



Crystal structure of {2,2'-[*N,N'*-bis(pyridin-2-ylmethyl)cyclohexane-*trans*-1,2-diyl]di(nitrilo)]diacetato}cobalt(III) hexafluoridophosphate

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Received 24 February 2015

Accepted 13 March 2015

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Edited by M. Zeller, Youngstown State University, USA

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Keywords: crystal structure; polyaminocarboxylic acid; cobalt(III); chelating ligand

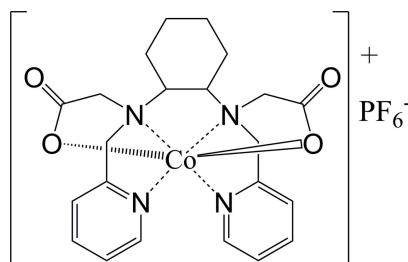
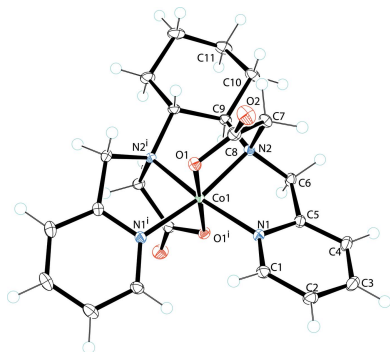
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The title compound [Co(C₂₂H₂₆N₄O₄)]PF₆, commonly known as [Co(bpcd)]PF₆, where bpcd²⁻ is derived from the historical ligand name *N,N'*-bis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane-*N,N'*-diacetate, crystallized by slow evaporation of a saturated acetonitrile solution in air. The cation of the hexafluoridophosphate salt has the Co^{III} atom in a distorted octahedral coordination geometry provided by an N₄O₂ donor atom set. The acetate groups, which are oriented *trans* with respect to each other, exhibit monodentate coordination whereas the pyridyl N atoms are coordinating in a *cis* configuration. The geometry of the cation is compared to the geometries of other diamino diacetate complexes with Co^{III}.

1. Chemical context

Polyaminocarboxylic acids are of considerable interest as complexation reagents for a variety of metal ions in a wide range of applications (Weaver & Kappelmann, 1964; Weiner & Thakur, 1995; Caravan *et al.*, 1997*a,b*; Gerald, 1999; Heitzmann *et al.*, 2009). The title compound, [Co(bpcd)]PF₆, (I), was prepared from *N,N'*-bis(2-pyridylmethyl)-*trans*-1,2-diaminocyclohexane-*N,N'*-diacetic acid (H₂bpdc), a symmetrically disubstituted polyaminocarboxylic acid featuring a chiral *trans*-diaminocyclohexane backbone.



The ligand precursor, H₂bpdc, belongs to a relatively small group of diamino diacetic acids that contain softer aromatic nitrogen donor groups (Fig. 1) (Caravan *et al.*, 1997*a*; Heitzmann *et al.*, 2009; Kissel *et al.*, 2014). The preorganized ligand precursor H₂bpdc is of interest as a novel candidate for selective and efficient actinide(III)/lanthanide(III) separations. Preorganization of a ligand can reduce the pre-orientation energy required for metal ion complexation and provide improved metal–ligand complex stability (Rizkalla *et al.*, 1987; Choppin *et al.*, 2006; Ogden *et al.*, 2012). The addition of aromatic functionalities, such as pyridine and pyrazine, may increase ligand selectivity for softer metal ions and provide

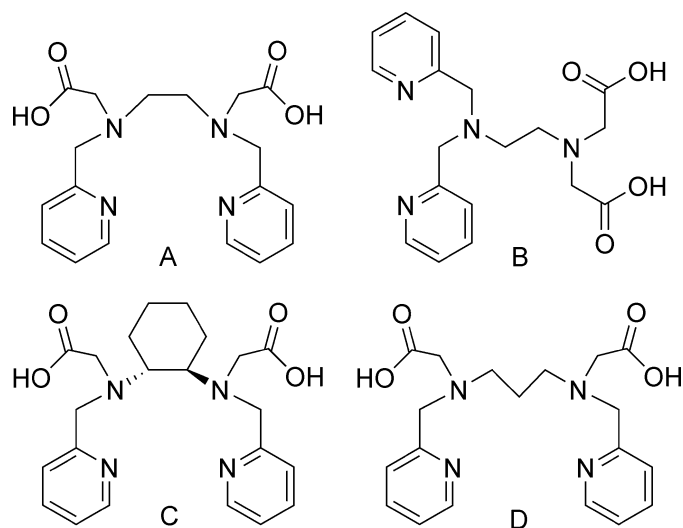


Figure 1

The diamino diacetic acids, H_2bped (A) and *gem*- H_2bped (B), where bped stands for bis(2-pyridylmethyl)-1,2-diaminoethane diacetate, H_2bpcd (C), and H_2bppd (D), where bppd stands for bis(2-pyridylmethyl)-1,3-diaminopropane diacetate.

greater stability towards radiolysis (Heitzmann *et al.*, 2009). The members of this group of diacetic acids, however, differ in the nature of the diamine backbone.

