

Syntheses and crystal structures of three cesium salts: Cesium 5-sulfosalicylate, cesium 3,5-dinitrosalicylate and cesium 2,4-dinitrophenoxide monohydrate

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Abstract

In an attempt to probe a potential template role of the large alkali-metal cation cesium in organization of biorelevant ligands, 5-sulfosalicylate, 3,5-dinitrosalicylate and 2,4-dinitrophenol complexes of cesium were prepared and structurally investigated. The structures of cesium 5-sulfosalicylate, cesium 3,5-dinitrosalicylate and cesium 2,4-dinitrophenoxide monohydrate have been determined through X-ray diffraction analysis. The 5-sulfosalicylate anion has lost the proton at the $-\text{SO}_3\text{H}$ group while the 3,5-dinitrosalicylate anion at $-\text{COOH}$ group but both retains the usual intermolecular hydrogen bond between phenolic and carboxylic oxygen. In cesium 2,4-dinitrophenoxide monohydrate, the Cs^+ cation is 12-coordinate by O atoms in anions and water molecules while the metal atoms in cesium 5-sulfosalicylate and cesium 3,5-dinitrosalicylate have coordination numbers 10 and 11, respectively, with an irregular coordination sphere made up exclusively of oxygen atoms. Even more in cesium 2,4-dinitrophenoxide monohydrate, the water molecules are in rare triply bridging positions between these cations. Both complexes have layer structures containing the cations and polar groups of the ligands in core domains sandwiched by the aromatic rings above and below. The organization of all layer structures appears to be governed mainly by steric effects and electrostatic forces with very little directional influence of the cations.

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1. Introduction

Binding of the common alkali-metal (Na^+ , K^+) cations to biorelevant ligands is of great current interest since these metals are abundant in biological systems [1]. They are known to determine or codetermine not only the structures of biominerals, but also the folding and function of proteins and other biopolymers [2–4]. They also act as cofactors for many processes of prime importance [5–7]. Obviously the two metals are “essen-

tial”, and an undersupply causes deficiency syndromes [8]. Recent work has contributed significantly to a better understanding of the action of these cations on a molecular level, although many details remain unexplored. By contrast, the role of the heavier alkali (Rb^+ , Cs^+) metals has received much less attention, because according to present knowledge these elements are rare or absent in biological systems and therefore are not considered essential. Because salicylic acid (2-oxybenzoic acid) and its derivatives have been known for a long time to possess anti-inflammatory activity and have also been considered of interest from a structural point of view [9]. The complexes of them have been found to have biological activity and exhibited antimicrobial activity

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stronger than that of the free ligand [10,11]. The reactivity and structure of the complexes are intimately related, and thus, knowledge of their structures is important for an understanding of their reactivity.

We have recently investigated the coordination chemistry of the heavy alkali metal (Cs) with the 5-sulfosalicylic acid, 3,5-dinitrosalicylic acid and 2,4-dinitrophenol. In the present paper, the preparation and structures of heavy alkaline metal salts, the rubidium and cesium anthranilates and salicylates [12] and sodium 5-sulfosalicylate dihydrate [13] have already been reported. In another current study [14,15], the structures of thallium(I) salicylates have been determined and shown to feature a marked asymmetry in the coordination sphere of the metal atom, which has an ionic radius between those of rubidium and cesium.

2. Material and methods

2.1. Materials and general laboratory equipment

Analysis grade 5-sulfosalicylic acid, 3,5-dinitrosalicylic acid, 2,4-dinitrophenol, analytical grade cesium sulfate (purity >99.5%), analytical grade barium hydroxide and bidistilled water were used in all experiments.

The CsOH solution was prepared from analytical grade Cs_2SO_4 and $\text{Ba}(\text{OH})_2$ and bidistilled water [16].

IR spectra were measured with a Bruker Equinox 55 spectrometer with KBr pellets in 4000–400 cm^{-1} ranges at room temperature.

