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Key indicators

Single-crystal X-ray study
T = 180 K
Mean $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.069
wR factor = 0.165
Data-to-parameter ratio = 15.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Hexaamminecobalt(III)–4-hydroxybenzene-sulfonate–chloride–water (3/8/1/13)

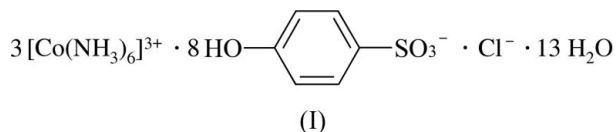
The title compound, $[\text{Co}(\text{NH}_3)_6]_3(\text{C}_6\text{H}_5\text{O}_4\text{S})_8\text{Cl}\cdot 13\text{H}_2\text{O}$, contains one and a half hexaamminecobalt(III) cations, four 4-hydroxybenzenesulfonate anions, one half chloride anion and six and a half water molecules in its asymmetric unit. One $[\text{Co}(\text{NH}_3)_6]^{3+}$ cation lies on a centre of inversion. The $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations and 4-hydroxybenzenesulfonate anions are linked by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds into 'triple-stranded ribbons'. The chloride anion is disordered in sites between these ribbons.

Received 4 July 2006

Accepted 31 July 2006

Comment

We and others have reported previously the crystal structures of some hexaamminecobalt(III) salts with organic sulfonate anions (Dalrymple *et al.*, 2002; Reddy *et al.*, 2003; Sharma *et al.*, 2004). In continuation of this work, we describe here the crystal structure of the title compound, hexaamminecobalt(III)–4-hydroxybenzenesulfonate–chloride–water (3/8/1/13), (I), containing 4-hydroxybenzenesulfonate counter-ions (Fig. 1).



There are two distinct $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations in (I) (Table 1), with atom Co1 occupying an inversion centre. The cations are

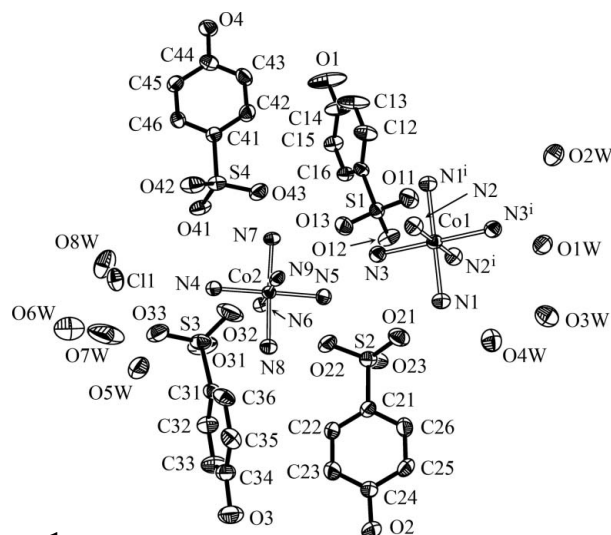
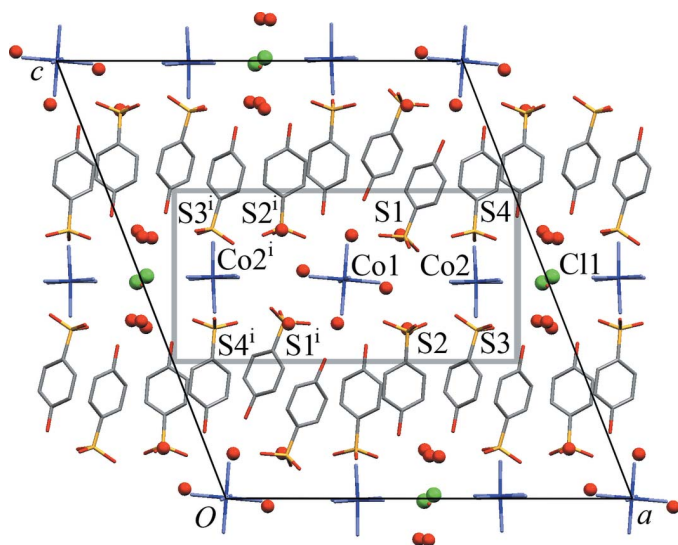


