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Crystal Structures of Rubidium and Cesium Anthranilates and Salicylates

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In an attempt to probe a potential template role of the large alkali-metal cations rubidium and cesium in the organization of biorelevant ligands, salicylate and anthranilate complexes of the two elements were prepared and structurally investigated. The studies were also expected to show the marked structural differences compared to the corresponding thallium(I) compounds. Rubidium anthranilate and cesium salicylate could be crystallized as the monohydrates Rb(Anth)(H_2O) and Cs(Sal)(H_2O). Both have layer structures containing the cations and the polar groups of the ligands in core domains sandwiched by the aromatic rings above and below. The metal atoms have coordination numbers 7 and 8, respectively, with an irregular coordination sphere made up exclusively of oxygen atoms. Crystalline material with a 1:2 stoichiometry, Cs[H(Anth)$_2$], is obtained from aqueous solutions of Cs(Anth) upon absorption of carbon dioxide with concomitant formation of cesium bicarbonate, Cs(HCO_3). The crystal structure of Cs(HCO_3) was redetermined to obtain precise benchmark data for cesium carbonates and carboxylates. The cesium hydrogen bisanthranilate also has a layer structure with eight-coordinate cesium atoms. The coordination sphere includes one nitrogen donor atom. 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. This result suggests that the large alkali metals have no efficient template effect for the organization of biological substrates and can explain the low toxicity of rubidium and cesium salts.

Introduction

Binding of the common alkali-metal (Na^+, K^+) and alkaline-earth-metal (Mg^{2+}, Ca^{2+}) 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 four metals are "essential", 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.[1-8] By contrast, the role of the heavier alkali (Rb^+, Cs^+) and alkaline-earth (Sr^{2+}, Ba^{2+}) 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. Only one of the four elements (Ba) is known to be toxic, while the other three have high tolerance doses.[9]

In a series of preparative and structural studies in our own laboratory we have recently investigated the coordination chemistry of the common alkali-metal and alkaline-earth-metal cations with the most important prototypes of amino and hydroxy acids. This program included in particular the α-aspartates and α- and β-glutamates of these metals, but also salicylates and anthranilates.[10-19] Several of these compounds are established drugs widely used for the

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(1) (a) Emsley, J. *The Elements*, 2nd ed.; Clarendon Press: Oxford, 1991. (b) Hartwig, A. *Chem. Unserer Zeit* **2000**, *34*, 224.
(2) Cowan, J. A. *Chem. Rev.* **1998**, *98*, 1067.
(3) Krampitz, G.; Graser, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1145.
(4) Cowan, J. A., Ed. *Biological Chemistry of Magnesium*; VCH: New York, 1995.
(5) Frausto da Silva, J. J. R., Williams, R. J. P., Eds. *The Biological Chemistry of the Elements*; Clarendon Press: Oxford, 1991.
(6) Sigel, H., Ed. *Metal Ions in Biological Systems*; Marcel Dekker: New York, 1976; Vol. 7.
(7) Williams, R. J. P. *Polyhedron* **1987**, *6*, 61.
(8) Williams, R. J. P. *Chem. Soc. Rev.* **1980**, *9*, 281.
(9) Hou, X. *J. Radioanal. Nucl. Chem.* **1999**, *242*, 49.
(10) Schmidbaur, H.; Mikulcik, P.; Müller, G. *Chem. Ber.* **1990**, *123*, 1599.

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treatment of deficiency disorders.[19,20] Complementary literature has been summarized in previous publications.

In the present paper we present the results of related studies with the two heavier alkali metals, rubidium and cesium, as coordination centers for anthranilic (AnthH) and salicylic (SalH) acid. The preparation and structures of the corresponding heavy alkaline-earth-metal salts, the strontium and barium anthranilates and salicylates, have already been reported.[21,22]

In another current study,[23,24] the structures of thallium(I) salicylates and anthranilates 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. The stereochemical activity of the $6s^2$ lone pair of electrons leads to a virtually empty hemisphere close to the metal center. Thallium(I) therefore appears to have a very special template effect which is probably responsible for the high toxicity of the salts of this metal.

