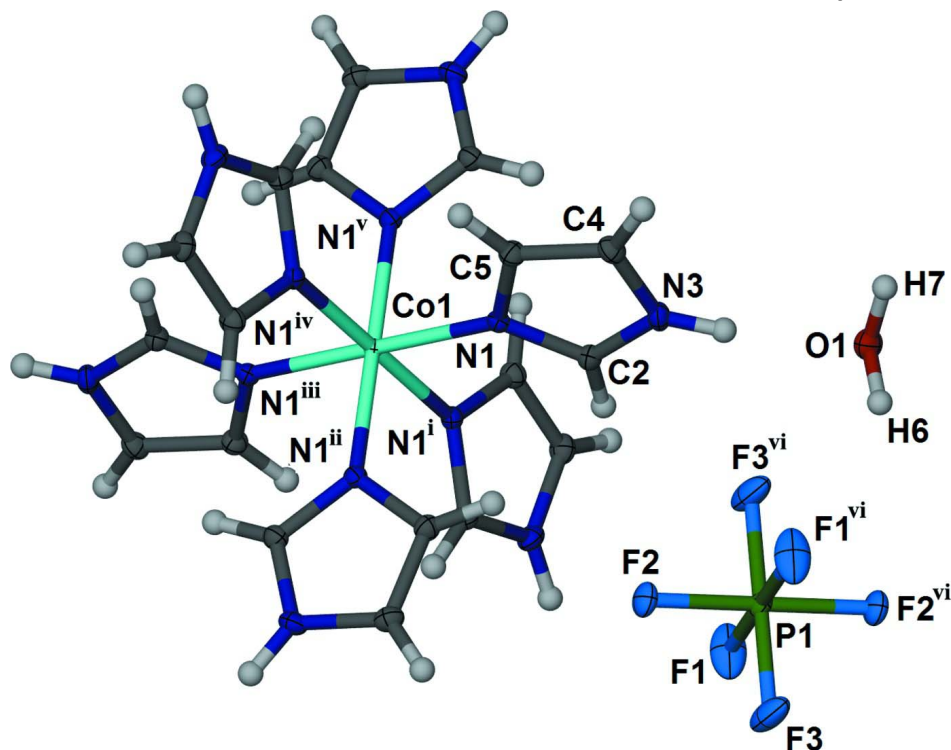

Figure 1

The molecular structure of (I), with the atom-numbering scheme [symmetry codes:(i) $y, -x + y, -z$; (ii) $-x + y, -x, z$; (iii) $-x, -y, -z$; (iv) $-y, x-y, z$; (v) $x-y, x, -z$; (vi) $-x + 2/3, -y + 1/3, -z + 1/3$]. Displacement ellipsoids are drawn at the 50% probability level.
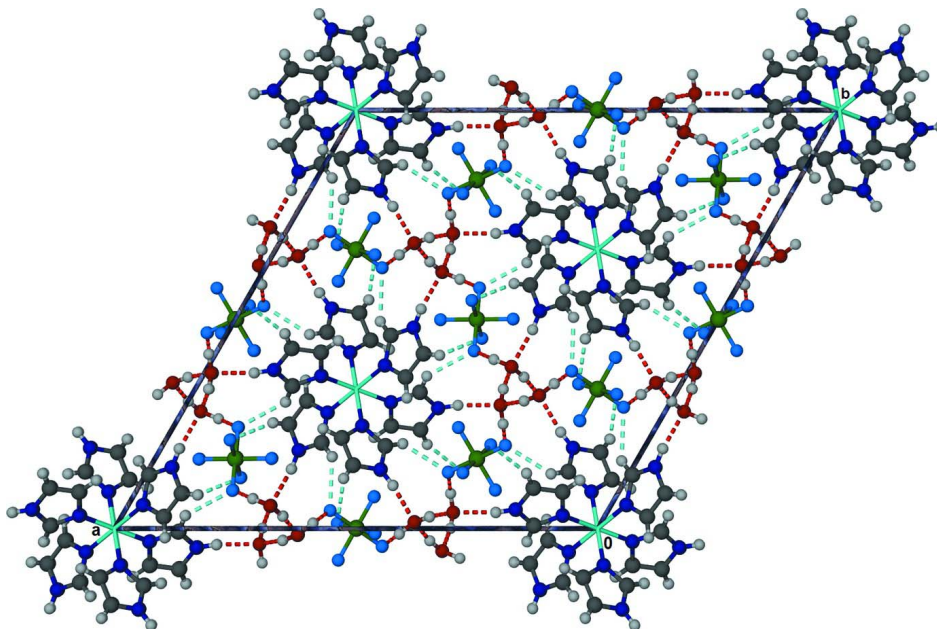
Figure 2

The crystal packing of (I) viewed down [001] with the extensive net of hydrogen bonds leading to a three-dimensional arrangement (the red dashed lines indicate strong hydrogen bonding and the blue weak ones).

