Poly[[aqua(1-aza-4-azoniabicyclo[2.2.2]octane)-cadmate(II)]-μ-5-sulfatoisophthalato]

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In the title compound, $[Cd(C_8H_3O_7S)(C_6H_{13}N_2)(H_2O)]_n$, the Cd atom is coordinated by one O atom of a carboxylate group of a 5-sulfatoisophthalato ligand, two O atoms of the carboxylate group group of an adjacent symmetry-related 5-sulfoisophthalato entity, one O atom of the sulfonyl group of yet another adjacent 5-sulfatooisophthalato entity, a water molecule and the N atom of the 1-aza-4-azoniabicyclo[2.2.2]-octane cation in a six-coordinate octahedral geometry. Thus, the mode of coordination of the 5-sulfatoisophthalato ligand leads to the formation of a linear ribbon motif; adjacent ribbons are linked by hydrogen-bonding interactions, giving rise to a three-dimensional network structure.

Comment

The 5-sulfatoisophthalato monoanion, $[C_6H_3-1,3-(CO_2H)_2-5-SO_3]^-$, reacts with copper nitrate in the presence of hexamethylenetetramine to form $[C_6H_3-1,3-(CO_2)_2-5-SO_3H](H_2O)_3Cu\cdot6H_2O\cdot0.5(CH_2)_6N_4$ (Sun et al., 2003) In the crystal structure, the $[C_6H_3-1,3-(CO_2)_2-5-SO_3H]^{2-}$ dianion links adjacent Cu atoms through both monodentate –CO_2 groups into a linear chain, and adjacent chains are linked by hydrogen bonds to the water and hexamethylenetetramine molecules into a network motif. The piperazine guest-host analog, $[C_6H_3-1,3-(CO_2)_2-5-SO_3H](H_2O)_2Cu\cdot6H_2O\cdot0.5N(CH_2)_4N$, follows a similar pattern (Sun et al., 2003). The other known metal complex of 5-sulfatoisophthalic acid is also a copper derivative, $[C_6H_3(CO_2)_2(SO_3)]_2Cu_3$, whose Cu atoms are coordinated by pyridine ligands (Kulynych & Shimizu, 2002).


(I)
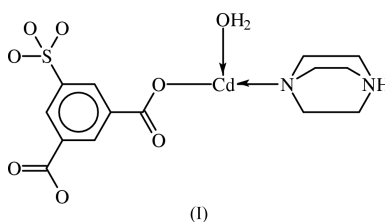
We have employed the anion to react with Cd^{2+} in the presence of 1,4-diazabicyclo[2.2.2]octane in the hope of synthesizing a similar guest–host hydrate, viz $[C_6H_3-1,3-(CO_2)_2-5-SO_3H]Cd-N(CH_2CH_2)_3N\cdot nH_2O$, (I), using a hydrothermal synthetic procedure. However, in the water-coordinated product, the H atom of the sulfonate group has protonated one of the N atoms of the 1,4-diazabicyclo[2.2.2]-octane; the resulting 1-aza-4-azoniabicyclo[2.2.2]octane cation then uses its free N atom to coordinate to the Cd atom, and a zwitterionic compound results (Fig. 1).

The $[C_6H_3-1,3-(CO_2)_2-5-SO_3]^{3-}$ trianion uses both –CO_2 groups to link to adjacent Cd atoms to form a chain, but one of

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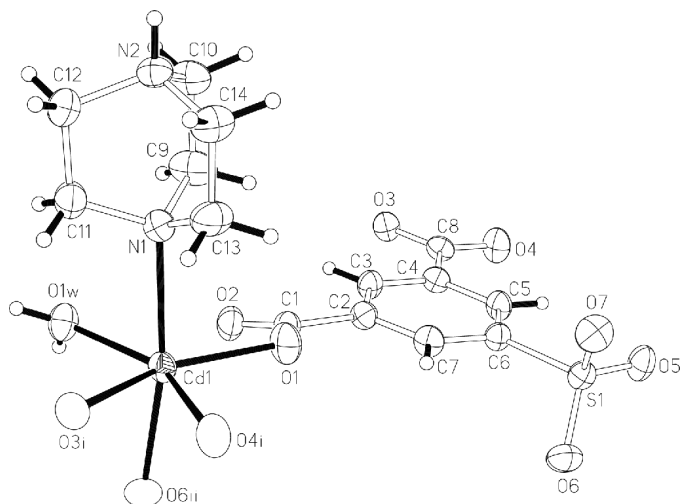
Figure 1
*ORTEP*II (Johnson, 1976) plot of a segment of the structure of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) ?$x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$;? (ii) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.
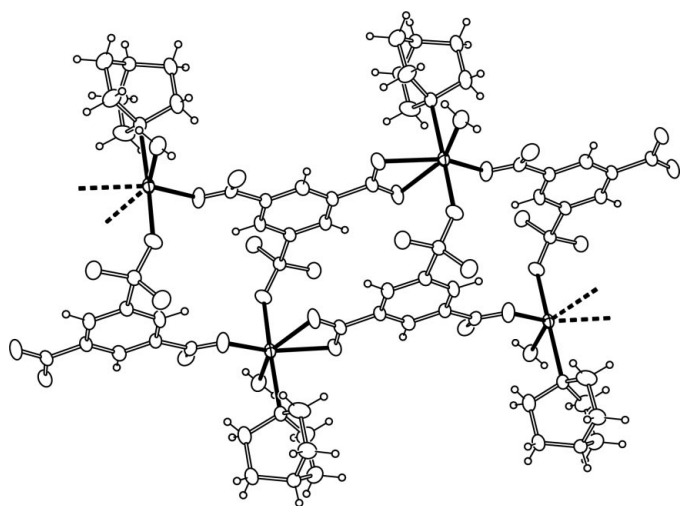
Figure 2
*ORTEP*II (Johnson, 1976) plot of the ribbon structure.