Experimental Section

General Procedures. All experiments were carried out in bidistilled water. Anthranilic acid, salicylic acid, and the metal salts are commercially available. Standard equipment was used throughout.

Cesium Salicylate Hydrate. Cesium hydroxide monohydrate (1.68 g, 10 mmol) is added to a suspension of salycilic acid (1.38 g, 10 mmol) in 10 mL of water. After the resulting suspension is stirred for 15 min at room temperature, the solution obtained is concentrated to a volume of 5 mL in a vacuum and set aside for crystallization. After 6 weeks colorless crystals of the monohydrate are collected, 0.49 g (17%). By removing the solvent in a vacuum, the anhydrous product can be obtained as a microcrystalline solid in quantitative yield. Anal. Calcd for Cs(Sal) ($C_7H_5CsO_3$): C, 31.14; H, 1.87; Cs, 49.21; O, 17.78. Found: C, 31.01; H, 1.97. IR (KBr, cm^{-1}): 3377, m (br), ν(O−H); 3066, w, ν(O−H); 2702, w, ν(O−H), 1629, s, ν_{asym}(C−O); 1586, s, ν(C=C), 1487, s, ν(C=C); 1462, s, ν(C=C); 1390, s, ν_{sym}(C−O); 1334, s, δ(O−H), ν(C−O); 1253, s, δ(=C−H); 1144, m, δ(=C−H); 1034, m, δ(=C−H); 861, s, γ(=C−H); 811, m, γ(=C−H); 745, s, γ(=C−H); 669, s, γ(O−H). MS (FAB, negative): $m/e = 407$, $[CsSal + Sal]^-$, 25.45; 269, $[CsSal - H]^-$, 2.50; 137, $[Sal]^-$, 100.0.

Cesium Hydrogen Dianthranilate and Cesium Bicarbonate. Anthranilic acid (0.88 g, 6.38 mmol) is added to a solution of cesium hydroxide monohydrate (1.07 g, 6.38 mmol) in 5 mL of water with vigorous stirring at room temperature. For the growth of single crystals, the vessel is set aside under atmospheric conditions. After four weeks, crystals of both cesium bicarbonate (needles, 0.16 g, 6.2%) and cesium hydrogen dianthranilate (plates, 0.12 g, 9.7%) are collected. Anal. Calcd for $Cs[H(Anth)_2]$ ($C_{14}H_{13}CsN_2O_4$): C, 41.40; H, 3.23; N, 6.90; Cs, 32.72; O, 15.75. Found: C, 40.37; H, 3.21; N, 6.58. IR (KBr, cm^{-1}): 3500−3100, m (br), H_2O, ν_{asym}(N−H), ν_{sym}(N−H); 1620−1480, s (br), δ(N−H), ν_{asym}(C−O), ν(C=C); 1444, s, ν(C=C); 1370, s, ν_{sym}(C−O); 1312, s, ν(C−H); 1254, s, δ(=C−H); 1150, s, δ(=C−H); 1028, m, δ(=C−H); 860, s, γ(=C−H); 808, s, γ(=C−H); 762, s, γ(=C−H); 708, s, γ(N−H). Anal. Calcd for $CsHCO_3$: C, 6.19; H, 0.52; Cs, 68.54; O, 24.75. Found: C, 6.79; H, 0.85.

