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Polymeric structures in the metal complexes of 5-sulfosalicylic acid: The rubidium(I), caesium(I) and lead(II) analogues

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Abstract

The complexes of 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid, H_3SSA) with rubidium(I), caesium(I) and lead(II) have been synthesized and characterized using single-crystal X-ray methods at 130 K. The rubidium(I) complex **1**, $[Rb_3(H_2SSA)(HSSA)(H_2O)_4]_n$, is an unstable hydrate variant of a previously described complex $[Rb(H_2SSA)(H_2O)]_n$, and comprises three independent and different seven-coordinate metal polyhedra interlinked through oxygen donors of the sulfonate, carboxylate and phenolate groups of the 5-sulfosalicylate ligands (one of which is dianionic, the other monoanionic), and one bridging water, giving a three-dimensional hydrogen-bonded framework polymer structure. The anhydrous caesium(I) complex **2** $[Cs(H_2SSA)]_n$, which has been previously described in a room-temperature determination, has a three-dimensional framework polymer structure based on an irregular Cs–O_9 repeating unit. Complex **3** with lead(II), $[Pb(H_2SSA)_2(H_2O)]_n$, forms helical step-polymer ribbon substructures having an irregular Pb–O_7 coordination centre comprising a single monodentate water and six sulfonate-O donors bridging three separate metals. The carboxylic acid and phenol substituent groups of the 5-sulfosalicylate ligand link the ribbons peripherally through hydrogen bonds, giving a three-dimensional layered framework polymer structure.

Keywords: 5-Sulfosalicylic acid; Rubidium(I); Caesium(I); Lead(II); Crystal structures; Coordination polymers

1. Introduction

The aromatic sulfonic acid 3-carboxy-4-hydroxybenzenesulfonic acid (5-sulfosalicylic acid = H_3SSA) and its compounds have unusual physical properties, e.g., fluorescence and proton conductivity. These properties are considered to be attributable mainly to its ability to protonate water and among the several known hydrate structures of the acid {the dihydrate [1,2], the dideuterate [3], the trihydrate [2,4], and the pentahydrate [5]} many protonated polyaqua oxonium species have been identified e.g. the $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$ cation species. The metal complexes having similar physical properties have therefore been studied since stable compounds with sulfosalicylic acid may be formed, involving coordination through the six potential donor sites of the three substituent groups of the H_3SSA molecule (the sulfonic acid, the carboxylic acid and the phenolic groups), which with controlled deprotonation give mono-, di- and trianionic ligand species (H_2SSA^-, $HSSA^{2-}$, SSA^{3-}). In addition the presence of the numerous oxygen acceptor atoms from all three substituent groups usually results in hydrogen-bonding associations, often requiring the incorporation of water molecules of solvation in the structures, thereby enhancing self-assembly during the crystallization process (see Scheme 1).

Crystallographically characterized structures of complexes with univalent, divalent and trivalent metal species mostly from the Groups 1 and 2 and the lanthanides are predominantly polymeric and include examples with all three of the possible anionic ligand types, e.g. $[Na(H_2SSA)$-

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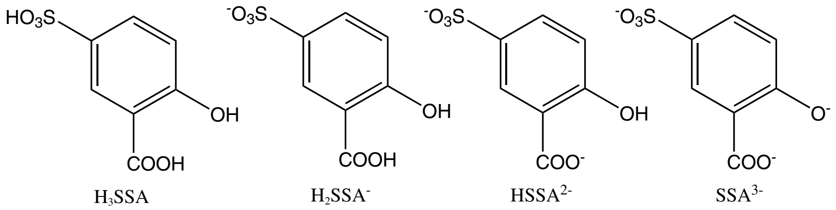

Scheme 1. The 5-sulfosalicylic acid species.

$(H_2O)]_n$ [6,7], $[K(H_2SSA)(H_2O)_2]_n$ [8], $[Rb(H_2SSA)(H_2O)]_n$ [9], $[Cs(H_2SSA)]_n$ [10], $[Ca(HSSA)(H_2O)_3]_n$ [8], $\{[Sr(H_2SSA)_2(H_2O)] \cdot H_2O\}_n$ [11], $[Ba(H_2SSA)_2(H_2O)_5]_n$ [12], $\{[La(SSA)(H_2O)_8] \cdot H_2O\}_n$ [13], $[Eu(H_2SSA)_2(H_2O)_5]_n$ [14], $\{[Yb(SSA)_3(H_2O)_8] \cdot H_2O\}_n$ [15], $[Sm(HSSA)_2(H_2O)_6]_n$ [16], and $[Nd(SSA)(H_2O)]_n$ [17]. Also, examples with mixed-metal species are known, e.g. $[NaCu(SSA)(H_2O)_4]_n$ [6], $[Na_3La_2Tb(SSA)_4(H_2O)_{26}]_n$ [18] and $[Na_3La_2Y(SSA)_4(H_2O)_{26}]_n$ [19]. Among the known examples are occasional complexes with mixed mono- and dianionic ligand species, e.g. $\{[Na_3(H_2SSA)(HSSA) \cdot H_2O]\}_n$ [20]. Also, in a number of these complexes the 5-sulfosalicylate species act as counter-anions without participating in coordination, e.g. the Yb^{III} complex which has the actual structural formula $\{[Yb(H_2O)_8(H_2SSA)_3] \cdot H_2O\}_n$ [15], while a series of first-row transition metal(II) complexes have a similar type of constitution, with a general formula $[M(H_2O)_6(H_2SSA)_2 \cdot nH_2O]$ [M = Mn, $n = 2$; M = Co, $n = 4$; M = Ni, $n = 4$; M = Cu, $n = 2$; M = Zn, $n = 4$ [21]. These differ from the polymeric structures shown in the Group 1 complexes and in the silver(I) complexes $[Ag_4(HSSA)_2(H_2O)_2]_n$ and $[Ag_2(HSSA)(H_2O)–Ag_2(H_2SSA)_2(H_2O)_3] \cdot H_2O\}_n$ [22].