2.2. Synthesis

2.2.1. Cesium 5-sulfosalicylate (I)

A mixture containing 10 mmol of CsOH solution was added slowly with stirring to a solution of 5-sulfosalicylic acid dihydrate ($\text{H}_3\text{Ssal} \cdot 2\text{H}_2\text{O}$) (10 mmol). After the resulting suspension is stirred for 30 min at room temperature, the solution obtained is concentrated to a volume of 5 ml and set aside for crystallization. After 4 weeks, colorless crystals of the $\text{Cs}(\text{H}_2\text{ssal})$ are collected. Anal. Calc. for **I**: C, 24.05; H, 0.57; Cs, 37.98. Found: C, 24.57; H, 1.24; Cs, 38.80%.

2.2.2. Cesium 3,5-dinitrosalicylate (II)

The complex was synthesized by adding 3,5-dinitrosalicylic acid solid under stirring an uncolored aqueous solution. The color changed immediately to yellow and the resulting suspension was stirring for 30 min under room temperature, then set aside for crystallization. After 6 weeks yellow crystals of $\text{Cs}(\text{Hn}_2\text{sal})$ were collected. Anal. Calc. for **II**: C, 23.34; H, 0.28; N, 7.78; Cs, 36.93. Found: C, 23.47; H, 0.65; N, 7.78; Cs, 37.07%.

2.2.3. Cesium 2,4-dinitrophenoxide monohydrate (III)

An aqueous solution of CsOH was added to the 2,4-dinitrophenol until a pH 7.0 was reached. After filtration, the filtrate evaporated at room temperature. The yellow crystals were obtained after several days. Anal. Calc. for **III**: C, 21.56; H, 0.95; N, 8.39; Cs, 39.79. Found: C, 21.63; H, 1.37; N, 8.35; Cs, 40.14%.

2.2.4. X-ray single-crystal studies for title compounds

The single crystal used for crystal structure measurement were mounted in Lindemann capillaries at 298.2 K. Diffraction data were collected on a Siemens CCD area-detector with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.071073$ nm). The structures were solved by direct methods using SHELXS-97 [17] and refined against F^2 by fullmatrix least-squares using SHELXL-97 [18]. Hydrogen atoms located on carbon atoms were calculated and allowed to ride on their parent atoms with fixed isotropic parameters, whereas the acidic protons situated on the oxygen atoms were located and refined with isotropic contributions. Crystal data, experimental details, and refinement results are listed in Table 1.

3. Result and discussion

3.1. Molecular and crystal structure of I

Cesium 5-sulfosalicylate (**I**) crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The asymmetric unit contains one cesium cation and one 5-sulfosalicylate anion. The 5-sulfosalicylic acid is deprotonated at the sulfonate group so that the crystal structure consists of Cs^+ and 5-sulfosalicylate anions. The Cs^+ cation is surrounded by the four sulfonate ligands (O1/O2, O2A, O1B/O3B, O3F), two carboxylate groups (O5C, O4D/O5D) and two hydroxy groups (O6E, O6G). The cesium atoms are 11-coordinated with Cs–O contacts in the range from 3.093 to 3.781 Å (for O3B and O4D, which is already excessively long and should be considered a borderline case) (Fig. 1). This is a constant feature of Cs^+ coordination as one can see for example in cesium salicylate and cesium mellitate [12,19].

Table 2 shows the selected bond lengths and angles of compound **I**. Fig. 1 shows the molecular structure with the atom-labeling scheme and the detailed coordination sphere around the Cs^+ ion. Fig. 2 shows the coordination modes of the 5-sulfosalicylate anions. The oxygen atoms are in double bridging position between the cesium cations except O4 atom in the carboxylate ligand. The carboxylate and hydroxy groups are tied together through an intraanionic hydrogen bond $\text{O6-H}\cdots\text{O5}$. The bond length and angle are 1.875 Å and 147.79°. Conversely, each cesium atom is associated with eight