Anhydrous Cesium Anthranilate. The preparation of the solution follows the procedure for cesium hydrogen dianthranilate. The solution is carefully layered with methanol, and the vessel is kept in an atmosphere of nitrogen to exclude carbon dioxide. After 4 weeks, a microcrystalline product is isolated, 1.03 g (56.1%). Anal. Calcd for Cs(Anth) ($C_7H_6CsNO_2$): C, 31.25; H, 2.25; N, 5.21; Cs, 49.40; O, 11.89. Found: C, 31.05; H, 2.24; N, 5.14. IR (KBr, cm^{-1}): 3428, m, ν(O−H); 3324, m, ν_{asym}(C−O); 3023, w, ν_{sym}(N−H); 1608, s, ν_{asym}(C−O), δ(N−H); 1579, s, ν(C=C); 1531, s, ν(C=C); 1448, m, ν(C=C); 1315, m, ν(C−N); 1254, m, δ(=C−H); 1150, m, δ(=C−H); 1028, w, δ(=C−H); 861, m, γ(=C−H); 806, m, γ(=C−H); 756, s, γ(=C−H); 662, m, γ(N−H). MS (FAB, negative): $m/e = 537$, $[2\ CsAnth - H]^-$, 2.72; 315 $[Hanth + H(Anth)_2 - CO_2 - 3NH_3]^-$, 32.21; 268, $[CsAnth - H]^-$, 5.57; 225, $[CsAnth - CO_2]^{\bullet -}$, 10.97; 151 $[H(Anth)_2 - 2CO_2 - 2NH_3]^-$, 44.67; 136, $[Anth]^-$, 100.0.

Rubidium Salicylate Monohydrate. A solution of rubidium hydroxide (1.0 mL, 50 wt %, $\rho = 1.740$ g·cm^{-3}, 8.50 mmol) is added to a suspension of salicylic acid (1.17 g, 8.50 mmol) in 4 mL of water with vigorous stirring. The vessel is set aside at room temperature. After 2 weeks, rubidium salicylate precipitates as the monohydrate from the solution. Anal. Calcd for $Rb(Sal)(H_2O)$ ($C_7H_7O_4Rb$): C, 34.94; H, 2.93; O, 26.61; Rb, 35.52. Found: C, 32.72; H, 2.40. IR (KBr, cm^{-1}): 3229, w (br), ν(O−H); 3064, w (br), ν(O−H); 1642, s, ν_{asym}(C−O); 1587, s, ν(C=C); 1489, s, ν(C=C); 1465, s, ν(C=C); 1393, s, ν_{asym}(C−O); 1322, m, δ(O−H); ν(C−O); 1253, m, δ(=C−H); 1142, w−m, δ(=C−H); 1033, w, δ(=C−H); 860, m, γ(=C−H); 811, m, γ(=C−H); 745, s, γ(=C−H); 669, m, γ(O−H). MS (FAB, neg.): $m/e = 361$, $[^{87}RbSal + Sal]^-$, 8.70; 359, $[^{85}RbSal + Sal]^-$, 20.31; 223, $[^{87}RbSal - H]^-$, 1.52; 221, $[^{85}RbSal - H]^-$, 3.42; 168, $[^{85}RbSal - CO_2]^{\bullet -}$, 5.83; 137, $[Sal]^-$, 100.0.

Rubidium Anthranilate Monohydrate. A solution of rubidium hydroxide monohydrate (0.75 mL, 50 wt %, $\rho = 1.740$ g·cm^{-3}, 6.38 mmol) is added to a suspension of anthranilic acid (0.88 g, 6.38 mmol) in 4.25 mL of water. The mixture is stirred for 15 min at room temperature. For the growth of single crystals, the vessel is set aside at room temperature. After four weeks, the product separates from the mother liquor in the form of colorless crystals, 1.61 g (79.1%). Anal. Calcd for $Rb(Anth)(H_2O)$ ($C_7H_8NO_3Rb$): C, 35.09; H, 3.37; N, 5.85; Rb, 35.66; O, 20.03. Found: C, 34.58; H, 3.20; N, 5.72. IR (KBr, cm^{-1}): 3422, s, ν(O−H); 3308, s, ν_{asym}(N−H); 3022, w, ν_{sym}(N−H); 1609, s, ν_{asym}(C−O), δ(N−H); 1581, s, ν(C=C); 1532, s, ν(C=C); 1446, s, ν(C=C); 1315, m, ν(C−N); 1252, m, δ(=C−H); 1158, m, δ(=C−H); 1029, m, δ-

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(11) Schmidbaur, H.; Bach, I.; Wilkinson, D. L.; Müller, G *Chem. Ber.* **1989**, *122*, 1433.

