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Second-sphere coordination in anion binding: sodium hexaammine-cobalt(III) tetrakis(4-fluorobenzoate) monohydrate

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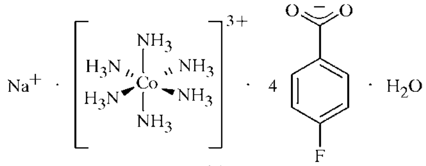
In sodium hexaamminecobalt(III) tetrakis(4-fluorobenzoate) monohydrate, $Na[Co(NH_3)_6](C_7H_4FO_2)_4 \cdot H_2O$, determined at 180 K, $[Co(NH_3)_6]^{3+}$ cations lie on centres of inversion and form layers in which their C_4 axes lie perpendicular to the layer planes. 4-Fluorobenzoate anions lie on twofold axes and general positions and adopt near-planar geometries. Na^+ cations and water molecules lie on twofold axes, forming $[NaO_5]$ square pyramids that lie between the $[Co(NH_3)_6]^{3+}$ cations. The second-sphere interactions between $[Co(NH_3)_6]^{3+}$ cations and 4-fluorobenzoate anions comprise edge-to-face and vertex-to-face arrangements. The structure is closely comparable with that of the benzoic acid salt, demonstrating that fluorination of the anion in the *para* position has no significant influence on the second-sphere interactions and minimal influence on the gross crystal structure.

Comment

We are currently engaged in studies to explore cobalt(III) complexes as potential anion receptors and have reported previously the crystal structures of some hexaammine-cobalt(III) salts with organic sulfonate (Sharma *et al.*, 2004) and benzoate anions (Sharma *et al.*, 2005). The cation $[Co(NH_3)_6]^{3+}$ has also been characterized previously in several



(I)

structures containing organic carboxylate anions, including $[Co(NH_3)_6]_2(Ox)_3 \cdot 4H_2O$ (Ox is oxalate; Gorol *et al.*, 2000) and $[Co(NH_3)_6][(NpO_2)_2(HMal)(Mal)](Mal)$ (Mal is malonate; Grigor'ev *et al.* 2004). In continuation of our interest in this class of compounds, we describe here the crystal structure of sodium hexaamminecobalt(III) 4-fluorobenzoate monohydrate, (I) (Fig. 1).

In (I), the $[Co(NH_3)_6]^{3+}$ cations lie on centres of inversion, with an approximately regular octahedral coordination geometry about atom Co1 (Table 1). There are three crystallographically distinct 4-fluorobenzoate anions: one (containing atom F1) lies on a general position, and two (containing atoms F2 and F3) lie on twofold axes; the bond distances and angles in each case are unremarkable. The dihedral angles between the least-squares plane through the six C atoms of the benzene ring and the plane of the carboxylate group are 8.6 (1), 13.4 (1) and 2.1 (1)° in the three distinct moieties, respectively. Similar near-planar geometry is observed for 4-fluorobenzoate or 4-fluorobenzoic acid in the relatively small number of crystal structures reported previously. Of 11 examples in the Cambridge Structural Database (November 2004 release, plus 2 updates; Allen, 2002), the maximum dihedral angle is *ca* 18° in the Cu^{II} complex salt $[Cu\{NH_2(CH_2)_2NH(CH_2)_2OH\}_2](FC_6H_4CO_2)_2$ (Qu *et al.*, 2004).

The $[Co(NH_3)_6]^{3+}$ cations in (I) are arranged into layers parallel to the *ac* plane, lying at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The C_4 axes of the cations lie approximately perpendicular to the layer planes (Fig. 2). The Na^+ cations and water molecules also lie within these layers, so that the hydrophobic and charged portions of the structure are segregated. The 4-fluorobenzoate anions display essentially two modes of interaction with the $[Co(NH_3)_6]^{3+}$ anions, namely edge-to-face and vertex-to-face (Fig. 3). In the first crystallographically distinct anion