Table 1
Crystallographic parameters for **I**, **II** and **III**

Complex	I	II	III
Crystal data			
Empirical formula	C7H4CsO6S	C7H3CsN2O7	C6H5CsN2O6
Formula weight	349.07	360.02	334.03
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions			
a (Å)	9.682(3)	7.710(2)	5.841(1)
b (Å)	7.317(2)	7.387(2)	21.715(2)
c (Å)	14.358(4)	17.644(5)	7.629(2)
α (°)	90	90	90
β (°)	90.641(4)	95.920(4)	92.048(3)
γ (°)	90	90	90
V (Å ³)	1017.2(5)	999.5(5)	967.0(3)
Z	4	4	4
D_{calc} (g cm ⁻³)	2.279	2.393	2.294
$F(000)$	660	680	632
Absorption coefficient (mm ⁻¹)	3.850	3.734	3.841
Crystal size (mm)	0.41 × 0.38 × 0.18	0.42 × 0.37 × 0.21	0.48 × 0.32 × 0.21
Color	Colorless	Yellow	Yellow
2θ max, range (°)	2.10–25.02	2.32–25.02	1.88–25.03
Index ranges	–10 ≤ h ≤ 11 –8 ≤ k ≤ 7 –17 ≤ l ≤ 15	–8 ≤ h ≤ 9 –8 ≤ k ≤ 8 –18 ≤ l ≤ 21	–6 ≤ h ≤ 6 –24 ≤ k ≤ 25 –9 ≤ l ≤ 8
Reflections collected/unique	4958/1796 [$R_{\text{int}} = 0.0342$]	5042/1767 [$R_{\text{int}} = 0.0289$]	5003/1705 [$R_{\text{int}} = 0.0394$]
Completeness to $\theta = 25.02$	99.6%	99.9%	99.8%
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.5441 and 0.3013	0.5077 and 0.3031	0.4993 and 0.2600
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	1796/0/140	1767/1/158	1705/5/142
Goodness-of-fit on F^2	1.028	0.999	1.006
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0281$ $wR_2^b = 0.0690$	$R_1^a = 0.0241$ $wR_2^b = 0.0615$	$R_1^a = 0.0378$ $wR_2^b = 0.0978$
R indices (all data)	$R_1^a = 0.0351$ $wR_2^b = 0.0735$	$R_1^a = 0.0296$ $wR_2^b = 0.0655$	$R_1^a = 0.0437$ $wR_2^b = 0.1022$
Largest difference in peak and hole (e Å ⁻¹)	0.661 and –1.063	0.496 and –0.562	0.577 and –1.699

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$$

$$^b wR_2 = \sum w[(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

salicylate anions, which all have a different mode of coordination. Three of them are bidentate, while others are monohapto ligands. The interactions among cations and anions in the lattice of **I** are largely unidirectional as it is shown in Fig. 3. Together with the cations, the polar groups of the ligands form an inner layer of a sandwich, which is covered on both sides by the nonpolar aromatic rings. These sandwich layers stack with long van der Waals contacts between the nonpolar covers.

3.2. Molecular and crystal structure of **II**

Cesium 3,5-dinitrosalicylate (**II**) crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The asymmetric unit contains one cesium

cation and one 3,5-dinitrosalicylate anion. Taking a larger domain of the crystal lattice, the 3,5-dinitrosalicylate anion is linked to eight cesium cations (Fig. 4), while the Cs⁺ cation is surrounded by the eight of the anions and reaches coordination number 10 (Fig. 5). The inner coordination sphere accommodates 10 oxygen atoms (O1, O2, O3A, O4A, O2B, O5C, O7D, O5E, O7F, O6G) (Fig. 5). The Cs–O distances are in the range from 2.913 for O3A to 3.513 Å for O6G. The bond lengths and angles are listed in Table 3. The shortest intra-anionic hydrogen bond is established between O3–H···O1 with the bond length is 1.612 Å. The geometry is rather distorted. The assembly of layers of the polar and nonpolar groups again leads to a stacking of sandwiches with the cesium cations, the carboxylate groups,