(12) Schmidbaur, H.; Bach, I.; Wilkinson, D. L. *Chem. Ber.* **1989**, *122*, 1445.

(13) Schmidbaur, H.; Müller, G.; Riede, J.; Manninger, G.; Helbig, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1013.

(14) Schmidbaur, H.; Wilkinson, D. L.; Schier, A.; Helbig, J.; Manninger, G. *New J. Chem.* **1994**, *18*, 507.

(15) Schmidbaur, H.; Mikulcik, P.; Müller, G. *Chem. Ber.* **1990**, *123*, 1599.

(16) Wiesbrock, F.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2002**, 3201.

(17) Wiesbrock, F.; Nogai, S.; Schier, A.; Schmidbaur, H. *Helv. Chim. Acta* **2002**, *85*, 1151.

(18) Wiesbrock, F.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2002**, 4703.

(19) Schmidbaur, H.; Classen, H.-G.; Helbig, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1090.

(20) Müller-Örlinghausen, B.; Imiela, M. *Pharmacopsychatrie* **1986**, *19*, 284.

(21) Murugavel, R.; Karambelkar, V. V.; Anantharaman, G.; Walawalkar, M. G. *Inorg. Chem.* **2000**, *39*, 1381.

(22) Debuyst, R.; Dejehet, F.; Dekandelaer, M.-C.; Declercq, J.-P.; Germain, G.; Meerssche, M. V. *J. Chim. Phys. Phys.-Chim. Biol.* **1979**, *76*, 1117.

(23) Wiesbrock, F.; Schmidbaur, H. *J. Am. Chem. Soc.* **2003**, *125*, 3622.

(24) Kristiansson, O. *Eur. J. Inorg. Chem.* **2002**, 2355.

Table 1. Crystal Data, Data Collection, and Structure Refinement of the Compounds

	$Cs(Sal)(H_2O)$	$Cs[H(Anth)_2]$	$Rb(Anth)(H_2O)$
	Crystal Data		
empirical formula	$C_7H_7Cs_1O_4$	$C_{14}H_{13}Cs_1N_2O_4$	$C_7H_8N_1O_3Rb_1$
fw	288.04	406.17	239.61
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	Pbca
a (Å)	11.6238(4)	14.9803(5)	7.5311(2)
b (Å)	5.8212(2)	7.7142(2)	7.9335(2)
c (Å)	13.2502(5)	13.4919(3)	29.0604(8)
β (deg)	99.864(2)	108.377(1)	90
V (Å^3)	883.31(5)	1479.63(7)	1736.30(8)
ρ_{calcd} (g·cm^{-3})	2.166	1.823	1.833
Z	4	4	8
F(000)	544	792	944
μ(Mo Kα) (cm^{-1})	4.164	2.519	5.668
	Data Collection		
no. of measured reflns	33967	23196	47628
no. of unique reflns (R_{int})	1960 (0.0457)	3236 (0.0510)	1881 (0.0419)
	Absorption Correction		
$T_{\mathrm{min}}/T_{\mathrm{max}}$	0.386/0.788	0.481/0.833	0.653/0.899
	Refinement		
no. of ref params	121	242	141
	Final R Values [$I \geq 2\sigma(I)$]		
R1[a]	0.0325	0.0335	0.0252
wR2[b]	0.0874	0.0860	0.0600
final diff map (e·Å^{-3})	1.363/−1.767	1.189/−1.336	0.497/−0.290

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$. $p = (F_o^2 + 2F_c^2)/3$. a and b are free variables.