The ethylenediamine backbone is a classic scaffold that has been used for the construction of many polydentate ligands. The amine N atoms are ideal for functionalization, which allows different donor atom groups to be incorporated into a ligand's design. The close proximity of the diamine nitrogens also maximizes the number of possible five- and six-membered chelate rings capable of forming upon metal ion complexation. H_2bped (A) is a hexadentate 2-pyridylmethyl-substituted diacetic acid based on this classic scaffold (Lacoste *et al.*, 1965; Caravan *et al.*, 1997a). *gem*- H_2bped (B) is a very closely related 2-pyridylmethyl-substituted diacetic acid that is also based on the ethylenediamine scaffold. In this case, however, both pyridine substituents are bonded to the same amine N atom (Heitzmann *et al.*, 2009). The C–C chain length between

the N atoms in the diamine backbone of these ligands allows for the formation of five-membered chelate rings. Hancock has shown the formation of five-membered chelate rings to be more favourable for larger metal ions than for smaller metal ions (Hancock & Martell, 1989). The ligand precursor, H_2bpcd (C), for the title compound is similar to A and B, but it incorporates the ethylenediamine backbone into a cyclohexyl group. Restricted rotation about the C–C bonds in the cyclohexane ring fixes the positions of the trans diamine nitrogen atoms and favourably preorganizes these donor groups for metal ion complexation. Consequently, the trans amine groups are constrained into a conformation that is pre-oriented favorably for binding and results in a complex of increased stability (Rizkalla *et al.*, 1987; Choppin *et al.*, 2006; Ogden *et al.*, 2012). In contrast, H_2bppd (D) features a 1,3-diaminopropane backbone that provides greater flexibility compared to A, B, or C with their shorter backbones. Further, the increased chain length of the propylene linker allows a six-membered chelate ring to form upon metal complexation. Formation of six-membered chelate rings in complexes with smaller metal ions has been shown to increase the stability of the complex relative to five-membered rings (Hancock & Martell, 1989). Here, we report the structure of a Co^{III} complex with $bpcd^{2-}$, C.

2. Structural commentary

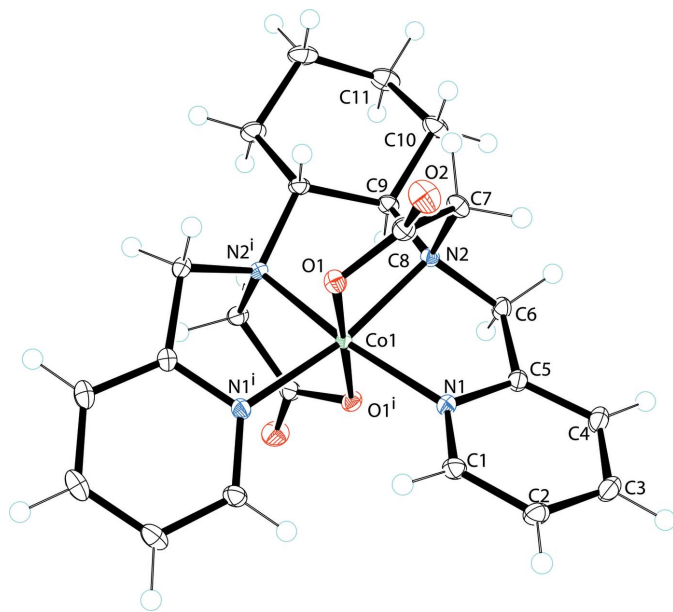
The structure of the $[Co(bpcd)]^+$ cation in the title compound is shown in Fig. 2 and selected geometric parameters are listed in Table 1. The cation is very similar to the structures of the $[Co(bped)]^+$ and $[Co(bppd)]^+$ complex ions. Nearly all of the Co–O_{ac} bond lengths for the five structures given in Table 1 are within experimental error of each other. One of the Co–O_{ac} bond lengths in the $[Co(bppd)]^+$ cation, however, is slightly shorter than the others. The C–O and C=O bond lengths are also quite similar. There are, however, some variations in the bond lengths and angles as shown in Tables 1 and 2. The Co–N_{am} bond length in the $[Co(bpcd)]^+$ cation is slightly shorter than the Co–N_{am} bond lengths reported for the two $[Co(bppd)]^+$ cations given in Table 1. They are,

Table 1

Bond distances (Å) and experimental data for different $[Co(bpad)]^+$ structures.