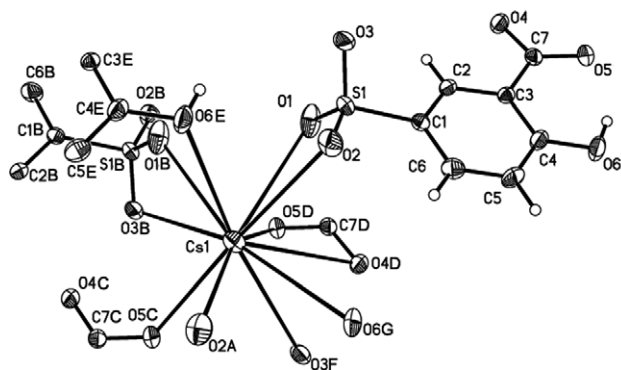


Fig. 1. 11-Coordination cesium cation of **I**. Displacement ellipsoids are drawn at the 30% probability level. Atoms marked with an A, B, C, D, E, F and G are at the symmetry positions $(-x, y - 1/2, -z + 1/2)$, $(-x, -y + 1, -z)$, $(x - 1, y - 1, z)$, $(-x + 1, -y + 1, -z)$, $(x - 1, y, z)$, $(x, y - 1, z)$ and $(-x + 1, y - 1/2, -z + 1/2)$, respectively.

hydroxy groups, nitrogen groups forming a core structure (Fig. 6).

The crystal structures of **II** are found to base on electrostatic forces and steric requirement of the components. π - π -stacking of arenas can be ruled out owing to long distances (3.707 Å). The details of ion packing (coordination number, coordination geometry) are variable, the bulk layer structure is always preserved.

3.3. Molecular and crystal structure of **III**

Compound (**III**) crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The asymmetric unit contains one cesium cation, one 2,4-dinitrophenoxide anion, and one water molecule. Forming an extend array of groups assemble in a parallelogram structure (Fig. 7). The individual fragments consist of a planar four-member ring containing two cesium atoms and two bridging oxygen atoms forming Cs_2O_2 . The cesium cations are 12-coordinate with Cs–O contacts in the range from 3.120(4) Å (for O1) to 3.805(5) Å (for O4C, which is already excessively long and should be considered a borderline case) (Fig. 8). The selected bond lengths and angles are listed in Table 4. The coordination sphere of the cesium atom is completed by three water molecules, which are all completed in bridging positions to three neighboring metal atoms.

Compound (**III**) is generally an exceptional cesium salt in that it contains water coordinated to the cation

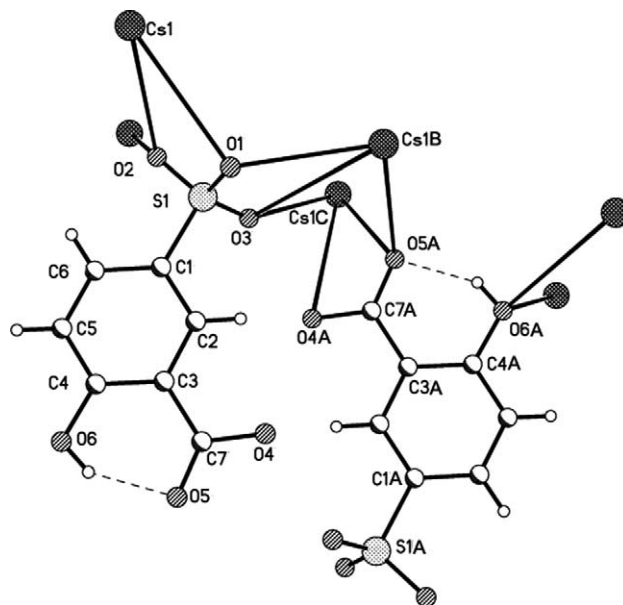


Fig. 2. Coordination modes of the 5-sulfosalicylate anions toward cesium cations in **I**.

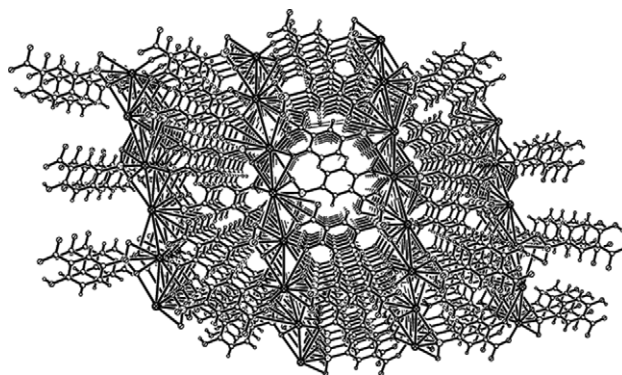


Fig. 3. Formation of layers in **I**. The inner domains formed of the cesium ions, the polar groups of 5-sulfosalicylate anions are shielded by the benzene rings.