Table 2. Hydrogen Bonding in the Compounds

D−H−A	d(D−H) (Å)	d(H···A) (Å)	D−H···A (deg)	d(D···A) (Å)	symmetry operation[a]
		$Cs(Sal)(H_2O)$			
O01−H02−O2	0.88(1)	1.88(2)	2.736(4)	164(5)	
O01−H01−O2	0.88(1)	1.92(2)	2.752(4)	158(5)	1
O3−H03−O1	0.92(8)	1.63(8)	2.521(4)	160(7)	
		$Cs[H(Anth)_2]$			
N1−H1B−O11	0.71(3)	2.29(4)	2.698(5)	118(4)	
N2−H2A−O21	0.89(5)	1.97(4)	2.677(4)	135(4)	
O22−H01−O11	0.99(7)	2.42(8)	3.230(4)	139(5)	
O22−H01−O12	0.99(7)	1.52(7)	2.459(3)	156(7)	
		$Rb(Anth)(H_2O)$			
N1−H1−O1	0.77(3)	2.11(3)	2.669(3)	129(3)	
O01−H01−N1	0.81(1)	2.32(2)	3.062(3)	153(3)	
O01−H02−O2	0.81(1)	1.96(1)	2.739(3)	161(4)	2

[a] (1) $-x + 1, y - 0.5, -z + 0.5$, (2) $x + 1, y, z$.

(=C−H); 864, m, γ(=C−H); 806, m, γ(=C−H); 757, s, γ(=C−H); 663, s, γ(N−H). MS (FAB, negative): $m/e = 359$, $[^{87}\mathrm{Rb(Anth)}_2]^-$, 10.01; 357, $[^{85}\mathrm{Rb(Anth)}_2]^-$, 22.43; 222, $[^{87}\mathrm{RbAnth} - \mathrm{H}]^-$, 1.13; 220 $[^{85}\mathrm{RbAnth} - \mathrm{H}]^-$, 2.19; 177 $[^{85}\mathrm{RbAnth} - \mathrm{CO_2}]\bullet^-$, 4.26; 136, $[\mathrm{Anth}]^-$, 100.0.

Single-Crystal X-ray Diffraction Analyses. The crystalline samples were placed in an inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated with an Enraf-Nonius DIP-2020 image plate system (Silicon Graphics O2 workstation) with monochromated Mo Kα (λ = 0.71073 Å) radiation at −130 °C. The structures were solved by direct methods using SHELXS-97[25a] and refined by full-matrix least-squares calculations on F^2 with SHELXL-97.[25b] Non-H-atoms were refined with anisotropic thermal parameters. H-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 nitrogen and oxygen atoms were located and refined with isotropic contributions. The protons of the water molecules were not stable toward refinement unless the O−H distances were fixed to the values found before refinement. Absorption corrections were applied for all compounds using DELABS. Crystal data, experimental details, and refinement results are listed in Table 1. Important interatomic distances and angles are given in the corresponding figure captions. Prominent hydrogen bonds are summarized in Table 2. Thermal parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1 EZ, U.K. The data are available on request by quoting CCDS-217532 to CCDS-217534.

Preparations

Aqueous solutions of rubidium and cesium anthranilates and salicylates are readily prepared by neutralization of the two carboxylic acids by the metal hydroxides or carbonates. However, the products are highly soluble in water, and single-crystal growth was only successfully accomplished under empirically modified conditions in selected cases. Rubidium anthranilate was obtained as a monohydrate, Rb(Anth)(H_2O), but with the same 1:1 stoichiometry no cesium salt could be crystallized. It was only with the 1:2 stoichiometry that a macrocrystalline anhydrous cesium hydrogen bisanthranilate, Cs[H(Anth)$_2$], could be isolated. This stoichiometry is also achieved upon absorption of carbon dioxide by an aqueous cesium anthranilate solution (Cs:Anth = 1:1). The equilibrium is thereby shifted to the 1:2 product by the formation of cesium bicarbonate, Cs(HCO_3), which is known to be one of the very few cesium salts which show low solubility in water.[26]

$$\mathrm{RbOH + AnthH \xrightarrow{H_2O} Rb(Anth)(H_2O)} \tag{1}$$

$$\mathrm{2CsOH + 2AnthH + CO_2 \xrightarrow{H_2O} Cs[H(Anth)_2] + CsHCO_3} \tag{2}$$

Aqueous solutions of rubidium salicylate, Rb(Sal), did not yield suitable single crystals even after extensive variation of the crystal growth conditions. By contrast, crystals of a cesium salicylate hydrate, Cs(Sal)(H_2O), were readily obtained.

$$\mathrm{CsOH + SalH \xrightarrow{H_2O} Cs(Sal)(H_2O)} \tag{3}$$

The compounds were identified through their elemental analysis data. Infrared and mass spectra were found to be of low diagnostic value due to extremely complicated vibrational patterns and extensive fragmentation, respectively. The crystals are stable in air and not hygroscopic, but readily lose water when exposed to a vacuum.