Hexakis(1*H*-imidazole-*κN*³)cobalt(III) tris(hexafluoridophosphate) hexahydrate

Crystal data

$[Co(C_3H_4N_2)_6](PF_6)_3 \cdot 6H_2O$

$M_r = 1010.43$

Trigonal, $R\bar{3}$

Hall symbol: -R 3

$a = 20.9911 (13)$ Å

$c = 7.0156 (9)$ Å

$V = 2677.1 (4)$ Å³

$Z = 3$

$F(000) = 1530$

$D_x = 1.880$ Mg m⁻³

Mo *Kα* radiation, $\lambda = 0.71073$ Å

Cell parameters from 3782 reflections

$\theta = 3.1–28.2°$

$\mu = 0.77$ mm⁻¹

$T = 100$ K

Block, red

$0.25 \times 0.25 \times 0.21$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)

$T_{min} = 0.832$, $T_{max} = 0.856$

4893 measured reflections

1373 independent reflections

1288 reflections with $I > 2\sigma(I)$

$R_{int} = 0.026$

$\theta_{max} = 28.2°$, $\theta_{min} = 3.1°$

$h = -22 \rightarrow 27$

$k = -26 \rightarrow 26$

$l = -9 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.083$

$S = 1.08$

1373 reflections

98 parameters

3 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map	$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 4.9022P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Hydrogen site location: inferred from neighbouring sites	$(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 0.54$ e Å^{-3}	
H atoms treated by a mixture of independent and constrained refinement	$\Delta\rho_{min} = -0.31$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Co1	0.0000	0.0000	0.0000	0.01001 (15)
F2	0.25776 (5)	0.09189 (5)	0.20301 (16)	0.0242 (3)
N1	0.05651 (7)	0.08788 (7)	0.15758 (19)	0.0126 (3)
N3	0.14686 (7)	0.19255 (7)	0.2646 (2)	0.0161 (3)
H3	0.1914	0.2302	0.2812	0.019*
C5	0.02873 (8)	0.11667 (8)	0.2899 (2)	0.0155 (3)
H5	−0.0213	0.0945	0.3285	0.019*
C2	0.12841 (8)	0.13594 (8)	0.1462 (2)	0.0150 (3)
H2	0.1618	0.1307	0.0653	0.018*
C4	0.08453 (9)	0.18177 (8)	0.3556 (2)	0.0171 (3)
H4	0.0810	0.2134	0.4464	0.020*
P1	0.3333	0.1667	0.1667	0.01496 (16)
F1	0.34563 (7)	0.13360 (7)	−0.02524 (19)	0.0421 (4)
F3	0.37650 (6)	0.13458 (7)	0.2841 (2)	0.0402 (4)
O1	0.27980 (6)	0.31811 (6)	0.37976 (18)	0.0203 (3)
H6	0.3046 (15)	0.3048 (15)	0.473 (4)	0.052 (8)*
H7	0.2625 (15)	0.3462 (14)	0.447 (4)	0.051 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.00877 (17)	0.00877 (17)	0.0125 (3)	0.00438 (9)	0.000	0.000
F2	0.0135 (4)	0.0191 (5)	0.0324 (6)	0.0026 (4)	0.0030 (4)	0.0038 (4)
N1	0.0126 (6)	0.0113 (6)	0.0144 (6)	0.0063 (5)	−0.0004 (5)	0.0004 (5)
N3	0.0148 (6)	0.0122 (6)	0.0179 (7)	0.0041 (5)	−0.0023 (5)	−0.0005 (5)
C5	0.0158 (7)	0.0158 (7)	0.0158 (8)	0.0085 (6)	−0.0001 (5)	−0.0015 (6)
C2	0.0137 (7)	0.0137 (7)	0.0171 (7)	0.0063 (6)	−0.0016 (5)	−0.0009 (5)
C4	0.0205 (8)	0.0153 (7)	0.0161 (8)	0.0095 (6)	−0.0020 (6)	−0.0023 (6)
P1	0.0104 (3)	0.0156 (3)	0.0172 (3)	0.0052 (2)	0.00177 (19)	0.0010 (2)
F1	0.0372 (7)	0.0354 (7)	0.0378 (7)	0.0062 (5)	0.0167 (5)	−0.0130 (5)

F3	0.0160 (5)	0.0422 (7)	0.0588 (9)	0.0118 (5)	0.0027 (5)	0.0283 (6)
O1	0.0192 (6)	0.0197 (6)	0.0207 (6)	0.0086 (5)	−0.0039 (5)	−0.0035 (5)

Geometric parameters (Å, º)