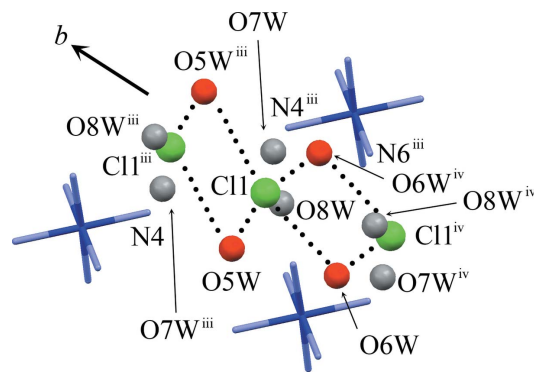
Figure 1
Structural components of (I), showing displacement ellipsoids at the 50% probability level. H atoms have been omitted. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]


Figure 2

Projection of (I) along b , showing the $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations lying with one of their C_4 axes approximately perpendicular to (001). A 'triple-stranded ribbon' is enclosed within the central rectangular box. H atoms have been omitted. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

arranged into layers parallel to (001), with one of their C_4 axes lying approximately perpendicular to the plane of the layers. The 4-hydroxybenzenesulfonate anions lie between these layers with their long axes also oriented approximately perpendicular to the layer plane. Viewed in projection along the b direction (Fig. 2), groups of three $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations can be distinguished within a (001) layer. Thus, the structure of (I) can be described in terms of 'triple-stranded ribbons' of stoichiometry $\{[\text{Co}(\text{NH}_3)_6]_3(\text{C}_6\text{H}_5\text{SO}_4)_8\}^+$. Four crystallographically distinct 4-hydroxybenzenesulfonate anions are present. In two of these (containing S2 and S4), the C—S bond of the sulfonate unit lies approximately parallel to the C_4 axes of the $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations. In two others (containing S1 and S3), the C—S bonds form small angles to the C_4 axes.

The hydrogen-bonding interactions between the cations and anions (Table 2) comprise an assortment of vertex-to-face and edge-to-face arrangements. In the former, one S—O bond of the sulfonate anion is directed approximately towards the centroid of one $(\text{NH}_3)_3$ face of the octahedral $[\text{Co}(\text{NH}_3)_6]^{3+}$ cation, so that the O atom at the vertex of the tetrahedral sulfonate anion accepts hydrogen bonds from all three NH_3 groups. In the edge-to-face arrangement, one $\text{O} \cdots \text{O}$ edge of the sulfonate unit lies across one $(\text{NH}_3)_3$ face of the $[\text{Co}(\text{NH}_3)_6]^{3+}$ cation, so that one O atom accepts a hydrogen bond from one NH_3 group and the other O atom lies over the mid-point of the opposite $\text{NH}_3 \cdots \text{NH}_3$ edge, accepting hydrogen bonds from both NH_3 groups. In the two (equivalent) outer strands of each triple-ribbon, the 4-hydroxybenzenesulfonate anion containing S3 forms two edge-to-face interactions on one side of the ribbon. On the other side, S4 forms one edge-to-face interaction and one vertex-to-face interaction in which the S4—O42 bond lies parallel to the direction of propagation of the chains. The central (Co1) strand in the triple-ribbons is linked to the outer strands through the 4-hydroxybenzenesulfonate anions containing S1


Figure 3

Disordered region of (I), between two triple-stranded ribbons. Atom O5W is always present. Either atoms Cl1 and O6W (coloured) or atoms O7W and O8W (grey) are present in any one site. Dotted lines denote hydrogen bonds between Cl1 and O6W, and H atoms have been omitted. [Symmetry codes: (iii) $2 - x, 1 - y, 1 - z$; (iv) $2 - x, 2 - y, 1 - z$.]

and S2. These two anions lie on opposite sides of the ribbons and interact in an essentially identical manner: they bridge between two $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations, with one $\text{O} \cdots \text{O}$ edge of the sulfonate group forming an edge-to-face interaction, and the opposite O atom forming a vertex-to-face interaction.