Structures

In the structural studies, the crystal structure of cesium bicarbonate, Cs(HCO_3), was redetermined[26,27] to obtain state-

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(25) (a) Sheldrick, G. M. *SHELXS-97, Program for structure solution*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL-97, Program for crystal structure analysis*; University of Göttingen: Göttingen, Germany, 1997. (c) Johnson, C. K. *ORTEP*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(26) Caranoni, C. *J. Appl. Crystallogr.* **1972**, *5*, 247.

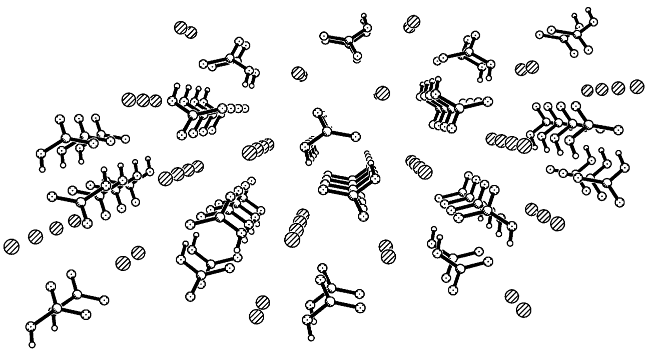

Figure 1. Cell plot of $CsHCO_3$, showing the mutual arrangement of cesium cations and dimers of bicarbonate anions.

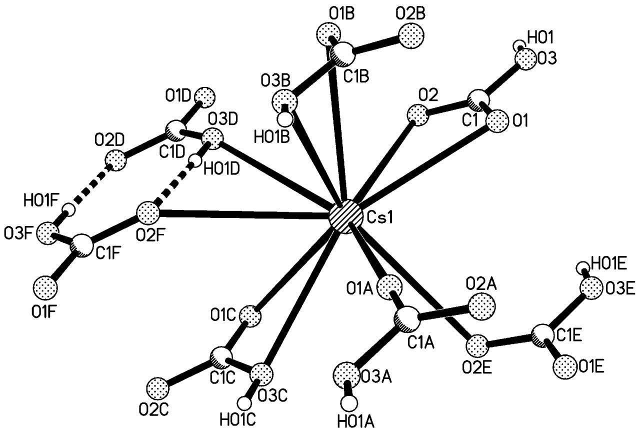

Figure 2. Coordination sphere around the cesium cations in $CsHCO_3$. Selected bond lengths (Å), angles (deg), and symmetry transformations (indicated by superscript numbers): Cs−O1 3.152(3), Cs−O2 3.116(3), Cs−O1A^{1} 3.061(3), Cs−O1B^{2} 3.261(3), Cs−O3B^{2} 3.482(3), Cs−O1C^{3} 3.206(3), Cs−O3C^{3} 3.119(3), Cs−O3D^{4} 3.239(3), Cs−O2E^{5} 3.288(3), Cs−O2F^{6} 3.426(3); O1−Cs−O2 41.83(7), O^{3}−C^{3-}Cs−O1C^{3} 41.02(8), O2−Cs−O3C^{3} 138.96(7), O1−Cs−O3C^{3} 150.12(7); (1) $-x - 1, -y + 2, -z - 1$, (2) $-x, -y + 2, -z - 1$, (3) $-x - 0.5, y - 0.5, -z - 0.5$, (4) $-x + 0.5, y - 0.5, -z - 0.5$, (5) $x - 1, y, z$, (6) $x - 0.5, -y + 1.5, z - 0.5$.

of-the-art reference data for a cesium “carboxylate”. The crystal system and the cell constants published in a more recent study were confirmed.[27] The crystal is composed of isolated cesium cations and anion dimers featuring the typical ring structure arising from double hydrogen bonding between two carbonate/carboxylate units. Six parallel strings of cesium cations surround a column of dimeric bicarbonate anions in a distorted hexagonal array (Figure 1).