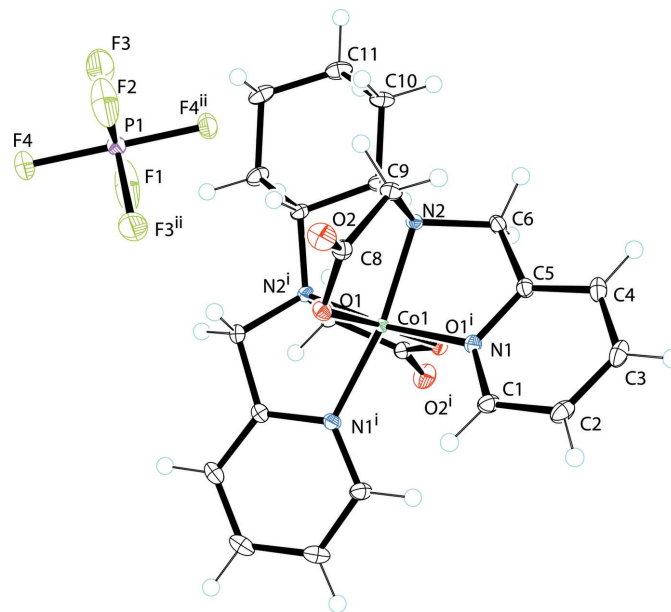
Bond (Å)	Co(bped) ⁺ ^a	Co(bped) ⁺ ^b	Co(bppd) ⁺ ^c 1	Co(bppd) ⁺ ^c 2	Co(bpcd) ⁺ ^d
Co–O _{ac1}	1.888 (1)	1.878 (2)	1.8828 (11)	1.8875 (10)	1.8869 (8)
Co–O _{ac2}	1.889 (2)	1.888 (2)	1.8899 (11)	1.8830 (11)	*
Co–N _{am1}	1.941 (2)	1.937 (2)	1.9625 (13)	1.9654 (12)	1.9548 (9)
Co–N _{am2}	1.974 (2)	1.941 (2)	1.9641 (13)	1.9645 (12)	*
Co–N _{pyr1}	1.944 (2)	1.960 (2)	1.9484 (13)	1.9403 (13)	1.9448 (9)
Co–N _{pyr2}	1.954 (2)	1.958 (2)	1.9397 (13)	1.9576 (13)	*
C–O _{ac1}	1.294 (2)	1.298 (4)	1.2973 (18)	1.3054 (18)	1.3029 (13)
C=O _{ac1}	1.212 (3)	1.218 (3)	1.2265 (18)	1.219 (2)	1.2212 (14)
C–O _{ac2}	1.289 (3)	1.299 (3)	1.3035 (19)	1.2971 (19)	*
C=O _{ac2}	1.210 (3)	1.213 (3)	1.2201 (19)	0.0030 (6)	*
Co above N/N/N plane	0.000 [†]	0.012 [†]	0.0026 (6)	0.0030 (6)	0**
Temp, K	298	293	100	100	100

Notes: (a) Mandel & Douglas (1989); (b) Caravan *et al.* (1997a); (c) two cations in asymmetric unit (McLauchlan *et al.*, 2013); (d) this work; (*) N/A – symmetry equivalent; (†) standard uncertainty unavailable; (**) N/A – sits on a special position.


Figure 2

View of the cation of the title structure, $[\text{Co}(\text{bpcd})]^+$. Here and in subsequent figures, displacement ellipsoids are shown at the 50% probability level. H atoms are shown as circles of arbitrary size. [Symmetry code: (i) $-x + 1, -y + \frac{1}{2}, z$.]

however, slightly longer than those reported for the $[\text{Co}(\text{bped})]^+$ structures. Similarly, the $\text{N}_{\text{am}1}-\text{Co}-\text{N}_{\text{am}2}$ bond angle in $[\text{Co}(\text{bpcd})]^+$ is close to ideal (90°), whereas the $\text{N}_{\text{am}1}-\text{Co}-\text{N}_{\text{am}2}$ angles in the $[\text{Co}(\text{bppd})]^+$ structures are somewhat larger than ideal and somewhat smaller than ideal in the $[\text{Co}(\text{bped})]^+$ structures (Table 2). The $\text{O}_{\text{ac}1}-\text{Co}-\text{O}_{\text{ac}2}$ bond angles for the five structures in Table 2 are all close to ideal (180°), with the largest deviation from linearity observed in the $[\text{Co}(\text{bpcd})]^+$ cation. The 176.1° $\text{O}_{\text{ac}1}-\text{Co}-\text{O}_{\text{ac}2}$ bond angle in $[\text{Co}(\text{bpcd})]^+$ is 2° smaller than the average (178.5°) of the bond angles reported for the $[\text{Co}(\text{bped})]^+$ and $[\text{Co}(\text{bppd})]^+$ cations. Finally, the Co^{III} in the title compound is situated directly in the N_4 plane of the equatorial nitrogen atoms, whereas in three of the other four structures the Co^{III} lays slightly out-of the plane (Table 1). The solid-state structural parameters for $[\text{Co}(\text{bpcd})]^+$, which are very similar to those for


Figure 3

View of the molecular components of the title structure, $[\text{Co}(\text{bpcd})]\text{PF}_6$. [Symmetry code: (i) $-x + 1, -y + \frac{1}{2}, z$.]

$\text{Co}(\text{bped})^+$, suggest that the ligand precursor $\text{H}_2(\text{bpcd})$, with its preorganized arrangement, may provide greater metal ion complex stability as well as be selective for actinides(III) over lanthanides(III) as demonstrated for *gem*- $\text{H}_2(\text{bped})$. (Heitzmann *et al.*, 2009)

3. Supramolecular features

The structure of the title compound (Fig. 3) exists in the solid state as an intricate network of anions and cations closely associated through many short interactions. Hydrogen-bonding interactions are listed in Table 3. Each PF_6^- anion is in close contact with six cations: three of the four unique F atoms interact with two neighboring cations while the remaining atom, F4, has a long interaction (2.29 \AA) with only the $\text{C}-\text{H9A}$ bond of the cyclohexyl ring of one cation. This $\text{F4} \cdots \text{H9A}$ interaction is the shortest of the $\text{F} \cdots \text{H}$ interactions present with two other weaker $\text{F} \cdots \text{H}$ interactions of 2.49

Table 2

Selected bond angles ($^\circ$) for different $[\text{Co}(\text{bpad})]^+$ structures.