The triple-stranded ribbons in (I) are arranged with the hydroxybenzene portions of the 4-hydroxybenzenesulfonate anions interdigitating between them. A complex pattern of additional $\text{O} - \text{H} \cdots \text{O}$ interactions is formed between the hydroxyl groups, the O atoms of the sulfonate anions and the uncoordinated water molecules. Where the edges of adjacent triple strands meet, regions are formed that are rich in N—H hydrogen-bond donors. These regions are occupied by chloride anions. A disordered description of the structure is suggested by refinement of the site-occupancy factor for Cl1 to 0.52 (1), and is a requirement for overall charge balance. The Cl^- anions occupy positions that bridge $\text{NH}_3 \cdots \text{NH}_3$ edges in one triple strand, and bridge between two NH_3 vertices of the adjacent triple strand (Fig. 3). The Cl1 sites are spaced at *ca* 4 Å intervals along the b -axis direction, which does not preclude occupation of all of them in any one channel, *i.e.* the disorder is not necessarily a result of occupation of only every other Cl1 site along b . Water molecules O5W and O6W (the latter modelled as disordered over two closely spaced sites) lie in suitable positions to bridge between adjacent Cl^- anions *via* $\text{O} - \text{H} \cdots \text{Cl}^-$ hydrogen bonds.

Experimental

Hexaamminecobalt(III) chloride (0.5 g, 0.0018 mol) was dissolved in hot water (15 ml) by mechanical stirring. In a second beaker, sodium 4-hydroxybenzenesulfonate dihydrate (1.3 g, 0.0056 mol) was dissolved in hot water (20 ml). These solutions were mixed and allowed to cool slowly to room temperature. After 2 h, orange crystals of (I) were formed, which were filtered and dried in air. The overall yield is quantitative. Elemental analysis is consistent with the composition $[\text{Co}(\text{NH}_3)_6]_3(\text{C}_6\text{H}_5\text{SO}_4)_8\text{Cl} \cdot 13\text{H}_2\text{O}$; found: C 27.30, H 4.40, N 11.81, Co 8.20, Cl 1.62%; calculated: C 27.39, H 5.70, N 11.99, Co 8.40, Cl 1.68%. IR (KBr, ν , cm^{-1}): 3243 (*br*), 1605 (*m*), 1324 (*s*, for coordinated NH_3) and 1119 (*s*), 1004 (*s*), 693 (*s*, for sulfonate anions).

¹H NMR (D₂O): δ 6.12–6.15 (*d*, 16H). ¹³C NMR (D₂O): δ 159.6 (1-C), 136.3 (4-C), 129.0 (2,6-C), 116.8 (3,5-C).

Crystal data

[Co(NH₃)₆]₃(C₆H₅O₄S)₈Cl·13H₂O
M_r = 2138.34
 Monoclinic, *P*2₁/*n*
a = 22.980 (1) Å
b = 7.8559 (3) Å
c = 26.5747 (11) Å
 β = 111.203 (2)°
V = 4472.7 (3) Å³
Z = 2
D_x = 1.588 Mg m⁻³
 Mo *K*α radiation
 μ = 0.87 mm⁻¹
T = 180 (2) K
 Lath, orange
 0.25 × 0.08 × 0.02 mm

Data collection

Bruker–Nonius X8APEX-II CCD diffractometer
 Thin-slice ω and φ scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
T_{min} = 0.773, *T_{max}* = 0.983
 25759 measured reflections
 9053 independent reflections
 6268 reflections with *I* > 2σ(*I*)
R_{int} = 0.053
 θ_{\max} = 26.4°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.069
wR (*F*²) = 0.165
S = 1.11
 9053 reflections
 574 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + 28.5287P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.92 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.62 \text{ e \AA}^{-3}$

Table 1

Selected bond lengths (Å).