Selected bond lengths and angles are listed in the caption to Figure 2, which shows one complete anion dimer and the coordination of a cesium cation. The metal atom is 10-coordinate with three chelating bicarbonate ligands (O1/O2, O1B/O3B, O1C/O3C), two anions acting as monodentate contacts (O1A, O2E), and an anion dimer coordinated side-on (O2F, O3D). The Cs−O distances cover a wide range from 3.061(3) Å (for O1A) to 3.482(3) Å (for O3B). The O−Cs−O angles are smallest for the chelating units (e.g., 41.83(7)° for O1−Cs−O2), and otherwise appear to be determined by the ion packing.

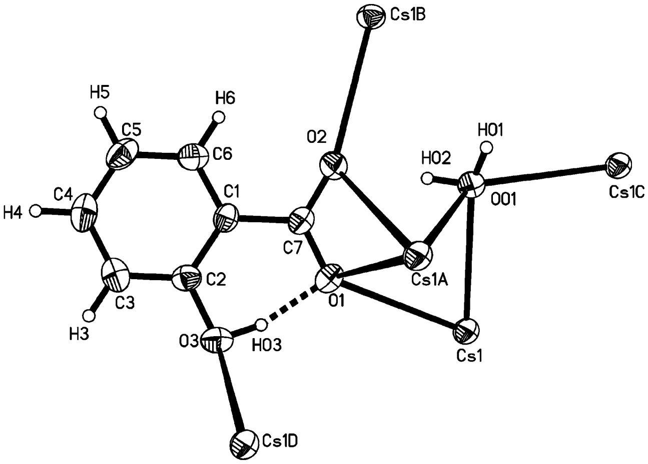

Figure 3. Coordination modes of the salicylate anion toward cesium cations in Cs(Sal)(H_2O) (ORTEP[25c] drawing with 50% probability ellipsoids and atomic numbering).

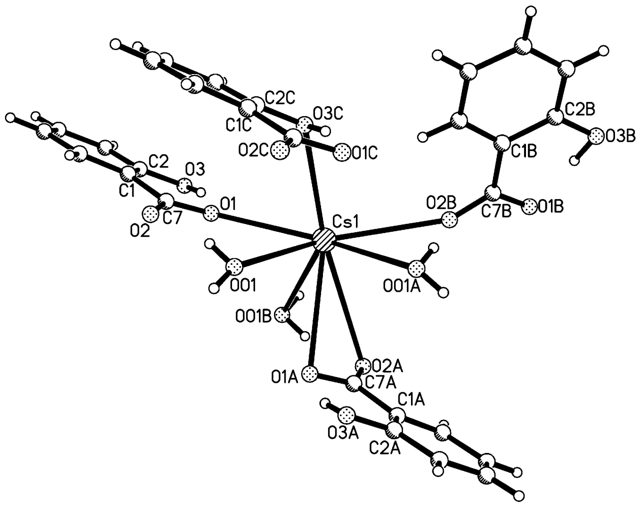

Figure 4. Coordination sphere of the cesium cations in Cs(Sal)(H_2O). Selected bond lengths (Å), angles (deg), and symmetry transformations (indicated by superscript numbers): Cs−O1 3.063(2), Cs−O01 3.071(3), Cs−O1A^{1} 3.341(3), Cs−O2A^{1} 3.584(2), Cs−O2B^{2} 3.155(2), Cs−O01A^{3} 3.173(3), Cs−O01B^{1} 3.308(3), Cs−O3C^{4} 3.183(3); O1−Cs−O01 66.24(7), O1−Cs−O2B^{2} 151.65(6), O0^{1}−B^{1-}Cs−O1A^{1} 60.54(7); (1) $-x + 1, -y - 1, -z + 1$, (2) $x, -y - 1.5, z + 0.5$, (3) $-x + 1, -y - 2, -z + 1$, (4) $x, y - 1, z$.