Angle, $^\circ$	$\text{Co}(\text{bped})^+{}^a$	$\text{Co}(\text{bped})^+{}^b$	$\text{Co}(\text{bppd})^+{}^c$ 1	$\text{Co}(\text{bppd})^+{}^c$ 2	$\text{Co}(\text{bpcd})^+{}^d$
$\text{O}_{\text{ac}1}-\text{Co}-\text{O}_{\text{ac}2}$	178.8 (1)	178.53 (8)	178.47 (5)	178.36 (5)	176.08 (5)
$\text{N}_{\text{am}1}-\text{Co}-\text{N}_{\text{am}2}$	82.0 (1)	88.87 (9)	95.91 (5)	95.92 (5)	89.33 (5)
$\text{N}_{\text{pyr}1}-\text{Co}-\text{N}_{\text{pyr}2}$	82.3 (1)	107.01 (9)	98.52 (6)	98.55 (5)	106.74 (5)
$\text{N}_{\text{am}1}-\text{Co}-\text{N}_{\text{pyr}1}$	89.3 (1)	82.14 (9)	82.36 (6)	83.23 (5)	82.17 (4)
$\text{N}_{\text{am}2}-\text{Co}-\text{N}_{\text{pyr}2}$	107.0 (1)	82.51 (9)	83.28 (6)	82.39 (5)	*
$\text{N}_{\text{am}1}-\text{Co}-\text{O}_{\text{ac}1}$	86.9 (1)	87.36 (9)	88.81 (5)	87.96 (5)	87.84 (4)
$\text{N}_{\text{pyr}1}-\text{Co}-\text{O}_{\text{ac}1}$	92.8 (1)	92.34 (8)	86.51 (5)	87.72 (5)	89.92 (4)
$\text{O}=\text{C}-\text{O}_{\text{ac}}$	124.4 (2)	123.9 (3)	123.87 (14)	123.80 (14)	124.95 (10)
	124.7 (2)	124.8 (3)	123.95 (15)	123.82 (14)	*
$\text{C}(\text{O})-\text{O}_{\text{ac}}-\text{Co}$	116.4 (1)	116.4 (2)	114.32 (9)	115.33 (10)	114.57 (7)
	115.9 (1)	115.3 (2)	115.11 (10)	114.38 (9)	*

Notes: (a) Mandel & Douglas (1989); (b) Caravan *et al.* (1997a); (c) two cations in asymmetric unit (McLauchlan *et al.*, 2013); (d) this work; (*) N/A – symmetry equivalent; (**) N/A – sits on a special position.

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

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
C1—H1A···O2 ⁱⁱ	0.95	2.84	3.4475 (15)	122
C2—H2A···F3 ⁱⁱⁱ	0.95	2.51	3.2928 (15)	139
C4—H4A···O2 ^{iv}	0.95	2.70	3.5907 (15)	157
C6—H6A···F2 ^v	0.99	2.52	3.4243 (13)	152
C6—H6B···F1 ^{vi}	0.99	2.74	3.3824 (13)	123
C6—H6B···F3 ^{vi}	0.99	2.84	3.8229 (18)	170
C7—H7A···F4 ^{vii}	0.99	2.68	3.3879 (13)	128
C7—H7A···F4 ^{iv}	0.99	2.67	3.2436 (13)	117
C7—H7B···F3 ^v	0.99	2.62	3.4982 (16)	147
C9—H9A···F1 ^{vi}	1.00	2.64	3.2790 (12)	122
C9—H9A···F4 ^{vi}	1.00	2.29	3.2336 (13)	157
C10—H10A···F1 ^{vi}	0.99	2.49	3.1429 (15)	123
C10—H10A···F2 ^v	0.99	2.35	3.0728 (14)	129
C10—H10B···F4 ^{iv}	0.99	2.77	3.5399 (14)	135

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

(F1···H10A) and 2.64 Å (F1···H9A) to cyclohexyl H atoms. There are also several interactions between pyridyl ring H atoms and carboxylate O atoms from neighboring cations, *i.e.* a 2.408 Å interaction with Co-bound oxygen O1, and a 2.700 Å interaction with terminal oxygen O2. The short interaction has a C—H···O angle of 140.7° so it does not appear in Table 3. There also exists π – π stacking for each of the two pyridyl rings with neighboring cations stacked anti-parallel. Each has a distance of 3.829 (13) Å between ring centroids.

4. Database survey

There is very little information in the literature about H₂bpcd and its metal complexes. There is a structurally characterized heptacoordinate [Fe^{II}(H₂bpcd)(C₃H₆O)](ClO₄)₂ complex with trans pyridine N atoms and cis carboxylic acid groups (Oddon *et al.*, 2012). In that case, Fe^{II} is coordinated in a distorted pentagonal–bipyramidal geometry with an unusual N₄O₃ donor atom set, including a bound acetone molecule. The carboxylic acid moieties are fully protonated with the H₂bpcd ligand coordinating through the carbonyl O atoms, which reside in the equatorial plane. The coordinating amine N atoms also lie in this plane, whereas the pyridyl N atoms are coordinating at the axial positions. This unique arrangement results in longer Fe—O and Fe—N_{py} bonds than are typically observed. In the present case, a fully deprotonated bpcd²⁻ ligand binds Co^{III} in a pseudo-octahedral fashion with trans acetate groups to form a hexacoordinate complex.