in the crystal, and even more in that the water molecules (such as O6D) are in rare triply bridging positions between these cations with quite different distances of 3.236(5) Å Cs1D, 3.200(4) Å Cs1, 3.370(4) Å for Cs1G. The water molecule is also engaged in hydrogen bonding with O1 and O4 atom of the anion. The water molecules are stabilized by intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds formed between

Table 2
Selected bond length (Å) and angles (°) for **I**

Cs(1)–O(1)	3.491(4)	Cs(1)–O(2)	3.130(4)	Cs(1)–O(2)A	3.093(3)
Cs(1)–O(1)B	3.168(4)	Cs(1)–O(3)B	3.771(4)	Cs(1)–O(5)C	3.176(3)
Cs(1)–O(4)D	3.781(3)	Cs(1)–O(5)D	3.236(3)	Cs(1)–O(6)E	3.345(4)
Cs(1)–O(3)F	3.407(3)	Cs(1)–O(6)G	3.449(3)		
O(2)–Cs(1)–O(1)	41.72(7)	O(1)B–Cs(1)–O(3)B	39.38(8)	O(5)D–Cs(1)–O(4)D	36.03(7)
O(2)A–Cs(1)–O(5)D	150.61(9)	O(2)–Cs(1)–O(5)C	173.24(8)	O(1)B–Cs(1)–O(6)G	160.65(9)

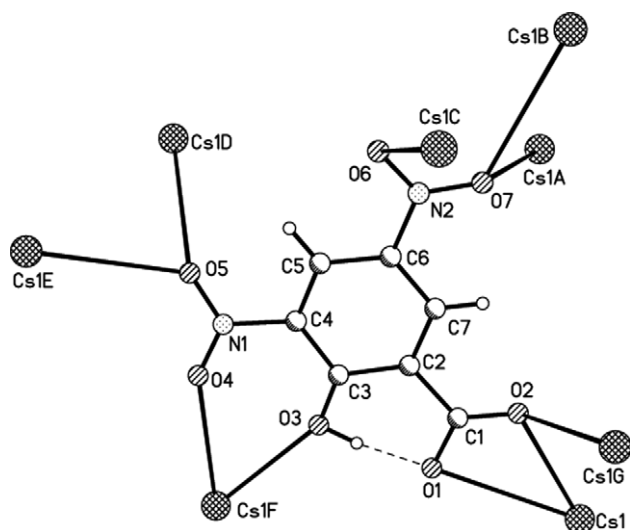


Fig. 4. Coordination modes of the 3,5-dinitrosalicylate anion toward cesium cations in **II**.

O6–H1···O4 and O6–H2···O1 of adjacent molecules. The bond lengths and angles are 2.06(5) Å, 158.47° and 2.13(4) Å, 136.43°, respectively. This result shows that the interactions among cations, anions, and water dipoles in the lattice of **III** are largely unidirectional and determined by steric effects and Coulomb forces. The ion packing (coordination number, coordination geometry) are variable. π – π -Stacking of arenes can be ruled out owing to excessively long distances ($d > 4$ Å) (Fig. 9).

3.4. Structure comparison

The crystal structure parameters of **I**, **II**, **III**, the reported cesium salicylate, sodium 5-sulfosalicylate dihydrate and potassium taurine–salicylic schiff base complexes are shown in Table 5. It is noticed that all the compared cesium compounds belong to monoclinic crystal system with space group $P2_1/c$. The bond lengths of these compounds are closed. The coordinate numbers of each cesium atom in these compounds are different. Both compounds have sandwich structures in which the cations and the polar groups of the ligands form a compact inner layer which is covered on both sides by the aromatic rings. The O atoms in carboxyl, hydroxyl