Co1–N2	1.949 (5)	Co2–N5	1.965 (5)
Co1–N1	1.960 (4)	Co2–N7	1.968 (4)
Co1–N3	1.965 (4)	Co2–N9	1.972 (5)
Co2–N4	1.952 (5)	Co2–N6	1.974 (5)
Co2–N8	1.964 (4)		

Table 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>
N1–H11···O11 ⁱ	0.91	2.36	2.989 (7)	127
N1–H13···O21	0.91	2.13	3.010 (6)	163
N2–H23···O11 ⁱ	0.91	2.09	2.978 (6)	164
N2–H22···O21 ⁱ	0.91	2.44	3.217 (6)	143
N3–H33···O13	0.91	2.50	3.279 (6)	144
N3–H32···O21	0.91	2.20	3.074 (7)	161
N4–H41···O31	0.91	2.02	2.910 (6)	166
N4–H42···O8W ⁱⁱ	0.91	2.13	3.031 (17)	171
N4–H43···O41	0.91	2.00	2.906 (6)	173
N4–H42···Cl1 ⁱⁱ	0.91	2.25	3.155 (7)	172
N5–H52···O12	0.91	2.43	3.108 (7)	131
N5–H52···O13	0.91	2.36	3.184 (7)	151
N5–H51···O23	0.91	2.47	3.204 (7)	138
N5–H51···O32 ⁱⁱⁱ	0.91	2.48	3.154 (8)	131
N5–H53···O42 ⁱⁱⁱ	0.91	2.32	3.136 (6)	150
N6–H62···O33 ⁱⁱⁱ	0.91	2.13	3.028 (6)	167
N6–H63···O42 ⁱⁱⁱ	0.91	2.12	2.987 (6)	158
N6–H61···Cl1 ⁱⁱ	0.91	2.49	3.396 (7)	172
N6–H61···O8W ⁱⁱ	0.91	2.14	3.021 (16)	162
N7–H73···O13	0.91	2.48	3.251 (6)	143
N7–H71···O41	0.91	2.39	3.068 (7)	132
N7–H72···O42 ⁱⁱⁱ	0.91	2.09	2.964 (6)	161
N7–H73···O43	0.91	2.50	3.157 (6)	130
N8–H82···O22	0.91	2.12	3.002 (6)	164
N8–H81···O31	0.91	2.21	2.951 (7)	138
N8–H83···O33 ⁱⁱⁱ	0.91	2.04	2.944 (7)	170

<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>
N9–H91···O13	0.91	2.30	2.917 (6)	125
N9–H91···O22	0.91	2.44	2.891 (6)	111
N9–H92···O32	0.91	2.33	3.146 (7)	149
N9–H93···O43	0.91	2.13	3.014 (6)	163

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

The C- and N-bound H atoms were positioned geometrically (C–H = 0.95 Å and N–H = 0.91 Å) and refined as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(N). The NH₃ groups were initially allowed to rotate around each local threefold axis. To assist convergence, this rotation was not allowed in the final cycles of refinement. The hydroxyl H atoms were placed along the O···O vector offering the shortest potential hydrogen bond. The H atoms of the uncoordinated water molecules were mostly located in difference Fourier maps. For the disordered O6W, O7W and O8W molecules, they were placed so as to form a reasonable hydrogen-bond network, with O–H distances of 0.84 Å. For the final cycles of refinement, all O–H distances were normalized to 0.84 Å and the H atoms were made to ride on their parent O atom, with *U*_{iso}(H) = 1.5*U*_{eq}(O). In a structure as complex as this, the water H atoms positions should be regarded as less certain.

The site-occupancy factor of Cl1 refined to 0.52 (1), but was subsequently constrained to be ½, since this is required for overall charge balance. Atom O8W is present when Cl1 is not, so its site-occupancy factor was also constrained to be 0.5. One further water molecule was modelled as disordered over two closely spaced sites, O6W and O7W. The site-occupancy factors of these atoms (constrained to sum to unity) were refined to 0.60 (2):0.40 (2). However, both were subsequently constrained to be ½, principally for the reason that this makes the structure conceptually much easier to comprehend: in any particular site, either Cl1 and O6W are present, or O7W and O8W are present. This moderate approximation is accommodated acceptably by the anisotropic displacement parameters of the atoms concerned.

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.

RB and RPS gratefully acknowledge the financial support of the CSIR, India [grant No. 01(1768)/02/EMR-II]. ADB is grateful to the Danish Natural Science Research Council (SNF) and Carlsbergfondet (Denmark) for provision of the X-ray equipment.

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