Although only one structure of a metal–H₂bpcd complex has been reported in the literature, there are several structures reported for related pseudo-octahedral Co^{III} complexes with bis-2-pyridylmethyl substituted diamino diacetic acids, *i.e.* H₂bped (A) and H₂bppd (D) in Fig. 1. We previously reported the structure of [Co(bppd)]PF₆ (McLauchlan *et al.*, 2013), and there are two structural reports for the [Co(bped)]⁺ complex ion with different counter-ions, *e.g.* BF₄⁻ and PF₆⁻ (Mandel & Douglas, 1989; Caravan *et al.*, 1997a). In these cases, the Co^{III}–

Table 4
Experimental details.

Crystal data	
Chemical formula	[Co(C ₂₂ H ₂₆ N ₄ O ₄)]PF ₆
<i>M_r</i>	614.37
Crystal system, space group	Orthorhombic, <i>Ibca</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.9848 (4), 14.6221 (4), 22.2177 (6)
<i>V</i> (Å ³)	4543.2 (2)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.92
Crystal size (mm)	0.44 × 0.36 × 0.21
Data collection	
Diffractometer	Bruker APEXII equipped with a CCD detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.691, 0.834
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	57644, 3630, 3401
<i>R_{int}</i>	0.017
(<i>sin</i> θ/ <i>λ</i>) _{max} (Å ⁻¹)	0.725
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.027, 0.079, 1.12
No. of reflections	3630
No. of parameters	174
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.66, -0.52

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *enCIFer* (Allen *et al.*, 2004) and *pubCIF* (Westrip, 2010).

bppd²⁻ and Co^{III}–bped²⁻ complexes form similar hexadentate structures with acetate O atoms in a trans orientation and pyridyl N atoms in a cis orientation.

5. Synthesis and crystallization

H₂bpcd (C) was prepared from *trans*-1,2-diaminocyclohexane using the procedure reported for H₂bppd (D) (Kissel *et al.*, 2014). The title compound was prepared using methods analogous to those previously reported for [Co(bppd)]PF₆ (McLauchlan *et al.*, 2013). Crystals suitable for diffraction were isolated by slow evaporation of a saturated acetonitrile solution (yield: 120 mg, 0.20 mmol, 40%).

Analysis observed (calculated) for CoC₂₂H₂₈N₄O₄PF₆: C 42.56 (43.00), H 3.85 (4.26), N 8.94 (9.11). IR (ν cm⁻¹, KBr): 3048 (*m*, C—H aryl str), 2945 (*m*, CH₂ str), 1665 (*vs*, COO⁻ str), 1612 (*m*, py str), 1477 (*w*, py str), 1445 (*m*, CH₂ def), 1384 (*s*, COO⁻ str).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. The structure of the title complex can be solved and refined in *Ibca* with well-separated cations and anions. There is a small amount of disorder that can be modelled for the PF₆⁻ anion. F2 and F3 can be moved in the plane. *R*1 can be reduced to 0.0252 by modeling this disorder,

but the occupancy is less than 10% and results in a less chemically satisfactory PF_6^- anion. Therefore, the disorder was not modelled. All H atoms were placed geometrically ($\text{C}-\text{H} = 0.93\text{--}0.97 \text{ \AA}$) and refined using a riding model.

Acknowledgements

This work was supported by Illinois State University and Loyola University Chicago. CCM acknowledges the National Science Foundation for the purchase of the Bruker APEXII diffractometer (CHE-10-39689). DSK wishes to thank Loyola University Chicago and the Schmitt Foundation for fifth year fellowship support.

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supporting information

Acta Cryst. (2015). E71, 380-384 [doi:10.1107/S2056989015005149]

Crystal structure of {2,2'-[N,N'-bis(pyridin-2-ylmethyl)cyclohexane-*trans*-1,2-diyl]di(nitrilo)]diacetato}cobalt(III) hexafluoridophosphate

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Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINTE* (Bruker, 2008); data reduction: *SAINTE* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *pubCIF* (Westrip, 2010).

{2,2'-[N,N'-Bis(pyridin-2-ylmethyl)cyclohexane-*trans*-1,2-diyl]di(nitrilo)]diacetato}cobalt(III) hexafluoridophosphate

Crystal data

[Co(C₂₂H₂₆N₄O₄)]PF₆

M_r = 614.37

Orthorhombic, *Ibca*

a = 13.9848 (4) Å

b = 14.6221 (4) Å

c = 22.2177 (6) Å

V = 4543.2 (2) Å³

Z = 8

F(000) = 2512

D_x = 1.796 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 9742 reflections

θ = 2.7–31.0°

μ = 0.92 mm⁻¹

T = 100 K

Parallelipiped, translucent dark red

0.44 × 0.36 × 0.21 mm

Data collection

Bruker APEXII

diffractometer equipped with a CCD detector

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm⁻¹

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2008)