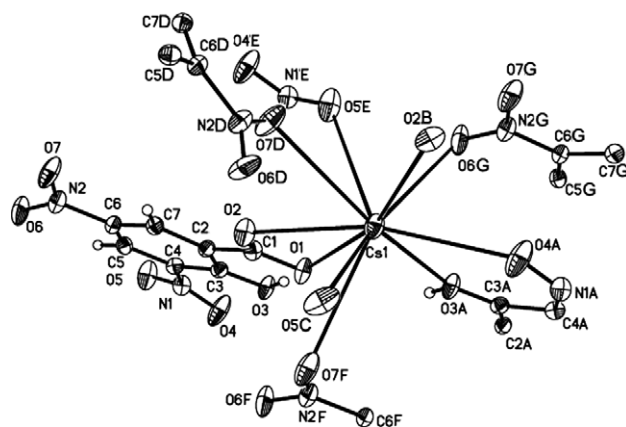


Fig. 5. 10-Coordination cesium cation of **II**. Displacement ellipsoids are drawn at the 30% probability level. Atoms marked with an A, B, C, D, E, F and G are at the symmetry positions $(-x+1, -y+2, -z)$, $(-x+1, y+1/2, -z+1/2)$, $(x+1, -y+3/2, z+1/2)$, $(-x, y+1/2, -z+1/2)$, $(-x, -y+2, -z)$, $(x+1, y, z)$ and $(x+1, y+1, z)$, respectively.

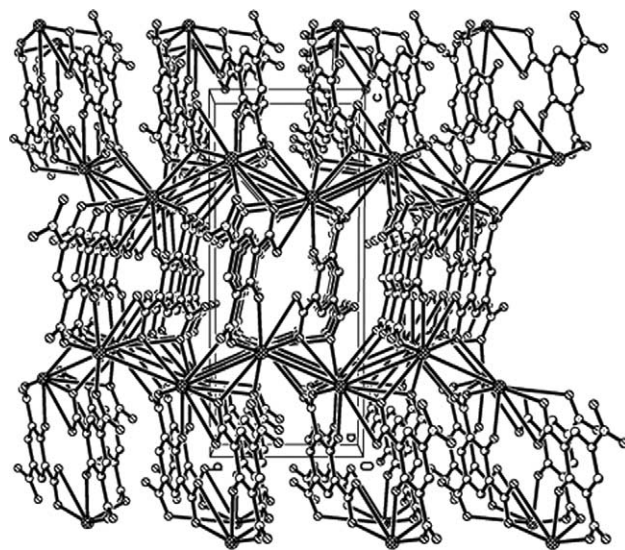


Fig. 6. Formation of layers in **II**. The inner domains formed of the cesium ions, the polar groups of 3,5-dinitrosalicylate anions are shielded by the benzene rings.

and water molecules are all in bridging positions between the metal atoms. The coordination sphere around the metal cesium atoms is quite irregular and appears to be governed solely by electrostatic and steric effects.

Table 3
Selected bond length (Å) and angles (°) for **II**

Cs(1)–O(1)	3.377(3)	Cs(1)–O(2)	3.121(3)	Cs(1)–O(3)A	2.963(3)
Cs(1)–O(4)A	3.179(3)	Cs(1)–O(2)B	3.021(3)	Cs(1)–O(5)C	3.258(3)
Cs(1)–O(7)D	3.322(3)	Cs(1)–O(5)E	3.340(4)	Cs(1)–O(7)F	3.399(4)
Cs(1)–O(6)G	3.513(3)				
O(2)–Cs(1)–O(1)	39.42(6)	O(3)A–Cs(1)–O(4)A	51.33(8)	O(2)B–Cs(1)–O(1)	161.76(7)
O(1)–Cs(1)–O(6)G	86.31(7)	O(2)–Cs(1)–O(3)A	105.82(7)	O(3)A–Cs(1)–O(7)D	158.55(8)
O(6)G–Cs(1)–O(7)F	138.06(7)	O(2)B–Cs(1)–O(7)F	133.28(7)		