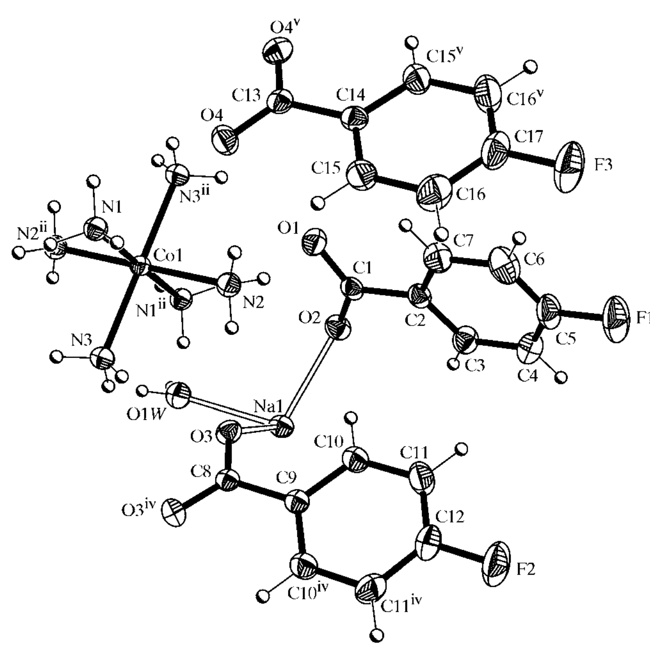


Figure 1
The molecular units in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iv) $-x, y, \frac{1}{2} - z$; (v) $1 - x, y, \frac{3}{2} - z$.]

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(containing atoms O1 and O2), the CO_2^- group forms an edge-to-face interaction with a neighbouring $[Co(NH_3)_6]^{3+}$ cation [N1—H11···O1^{iii}, N2—H21···O2^{iii} and N3—H31···O2^{iii}; symmetry code: (iii) $x, y, z - 1$; Table 2]. One O atom of the same CO_2^- group (O1) also forms a vertex-to-face interaction with a second $[Co(NH_3)_6]^{3+}$ cation, in which all three N···O contacts are of comparable magnitude [N1—H13···O1^{ii}, N2—H23···O1 and N3—H32···O1^{ii}; symmetry code: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$]. Atom O2 also forms two opposing corners in the basal plane of the square-pyramidal twofold symmetric coordination environment of Na1 (Table 1). In the other two crystallographically distinct 4-fluorobenzoate anions, the two O atoms of each CO_2^- group form identical interactions (related by twofold rotation axes). In the first anion, atom O3 forms a vertex-to-face interaction comprising one clear non-hydrogen-bonded N···O contact [N2···O3 = 3.4419 (16) Å], one intermediate N···O contact with a bent N—H···O geometry [N3···O3 = 3.1548 (16) Å and N3—H33···O3 = 122 (2)°], and one clear hydrogen bond (N1—H12···O3^{ii}; Table 2). The same O atom also forms the remaining two corners of the basal plane around Na1. In the second anion, atom O4 forms a more symmetrical vertex-to-face interaction with $[Co(NH_3)_6]^{3+}$, comprising two clear hydrogen bonds (N2—H22···O4 and N3—H33···O4^{ii}; Table 2) and one longer bent N—H···O contact [N1···H12 = 2.9533 (15) Å and N1—H12···O4 = 103 (1)°].

In projection on to the plane of a single layer (Fig. 4), the $[Co(NH_3)_6]^{3+}$ cations of (I) form an approximate primitive rectangular arrangement of dimensions *ca* 6.5 × 7.5 Å. The shorter side of the rectangular arrangement is formed by $[Co(NH_3)_6]^{3+}$ cations linked *via* the anions containing atoms O1 and O2, and the longer sides of the rectangles are linked by anions containing atoms O3 and O4. The centres of these rectangles are occupied by Na^+ ions. The axial coordination site of Na1 is occupied by a water molecule, which forms O—H···O hydrogen bonds to atom O4 (Table 2). The $[NaO_5]$ square pyramids are situated so that the axial water molecules lie on twofold axes and point into the centres of the layers. Between layers, the benzene rings of the 4-fluorobenzoate anions interdigitate in an edge-to-face manner similar to that observed in p-$FC_6H_4NH_3^+ \cdot X^-$ (X is Br or I) [see, for example, Klebe *et al.* (1983)].