T_{min} = 0.691, *T_{max}* = 0.834

57644 measured reflections

3630 independent reflections

3401 reflections with *I* > 2σ(*I*)

R_{int} = 0.017

θ_{max} = 31.0°, θ_{min} = 1.8°

h = -20→20

k = -21→21

l = -32→32

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.027

wR(*F*²) = 0.079

S = 1.12

3630 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 5.6191P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$$\Delta\rho_{\max} = 0.66 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$$

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. There is a small amount of disorder that can be modeled for the PF_6 anion. F2 and F3 can be moved in the plane, as one might imagine. R1 can be reduced to 0.0252 by modeling it, but the occupancy is less than 10% and results in a less chemically satisfactory PF_6 anion. Therefore, the disorder was not modeled.

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	0.5000	0.2500	0.09254 (2)	0.00761 (6)
N1	0.43958 (7)	0.15960 (6)	0.04005 (4)	0.01066 (16)
N2	0.43848 (6)	0.17734 (6)	0.15480 (4)	0.00930 (16)
O1	0.38813 (6)	0.32200 (5)	0.08964 (3)	0.01162 (15)
O2	0.23055 (6)	0.30823 (7)	0.10495 (4)	0.01942 (18)
C1	0.41181 (8)	0.16885 (8)	-0.01758 (5)	0.01342 (19)
H1A	0.4189	0.2265	-0.0369	0.016*
C2	0.37301 (8)	0.09611 (8)	-0.04959 (5)	0.0159 (2)
H2A	0.3555	0.1035	-0.0906	0.019*
C3	0.36018 (8)	0.01258 (8)	-0.02102 (6)	0.0160 (2)
H3A	0.3356	-0.0384	-0.0426	0.019*
C4	0.38383 (8)	0.00449 (8)	0.03974 (5)	0.0145 (2)
H4A	0.3729	-0.0511	0.0607	0.017*
C5	0.42361 (7)	0.07927 (7)	0.06891 (5)	0.01135 (18)
C6	0.44904 (8)	0.08027 (7)	0.13472 (5)	0.01223 (18)
H6A	0.4055	0.0399	0.1577	0.015*
H6B	0.5156	0.0590	0.1408	0.015*
C7	0.33453 (7)	0.20455 (8)	0.15563 (5)	0.01188 (19)
H7A	0.3164	0.2220	0.1971	0.014*
H7B	0.2951	0.1513	0.1439	0.014*
C8	0.31295 (8)	0.28378 (8)	0.11346 (5)	0.01202 (18)
C9	0.49132 (7)	0.19846 (8)	0.21257 (5)	0.01084 (18)
H9A	0.5551	0.1678	0.2102	0.013*
C10	0.44229 (8)	0.16490 (8)	0.27004 (5)	0.0154 (2)
H10A	0.4399	0.0972	0.2700	0.019*
H10B	0.3758	0.1882	0.2714	0.019*
C11	0.49688 (8)	0.19815 (10)	0.32563 (5)	0.0182 (2)
H11A	0.4637	0.1772	0.3625	0.022*
H11B	0.5621	0.1718	0.3256	0.022*

P1	0.30339 (3)	0.5000	0.2500	0.01160 (8)
F1	0.41712 (9)	0.5000	0.2500	0.0503 (5)
F2	0.19013 (9)	0.5000	0.2500	0.0417 (4)
F3	0.30336 (11)	0.49194 (7)	0.32124 (4)	0.0470 (3)
F4	0.30308 (5)	0.60985 (5)	0.25526 (4)	0.01831 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.00914 (10)	0.00719 (10)	0.00650 (10)	−0.00083 (6)	0.000	0.000
N1	0.0118 (4)	0.0103 (4)	0.0099 (4)	−0.0015 (3)	−0.0002 (3)	−0.0010 (3)
N2	0.0103 (4)	0.0095 (4)	0.0081 (4)	−0.0005 (3)	0.0000 (3)	0.0010 (3)
O1	0.0113 (3)	0.0106 (3)	0.0130 (3)	0.0008 (3)	−0.0004 (3)	0.0018 (3)
O2	0.0119 (4)	0.0223 (4)	0.0241 (4)	0.0033 (3)	−0.0017 (3)	0.0040 (3)
C1	0.0140 (4)	0.0167 (5)	0.0095 (4)	−0.0025 (4)	0.0000 (3)	−0.0006 (3)
C2	0.0133 (5)	0.0222 (5)	0.0123 (4)	−0.0031 (4)	0.0001 (4)	−0.0053 (4)
C3	0.0117 (4)	0.0167 (5)	0.0198 (5)	−0.0014 (4)	0.0007 (4)	−0.0087 (4)
C4	0.0129 (4)	0.0105 (4)	0.0200 (5)	−0.0008 (3)	0.0003 (4)	−0.0036 (4)
C5	0.0111 (4)	0.0100 (4)	0.0129 (4)	−0.0007 (3)	0.0004 (3)	−0.0008 (3)
C6	0.0156 (4)	0.0087 (4)	0.0124 (4)	−0.0011 (3)	−0.0010 (4)	0.0014 (3)
C7	0.0095 (4)	0.0143 (5)	0.0118 (4)	−0.0003 (3)	0.0000 (3)	0.0026 (3)
C8	0.0125 (4)	0.0125 (4)	0.0111 (4)	0.0001 (4)	−0.0010 (3)	−0.0002 (3)
C9	0.0115 (4)	0.0133 (5)	0.0077 (4)	−0.0004 (3)	−0.0007 (3)	0.0013 (3)
C10	0.0163 (5)	0.0208 (5)	0.0092 (4)	−0.0020 (4)	0.0011 (4)	0.0037 (4)
C11	0.0182 (5)	0.0277 (6)	0.0087 (4)	0.0011 (4)	−0.0006 (4)	0.0031 (4)
P1	0.01124 (17)	0.01151 (17)	0.01203 (17)	0.000	0.000	0.00031 (13)
F1	0.0127 (5)	0.0204 (6)	0.1178 (16)	0.000	0.000	−0.0134 (8)
F2	0.0128 (5)	0.0206 (6)	0.0916 (13)	0.000	0.000	−0.0056 (7)
F3	0.1008 (10)	0.0246 (5)	0.0157 (4)	0.0046 (5)	−0.0073 (5)	−0.0001 (3)
F4	0.0176 (3)	0.0116 (3)	0.0258 (4)	0.0001 (2)	−0.0029 (3)	−0.0010 (3)