them is monodentate [Cd—O = 2.190 (2) Å] whereas the other is chelating [Cd—O = 2.331 (2) and 2.399 (2) Å]. Two chains are then linked by a sulfonate bridge [Cd—O = 2.349 (2) Å] to furnish a ribbon motif (Fig. 2). The ribbons are further linked by hydrogen-bonding interactions (Table 2) to give rise to a three-dimensional network structure. Protonation of one of the two N atoms of the 1,4-diazabicyclo[2.2.2]octane probably raises the Lewis basicity of the other N atom to permit it to bind to Cd [Cd1—N1 = 2.437 (2) Å]; a Cd←N interaction of a similar length [Cd←N 2.446 (3) Å] is also found in {[NH(CH$_2$CH$_2$)N]$_2$Cd}-{Ni(CN)$_4$}$_2$·4C$_6$H$_5$NH$_2$ (Yuge & Iwamoto, 1995).

Experimental

A 1/1 water–ethanol solution (8 ml) of cadmium nitrate tetrahydrate (0.15 g, 0.5 mmol), the monosodium salt of 5-sulfatoisophthalic acid

Crystal data

[Cd(C$_8$H$_3$O$_7$S)(C$_6$H$_{13}$N$_2$)(H$_2$O)]	D_x = 1.974 Mg m^{-3}
M_r = 486.76	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 6969
a = 18.5885 (8) Å	reflections
b = 8.8265 (4) Å	θ = 2.0–28.2°
c = 21.7607 (9) Å	μ = 1.51 mm^{-1}
β = 113.408 (1)°	T = 298 (2) K
V = 3276.5 (2) Å^3	Block, colorless
Z = 8	0.40 × 0.08 × 0.04 mm

Data collection

Bruker AXS area-detector diffractometer	3750 independent reflections
φ and ω scans	3207 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.024
	θ_{max} = 28.2°
T_{min} = 0.689, T_{max} = 0.941	$h = -24 \rightarrow 24$
9529 measured reflections	$k = -11 \rightarrow 11$
	$l = -19 \rightarrow 28$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)]$ = 0.025	independent and constrained
$wR(F^2)$ = 0.056	refinement
S = 0.93	$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2]$
3750 reflections	where $P = (F_o^2 + 2F_c^2)/3$
247 parameters	$(\Delta/\sigma)_{max}$ = 0.001
	$\Delta\rho_{max}$ = 0.63 e Å^{-3}
	$\Delta\rho_{min}$ = -0.42 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.190 (2)	Cd1—O6^{ii}	2.349 (2)
Cd1—O3^i	2.331 (2)	Cd1—O1w	2.241 (2)
Cd1—O4^i	2.399 (2)	Cd1—N1	2.437 (2)
O1—Cd1—O3^i	145.5 (1)	O3^i—Cd1—N1	87.4 (1)
O1—Cd1—O4^i	91.0 (1)	O4^i—Cd1—O6^{ii}	90.5 (1)
O1—Cd1—O6^{ii}	99.3 (1)	O4^i—Cd1—O1w	150.8 (1)
O1—Cd1—O1w	118.1 (1	O4^i—Cd1—N1	94.6 (1)
O1—Cd1—N1	88.3 (1)	O6^{ii}—Cd1—O1w	87.7 (1)
O3^i—Cd1—O4^i	55.3 (1)	O6^{ii}—Cd1—N1	170.8 (1)
O3^i—Cd1—O6^{ii}	89.2 (1)	O1w—Cd1—N1	84.1 (1)
O3^i—Cd1—O1w	95.5 (1)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1w—H1w1$\cdots$O5^{iv}	0.85 (1)	1.91 (2)	2.700 (3)	155 (3)
O1w—H1w2$\cdots$O3^v	0.85 (1)	1.88 (1)	2.714 (2)	165 (3)
N2—H2$n\cdots$O2^{vi}	0.86 (1)	1.91 (1)	2.736 (3)	161 (3)

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

The water and ammonium H atoms were located and refined subject to constraints of O—H = N—H = 0.85 (1) and H···H = 1.39 (1) Å. The C-bound H atoms were generated geometrically (C—H = 0.95 Å for the aromatic H atoms and 0.97 Å for the aliphatic H atoms) and were included in the refinement in the riding-model approximation; their displacement parameters were set at 1.2 times U_{eq} of the equivalent isotropic displacement parameters of the parent C atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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