The structure of (I) is closely comparable with that of the benzoate salt $Na[Co(NH_3)_6](C_6H_5CO_2)_4 \cdot H_2O$ (Sharma *et al.*, 2005). The layers in the *ac* plane are essentially identical in

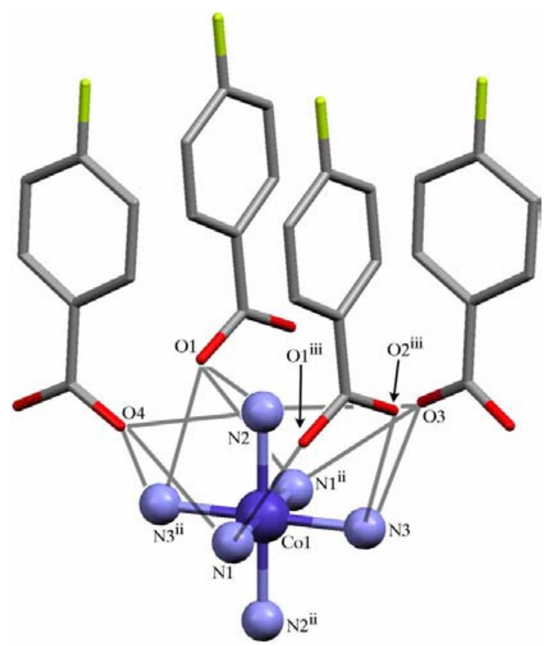

Figure 3
The second-sphere coordination of the $[Co(NH_3)_6]^{3+}$ cation in (I). The CO_2^- group containing atoms O1 and O2 forms an edge-to-face interaction, while the other three interactions shown are vertex-to-face. Atom Co1 lies on a centre of inversion so that a comparable arrangement is formed on the opposite side of the plane (not shown). H atoms have been omitted. [Symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $x, y, z - 1$.]

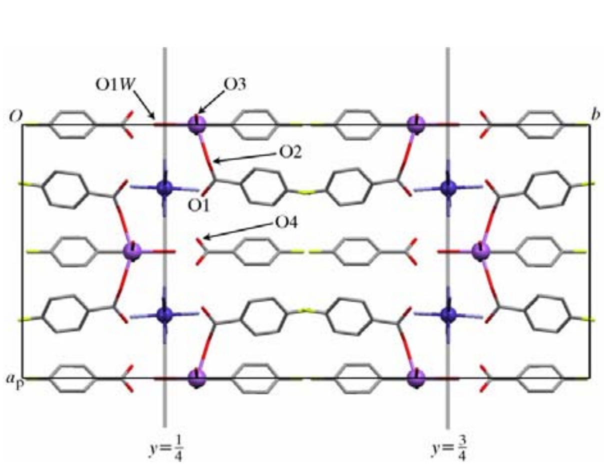

Figure 2
A projection of the unit cell of (I) along the *c* direction, showing layers of $[Co(NH_3)_6]^{3+}$ cations lying parallel to the *ac* plane at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The organic anions are interdigitated between these layers. H atoms have been omitted.

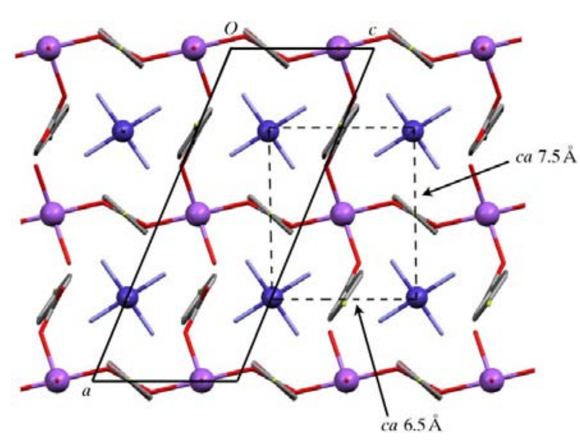

Figure 4
A projection on to the plane of a single layer, showing the approximate rectangular arrangement of $[Co(NH_3)_6]^{3+}$ cations, with Na^+ cations between them. The $[NaO_5]$ square pyramids are viewed in projection along their axial Na1—O1*W* vectors, which point upwards for $[NaO_5]$ lying close to the corners of the unit cell and downwards for $[NaO_5]$ lying close to the middle of the unit cell. H atoms have been omitted.

both cases, but the structure of (I) expands by *ca* 1 Å along the *b* direction to accommodate the fluoro substituents. This demonstrates that fluorination of the benzoate anion in the *para* position has no significant influence on its second-sphere interactions with $[Co(NH_3)_6]^{3+}$, and minimal influence on the gross crystal structure.