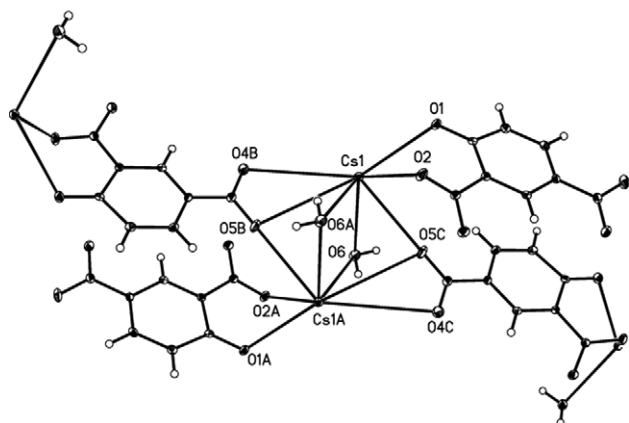
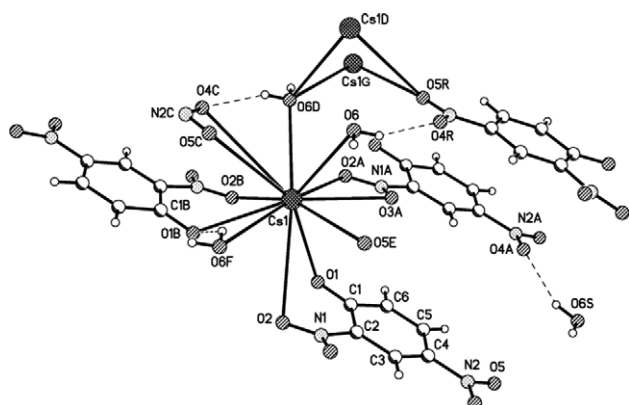
Fig. 7. Diagram illustrating the extended array of **III**.

Fig. 8. 12-Coordination cesium cation of the title compound. Atoms marked with an A, B, C, D, E and F are at the symmetry positions $(1+x, y, z)$, $(1-x, 1-y, 2-z)$, $(1-x, 1/2+y, 3/2-z)$, $(2-x, 1-y, 1-z)$, $(x, 1/2-y, -1/2+z)$ and $(1-x, 1-y, 1-z)$, respectively. Dashed lines indicate O–H...O hydrogen bonds.

From these details, it is obvious that large alkali-metal cations have very little directional influence on the coordination geometry. The arrangements appear to be governed by ion–ion and ion–dipole forces, which lead to an aggregation of all polar groups in layerlike domains covered by the organic groups. The most prominent difference from salts with the smaller alkali metals is the strict conservation of a certain coordination number and a more regular polyhedral geometry

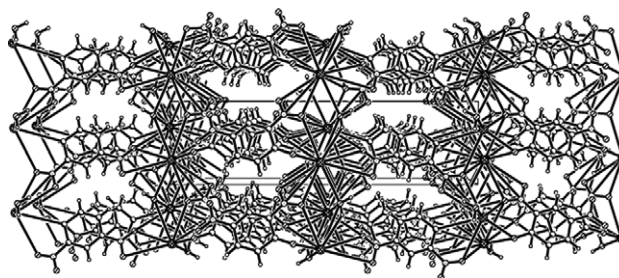


Fig. 9. Formation of layers in **III**. The inner domains formed of the cesium ions, the water molecules, and the polar groups of the dinitrophenoxide anions are shielded by the benzene rings.

for the smaller cations such as sodium and potassium with its strict geometry toward oxygen donor atoms [12]. Cesium therefore are among the least amenable to play a template role in biological systems, and therefore were discarded in the evolutionary process. By the same token they do not enforce nonstandard coordination geometries in biological substrates, which may be one reason for the low toxicity. These results are entirely similar with the structural characteristics recently found in the reference.