Geometric parameters (Å, °)

Co1—O1 ⁱ	1.8869 (8)	C5—C6	1.5050 (15)
Co1—O1	1.8869 (8)	C6—H6A	0.9900
Co1—N1	1.9548 (9)	C6—H6B	0.9900
Co1—N1 ⁱ	1.9548 (9)	C7—C8	1.5201 (15)
Co1—N2	1.9448 (9)	C7—H7A	0.9900
Co1—N2 ⁱ	1.9449 (9)	C7—H7B	0.9900
N1—C1	1.3448 (14)	C9—C9 ⁱ	1.527 (2)
N1—C5	1.3567 (14)	C9—C10	1.5300 (15)
N2—C6	1.4951 (14)	C9—H9A	1.0000
N2—C7	1.5073 (14)	C10—C11	1.5312 (16)
N2—C9	1.5130 (13)	C10—H10A	0.9900
O1—C8	1.3029 (13)	C10—H10B	0.9900
O2—C8	1.2212 (14)	C11—C11 ⁱ	1.519 (3)
C1—C2	1.3898 (15)	C11—H11A	0.9900
C1—H1A	0.9500	C11—H11B	0.9900

C2—C3	1.3882 (17)	P1—F2	1.5840 (13)
C2—H2A	0.9500	P1—F3	1.5872 (9)
C3—C4	1.3949 (17)	P1—F3 ⁱⁱ	1.5873 (9)
C3—H3A	0.9500	P1—F1	1.5905 (14)
C4—C5	1.3873 (15)	P1—F4	1.6106 (7)
C4—H4A	0.9500	P1—F4 ⁱⁱ	1.6106 (7)
O1 ⁱ —Co1—O1	176.08 (5)	C5—C6—H6B	110.5
O1 ⁱ —Co1—N2	94.95 (4)	H6A—C6—H6B	108.7
O1—Co1—N2	87.84 (4)	N2—C7—C8	112.65 (8)
O1 ⁱ —Co1—N2 ⁱ	87.84 (4)	N2—C7—H7A	109.1
O1—Co1—N2 ⁱ	94.95 (4)	C8—C7—H7A	109.1
N2—Co1—N2 ⁱ	89.33 (5)	N2—C7—H7B	109.1
O1 ⁱ —Co1—N1	87.75 (4)	C8—C7—H7B	109.1
O1—Co1—N1	89.92 (4)	H7A—C7—H7B	107.8
N2—Co1—N1	82.17 (4)	O2—C8—O1	124.95 (10)
N2 ⁱ —Co1—N1	170.04 (4)	O2—C8—C7	120.39 (10)
O1 ⁱ —Co1—N1 ⁱ	89.92 (4)	O1—C8—C7	114.65 (9)
O1—Co1—N1 ⁱ	87.75 (4)	N2—C9—C9 ⁱ	106.21 (7)
N2—Co1—N1 ⁱ	170.04 (4)	N2—C9—C10	115.07 (9)
N2 ⁱ —Co1—N1 ⁱ	82.17 (4)	C9 ⁱ —C9—C10	112.82 (7)
N1—Co1—N1 ⁱ	106.74 (5)	N2—C9—H9A	107.5
C1—N1—C5	119.30 (9)	C9 ⁱ —C9—H9A	107.5
C1—N1—Co1	128.67 (8)	C10—C9—H9A	107.5
C5—N1—Co1	112.01 (7)	C9—C10—C11	110.36 (9)
C6—N2—C7	110.46 (8)	C9—C10—H10A	109.6
C6—N2—C9	113.49 (8)	C11—C10—H10A	109.6
C7—N2—C9	114.01 (8)	C9—C10—H10B	109.6
C6—N2—Co1	105.23 (6)	C11—C10—H10B	109.6
C7—N2—Co1	106.93 (6)	H10A—C10—H10B	108.1
C9—N2—Co1	106.01 (6)	C11 ⁱ —C11—C10	110.22 (9)
C8—O1—Co1	114.57 (7)	C11 ⁱ —C11—H11A	109.6
N1—C1—C2	121.54 (10)	C10—C11—H11A	109.6
N1—C1—H1A	119.2	C11 ⁱ —C11—H11B	109.6
C2—C1—H1A	119.2	C10—C11—H11B	109.6
C3—C2—C1	119.32 (10)	H11A—C11—H11B	108.1
C3—C2—H2A	120.3	F2—P1—F3	89.98 (6)
C1—C2—H2A	120.3	F2—P1—F3 ⁱⁱ	89.98 (6)
C2—C3—C4	119.11 (10)	F3—P1—F3 ⁱⁱ	179.97 (11)
C2—C3—H3A	120.4	F2—P1—F1	180.0
C4—C3—H3A	120.4	F3—P1—F1	90.02 (6)
C5—C4—C3	118.70 (11)	F3 ⁱⁱ —P1—F1	90.02 (6)
C5—C4—H4A	120.6	F2—P1—F4	89.84 (3)
C3—C4—H4A	120.6	F3—P1—F4	90.09 (5)
N1—C5—C4	121.85 (10)	F3 ⁱⁱ —P1—F4	89.91 (5)
N1—C5—C6	114.31 (9)	F1—P1—F4	90.16 (3)
C4—C5—C6	123.80 (10)	F2—P1—F4 ⁱⁱ	89.84 (3)
N2—C6—C5	106.01 (8)	F3—P1—F4 ⁱⁱ	89.91 (5)