Experimental

Hexaamminecobalt(III) chloride (1 g, 0.003 mol) was dissolved in hot water (20 ml) with mechanical stirring. In a second beaker, the sodium salt of 4-fluorobenzoic acid (1.825 g, 0.011 mol) was dissolved in hot water (20 ml). These solutions were mixed and allowed to cool slowly to room temperature. After 1 d, the orange crystals which formed were filtered off and dried in air. The overall yield is quantitative (m.p. 478 K). Elemental analysis is consistent with the composition $Na[Co(NH_3)_6](FC_6H_4CO_2)_4 \cdot H_2O$.

Crystal data

$Na[Co(NH_3)_6](C_7H_4FO_2)_4 \cdot H_2O$
M_r = 758.55
Monoclinic, $C2/c$
a = 16.1930 (4) Å
b = 33.4500 (9) Å
c = 6.5169 (2) Å
β = 112.349 (1)°
V = 3264.77 (16) Å^3
Z = 4
D_x = 1.543 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6005 reflections
θ = 2.3–28.0°
μ = 0.62 mm^{-1}
T = 180 (2) K
Block, orange
0.40 × 0.30 × 0.20 mm

Data collection

Bruker–Nonius X8APEX-II CCD area-detector diffractometer
Thin–slice ω and φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.699, T_{max} = 0.886
11474 measured reflections
3531 independent reflections
2909 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 28.0°
$h = -20 \rightarrow 18$
$k = -40 \rightarrow 44$
$l = -7 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.085
S = 1.03
3531 reflections
269 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 1.8227P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.9510 (12)	Na1—O3	2.3444 (10)
Co1—N3	1.9562 (12)	Na1—O2	2.3861 (10)
Co1—N2	1.9643 (13)	Na1—O1*W*	2.4834 (19)
O3—Na1—O3^{i}	177.34 (6)	N2—Co1—N3	91.93 (5)
O3—Na1—O2	95.66 (4)	N1—Co1—N1^{ii}	180.0
O3—Na1—O2^{i}	85.08 (4)	N2—Co1—N2^{ii}	180.0
O2—Na1—O2^{i}	147.85 (6)	N3—Co1—N3^{ii}	180.0
O3—Na1—O1*W*	88.67 (3)	N1—Co1—N2^{ii}	90.39 (5)
O2—Na1—O1*W*	106.07 (3)	N1—Co1—N3^{ii}	91.94 (5)
N1—Co1—N2	89.61 (5)	N3—Co1—N2^{ii}	88.07 (5)
N1—Co1—N3	88.06 (5)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H12···O3^{ii}	0.87 (1)	2.11 (1)	2.8962 (15)	150 (2)
N1—H11···O1^{iii}	0.87 (1)	2.27 (1)	3.1000 (16)	159 (2)
N1—H13···O1^{ii}	0.88 (1)	2.06 (1)	2.9124 (16)	163 (2)
N2—H21···O2^{iii}	0.88 (1)	2.38 (2)	3.1357 (15)	144 (2)
N2—H22···O4	0.88 (1)	2.20 (1)	3.0108 (16)	153 (2)
N2—H23···O1	0.87 (1)	2.16 (1)	2.9867 (16)	158 (2)
N3—H31···O2^{iii}	0.88 (1)	2.10 (1)	2.9730 (15)	174 (2)
N3—H32···O1^{ii}	0.88 (1)	2.35 (1)	3.1335 (16)	149 (2)
N3—H33···O4^{ii}	0.86 (1)	2.43 (2)	3.0481 (16)	129 (2)
O1*W*—H1*W*···O4^{ii}	0.84 (2)	2.04 (2)	2.8519 (14)	163 (2)

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

H atoms bound to C atoms were placed in calculated positions and allowed to ride during subsequent refinement, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms of the NH_3 groups were located in difference Fourier maps and refined with isotropic displacement parameters. All nine independent N—H bond lengths were restrained to a common refined value with an s.u. of 0.01 Å. The single unique H atom of the water molecule was also located in a difference Fourier map and was refined isotropically without restraint.

Data collection: *APEX2* (Bruker–Nonius, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG1006). Services for accessing these data are described at the back of the journal.

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