Co1—N1	1.9605 (13)	C5—C4	1.361 (2)
Co1—N1^i	1.9605 (13)	C5—H5	0.9500
Co1—N1^{ii}	1.9605 (13)	C2—H2	0.9500
Co1—N1^{iii}	1.9605 (13)	C4—H4	0.9500
Co1—N1^{iv}	1.9605 (13)	P1—F1^{vi}	1.5939 (12)
Co1—N1^v	1.9605 (13)	P1—F1	1.5938 (12)
F2—P1	1.5985 (9)	P1—F2^{vi}	1.5985 (9)
N1—C2	1.3340 (19)	P1—F3^{vi}	1.6012 (11)
N1—C5	1.3854 (19)	P1—F3	1.6012 (11)
N3—C2	1.339 (2)	O1—H6	0.96 (3)
N3—C4	1.369 (2)	O1—H7	0.96 (3)
N3—H3	0.8800		
N1—Co1—N1^i	88.68 (5)	N1—C5—H5	125.5
N1—Co1—N1^{ii}	91.32 (5)	N1—C2—N3	110.48 (14)
N1—Co1—N1^v	88.68 (5)	N1—C2—H2	124.8
N1—Co1—N1^{iii}	180.00 (9)	N3—C2—H2	124.8
N1^v—Co1—N1^{iii}	91.32 (5)	C5—C4—N3	106.26 (14)
N1^v—Co1—N1^i	91.32 (5)	C5—C4—H4	126.9
N1^{iii}—Co1—N1^i	91.32 (5)	N3—C4—H4	126.9
N1^v—Co1—N1^{ii}	180.00 (9)	F1^{vi}—P1—F1	180.0
N1^{iii}—Co1—N1^{ii}	88.68 (5)	F1^{vi}—P1—F2	89.75 (6)
N1^i—Co1—N1^{ii}	88.68 (5)	F1—P1—F2	90.25 (6)
N1—Co1—N1^{iv}	91.32 (5)	F1^{vi}—P1—F2^{vi}	90.25 (6)
N1^v—Co1—N1^{iv}	88.68 (5)	F1—P1—F2^{vi}	89.75 (6)
N1^{iii}—Co1—N1^{iv}	88.68 (5)	F2—P1—F2^{vi}	179.997 (1)
N1^i—Co1—N1^{iv}	180.00 (5)	F1^{vi}—P1—F3^{vi}	90.13 (8)
N1^{ii}—Co1—N1^{iv}	91.32 (5)	F1—P1—F3^{vi}	89.86 (8)
C2—N1—C5	105.91 (12)	F2—P1—F3^{vi}	90.15 (6)
C2—N1—Co1	126.96 (11)	F2^{vi}—P1—F3^{vi}	89.85 (6)
C5—N1—Co1	126.84 (10)	F1^{vi}—P1—F3	89.86 (8)
C2—N3—C4	108.30 (13)	F1—P1—F3	90.14 (8)
C2—N3—H3	125.8	F2—P1—F3	89.85 (6)
C4—N3—H3	125.8	F2^{vi}—P1—F3	90.15 (6)
C4—C5—N1	109.04 (14)	F3^{vi}—P1—F3	180.0
C4—C5—H5	125.5	H6—O1—H7	105.7 (19)
N1^v—Co1—N1—C2	−98.46 (15)	C2—N1—C5—C4	0.10 (17)
N1^i—Co1—N1—C2	−7.11 (13)	Co1—N1—C5—C4	−174.02 (11)
N1^{ii}—Co1—N1—C2	81.54 (15)	C5—N1—C2—N3	0.45 (17)
N1^{iv}—Co1—N1—C2	172.89 (13)	Co1—N1—C2—N3	174.56 (10)
N1^v—Co1—N1—C5	74.46 (10)	C4—N3—C2—N1	−0.82 (18)
N1^i—Co1—N1—C5	165.81 (14)	N1—C5—C4—N3	−0.58 (18)

| N1ii—Co1—N1—C5 | −105.54 (10) | C2—N3—C4—C5 | 0.85 (18) |
| N1iv—Co1—N1—C5 | −14.19 (14) | | |

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H6···O1vii	0.96 (3)	1.98 (3)	2.913 (2)	163 (3)
N3—H3···O1	0.88	1.98	2.834 (2)	165
O1—H7···F3viii	0.96 (3)	2.10 (3)	2.945 (2)	146 (2)
C2—H2···F3vi	0.95	2.34	3.042 (2)	131
C4—H4···F1ix	0.95	2.40	3.303 (2)	158

Symmetry codes: (vi) $-x+2/3$, $-y+1/3$, $-z+1/3$; (vii) $-y+2/3$, $x-y+1/3$, $z+1/3$; (viii) $x-y$, x, $-z+1$; (ix) $-x+y+1/3$, $-x+2/3$, $z+2/3$.