N2—C6—H6A	110.5	F3 ⁱⁱ —P1—F4 ⁱⁱ	90.09 (5)
C5—C6—H6A	110.5	F1—P1—F4 ⁱⁱ	90.16 (3)
N2—C6—H6B	110.5	F4—P1—F4 ⁱⁱ	179.69 (6)
N2—Co1—O1—C8	-17.97 (8)	N1—C5—C6—N2	27.33 (12)
N2 ⁱ —Co1—O1—C8	-107.11 (8)	C4—C5—C6—N2	-150.39 (10)
N1—Co1—O1—C8	64.20 (8)	C6—N2—C7—C8	-119.41 (9)
N1 ⁱ —Co1—O1—C8	170.96 (8)	C9—N2—C7—C8	111.40 (10)
C5—N1—C1—C2	-4.46 (16)	Co1—N2—C7—C8	-5.42 (10)
Co1—N1—C1—C2	177.37 (8)	Co1—O1—C8—O2	-162.99 (10)
N1—C1—C2—C3	1.77 (17)	Co1—O1—C8—C7	18.41 (12)
C1—C2—C3—C4	1.97 (17)	N2—C7—C8—O2	173.28 (10)
C2—C3—C4—C5	-2.94 (16)	N2—C7—C8—O1	-8.05 (13)
C1—N1—C5—C4	3.43 (16)	C6—N2—C9—C9 ⁱ	156.93 (9)
Co1—N1—C5—C4	-178.11 (8)	C7—N2—C9—C9 ⁱ	-75.42 (11)
C1—N1—C5—C6	-174.34 (9)	Co1—N2—C9—C9 ⁱ	41.93 (10)
Co1—N1—C5—C6	4.12 (11)	C6—N2—C9—C10	-77.49 (11)
C3—C4—C5—N1	0.28 (16)	C7—N2—C9—C10	50.16 (12)
C3—C4—C5—C6	177.83 (10)	Co1—N2—C9—C10	167.51 (8)
C7—N2—C6—C5	69.87 (10)	N2—C9—C10—C11	-174.45 (9)
C9—N2—C6—C5	-160.66 (8)	C9 ⁱ —C9—C10—C11	-52.36 (14)
Co1—N2—C6—C5	-45.20 (9)	C9—C10—C11—C11 ⁱ	58.00 (14)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C1—H1A \cdots O2 ⁱⁱⁱ	0.95	2.84	3.4475 (15)	122
C2—H2A \cdots F3 ^{iv}	0.95	2.51	3.2928 (15)	139
C4—H4A \cdots O2 ^v	0.95	2.70	3.5907 (15)	157
C6—H6A \cdots F2 ^{vi}	0.99	2.52	3.4243 (13)	152
C6—H6B \cdots F1 ^{vii}	0.99	2.74	3.3824 (13)	123
C6—H6B \cdots F3 ^{vii}	0.99	2.84	3.8229 (18)	170
C7—H7A \cdots F4 ⁱⁱ	0.99	2.68	3.3879 (13)	128
C7—H7A \cdots F4 ^v	0.99	2.67	3.2436 (13)	117
C7—H7B \cdots F3 ^{vi}	0.99	2.62	3.4982 (16)	147
C9—H9A \cdots F1 ^{vii}	1.00	2.64	3.2790 (12)	122
C9—H9A \cdots F4 ^{vii}	1.00	2.29	3.2336 (13)	157
C10—H10A \cdots F1 ^{vii}	0.99	2.49	3.1429 (15)	123
C10—H10A \cdots F2 ^{vi}	0.99	2.35	3.0728 (14)	129
C10—H10B \cdots F4 ^v	0.99	2.77	3.5399 (14)	135

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