In an investigation of the complexes of sulfosalicylic acid with the Group 1 metal ions, it was found that not only were the reported complexes with K^I, Rb^I and Cs^I [8–10] isolated, a second presumably efflorescent form of the Rb complex, $[Rb_3(H_2SSA)(HSSA)(H_2O)_4]_n$ (**1**), was formed and its structure is reported here. This complex also has both H_2SSA^- and $HSSA^{2-}$ ligand species. A parallel determination using 5-sulfosalicylic acid and CsOH similarly gave an unstable compound which when recrystallized from water surprisingly gave the previously reported [10] anhydrous compound $[Cs(H_2SSA)]_n$ (**2**) confirmed by both elemental analysis and a low-temperature single-crystal X-ray diffraction analysis. The structure of the stable hydrated lead(II) complex $[Pb(H_2SSA)_2(H_2O)]_n$ (**3**) is also reported here, the only previous structure of a compound of lead(II) with 5-sulfosalicylic acid being a dimeric mixed-ligand complex with 1,10-phenanthroline, $[Pb_2(HSSA)_2(phen)_2(H_2O)_2]$ [23].

2. Experimental

2.1. Synthesis of compounds

Compound **1** $[Rb_3(H_2SSA)(HSSA)(H_2O)_4]_n$ was synthesized by adding 0.23 g (1 mmol) of 4-carboxy-3-hydroxybenzenesulfonic acid (5-sulfosalicylic acid) to 30 mL of an aqueous solution containing 0.10 g (1 mmol) of rubidium hydroxide. The mixture was heated for ca. 10 min at 90° and the resultant hot-filtered solution was then allowed to evaporate at room temperature. The colourless prisms of **1** which were obtained after several weeks were unstable in air, deteriorating slowly to a white powder, presumably due to loss of water of solvation, prompting the low-temperature X-ray diffraction analysis. No elemental analysis was therefore performed.

Compound **2** $[Cs(H_2SSA)]_n$ was synthesized using a parallel procedure to that in **1**, by adding 0.23 g (1 mmol) of 5-sulfosalicylic acid to 30 mL of an aqueous solution containing 0.15 g (1 mmol) of cesium hydroxide. The crystals obtained after several weeks of room temperature evapora-

Table 1
Cell data for compounds **1**–**3**

	Compound **1**	Compound **2**	Compound **3**
CCDC reference	637681	641976	637682
Formula	$C_{14}H_{19}O_{17}Rb_3S_2$	$C_7H_5CsO_6S$	$C_{14}H_{12}O_{13}PbS_2$
M_r	761.81	350.08	659.58
Crystal class	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/m$
a (Å)	15.0117(10)	9.6336(6)	8.5751(7)
b (Å)	23.0776(16)	7.1404(4)	5.9654(5)
c (Å)	7.0560(5)	14.3617(9)	17.8447(13)
β (°)	93.415(1)	91.842(1)	101.040(1)
V (Å^3)	2440.1(3)	987.4(1)	896.53(12)
$D_{calc.}$ (g cm^{-3})	2.074	2.355	2.436
Z	4	4	2
λ (Mo Kα) (mm^{-1})	6.238	3.966	9.716
Temperature (K)	130(2)	130(2)	130(2)
$2\theta_{max}$ (°)	50	50	50
Crystal size (mm)	$0.30 \times 0.30 \times 0.30$	$0.45 \times 0.25 \times 0.15$	$0.25 \times 0.15 \times 0.10$
Total data	12575	4986	4513
Collection range	$-17 \leqslant h \leqslant 17$, $-21 \leqslant k \leqslant 27$, $-8 \leqslant l \leqslant 7$	$-10 \leqslant h \leqslant 11$, $-8 \leqslant k \leqslant 8$, $-10 \leqslant l \leqslant 17$	$-10 \leqslant h \leqslant 9$, $-7 \leqslant k \leqslant 7$, $-14 \leqslant l \leqslant 21$
Unique data	4303	1742	1744
R_{int}	0.050	0.020	0.022
N [$I > 2.0\sigma(I)$]	3577	1683	1716
R_1^a	0.066	0.023	0.022
wR_2^a	0.168	0.061	0.060
S^a	1.09	1.09	1.12
A,B^b	0.052, 34.4	0.037, 0.998	0.035, 0.018

[a] $R_1 = (\sum|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum w[(F_o^2 - F_c^2)]^2/\sum[w(F_o^2)^2]\}^{1/2}$; $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$; $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ {where $P = [(\max.\ F_o^2, 0) + 2(F_c^2)]/3\}$.

[b] Cell parameters from Ref. [10] at 298 K: $a = 9.682(3)$, $b = 7.317(2)$, $c = 14.358(4)$ (Å), $\beta = 90.641(14)°$, $V = 1017.2(5)$ Å^3.