3.5. Infrared spectra of **I**, **II** and **III**

The IR spectra of the title compounds were recorded on Bruker Equinox 55 spectrometer with KBr pellets in 4000–400 cm^{-1} ranges at room temperature. The IR spectra are in good agreement with the crystallographic data. In compound **I**, the broad band in 3429 cm^{-1} was assigned to O–H stretching vibrations and hydrogen bond. The peaks in 3073, 1690, 1480 cm^{-1} were attributed to C–H stretching vibrations and C=C stretching vibrations of phenol, and 1663 cm^{-1} were C=O stretching vibration. The peaks, which were associated to the stretching vibration of the $-\text{SO}_3$ are in 1160 and 1023 cm^{-1} . All the peaks of compound **I** were closed to 5-sulfosalicylic acid [21], except for the $-\text{SO}_3$ which shows the 5-sulfosalicylate anion has lost the proton at the $-\text{SO}_3\text{H}$ group. In compound **II**, band assigned to O–H stretching vibrations and hydrogen bonds are in 3447 cm^{-1} . The $\nu(\text{C}=\text{O})$ carboxylate group stretching vibrations occur in 1689 cm^{-1} and $\nu(-\text{NO}_2)$ occur in 1571 and 1338 cm^{-1} . The bands at 3093, 1609,

Table 4

Selected bond length (\AA) and angles ($^\circ$) for **III**

Cs(1)–O(1)	3.120(4)	Cs(1)–O(2)	3.682(5)	Cs(1)–O(6)	3.236(5)
Cs(1)–O(2)A	3.291(4)	Cs(1)–O(3)A	3.300(4)	Cs(1)–O(1)B	3.140(4)
Cs(1)–O(2)B	3.140(4)	Cs(1)–O(4)C	3.805(5)	Cs(1)–O(5)C	3.679(5)
Cs(1)–O(6)D	3.200(4)	Cs(1)–O(5)E	3.176(4)	Cs(1)–O(6)F	3.370(4)
O(1)–Cs(1)–O(1)B	86.21(1)	O(1)–Cs(1)–O(2)B	76.09(1)	O(2)B–Cs(1)–O(5)E	156.76(1)
O(1)–Cs(1)–O(6)	130.86(1)	O(6)D–Cs(1)–O(6)	67.89(1)	O(2)A–Cs(1)–O(3)A	37.70(1)
O(6)D–Cs(1)–O(6)F	125.48(2)	O(2)B–Cs(1)–O(5)C	94.13(1)	O(1)–Cs(1)–O(2)	45.68(1)

Table 5
Crystal structure comparison of the title compounds with the cesium salicylate

Name	I	II	III	Cs(Sal) · H ₂ O [12]	Na(H ₂ Ssal) · H ₂ O [13]	K(taurine–salicylic) [20]
Chemical formula	C ₇ H ₄ CsO ₆ S	C ₇ H ₃ CsN ₂ O ₇	C ₆ H ₅ CsN ₂ O ₆	C ₇ H ₅ CsO ₃	C ₇ H ₉ NaO ₈ S	C ₉ H ₁₀ KNO ₄ S
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
Unit cell demensions						
<i>a</i> (Å)	9.682(3)	7.710(2)	5.841(1)	11.6238(4)	6.698(2)	20.292(8)
<i>b</i> (Å)	7.317(2)	7.387(2)	21.715(2)	5.8212(2)	7.065(2)	7.283(4)
<i>c</i> (Å)	14.358(4)	17.644(5)	7.629(2)	13.2502(5)	11.646(2)	7.540(4)
α (°)	90	90	90	90	77.80(3)	90
β (°)	90.641(4)	95.920(4)	92.048(3)	99.864(2)	83.20(3)	94.15(1)
γ (°)	90	90	90	90	77.90(3)	90
<i>Z</i>	4	4	4	4	2	4
Coordinate numbers	11	10	12	8	6	8

1494 cm⁻¹ were assigned to C–H stretching vibrations and C=C stretching vibrations of phenol. In compound **III**, the broad bands in 3419 and in 1607 cm⁻¹ were attributed to water molecule and intermolecular hydrogen bonds. The band at 3097 cm⁻¹ was assign to the C–H stretching vibrations. Bands at 1561, 1430, 1379, 1326 cm⁻¹ were assign to the anti-symmetric and symmetric stretch vibration of –NO₂.

4. Supplementary data

X-ray crystallographic files in CIF format for complexes **I**, **II** and **III** have been deposited at the Cambridge Crystallographic Data Center, CCDC Nos. 256661 for **I**, 256660 for complex **II** and 261542 for **III**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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