Cesium salicylate hydrate, Cs(Sal)(H_2O), 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 salicylate anion, and one water molecule. All atoms of the salicylate anion are virtually coplanar, and the carboxylate and hydroxy groups are tied together through an intraanionic hydrogen bond O3−H03···O1 (Table 2). Each anion has short contacts with four cesium cations through its oxygen atoms as shown in Figure 3. Conversely, each cesium atom is associated with four salicylate anions, which all have a different mode of coordination (Figure 4). Only one of them is bidentate (O1A/O2A), while the others are monohapto ligands (O1, O2B, O3C).

The coordination sphere of the cesium atom is completed by three water molecules, which are all in bridging positions to three neighboring metal atoms (H_2O with oxygen atom O01 in Figure 3). The water molecule is also engaged in hydrogen bonding with oxygen atoms (O2, O2A) of two carboxylate groups (Table 2 and Figure 5). The cesium atoms

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[27] Kaduk, J. A. *Z. Kristallogr.* **1993**, *204*, 319.

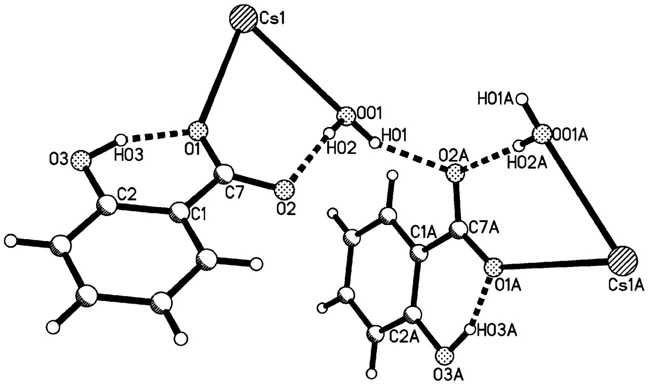

Figure 5. Hydrogen bonding in Cs(Sal)(H_2O). The water molecules link two cesium cations by their oxygen atoms (Cs−O−Cs, Figure 3) and two salicylate anions via their hydrogen atoms (O2···H02−O01−H01···O2A).

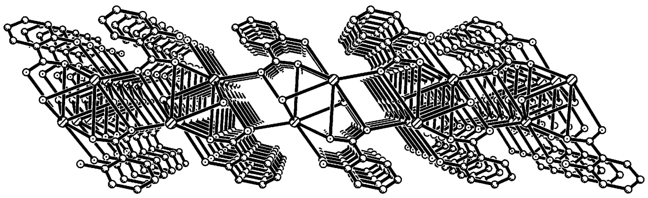

Figure 6. Formation of layers in Cs(Sal)(H_2O). The inner domains formed of the cesium ions, the water molecules, and the polar groups of the anthranilate anions are shielded by the benzene rings.

are eight-coordinate with Cs−O contacts in the range from 3.063(2) Å (for O1) to 3.584(2) Å (for O2A, which is already excessively long and should be considered a borderline case) (Figure 4). Note that these distances are very similar to those in the Cs(HCO_3) model structure (above). It is also worth observing that the Cs−O distances to carboxylate anions are not significantly different from those to water molecules: Cs−O1 = 3.063(2) Å, Cs−O01 = 3.071(3) Å.

Cs(Sal)(H_2O) is generally an exceptional cesium salt in that it contains water coordinated to the cation in the crystal, and even more so in that the water molecules are in rare triply bridging positions between these cations with quite different distances of 3.071(3) Å for Cs1, 3.173(3) Å for Cs1C, and 3.308(3) Å for Cs1B (Figure 4). This result shows that the interactions among cations, anions, and water dipoles in the lattice of Cs(Sal)(H_2O) are largely undirectional and determined by steric effects and Coulomb forces.

This concept is also supported by the overall structure of the compound as it is shown in Figure 6. 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 along the *a*-axis with long van der Waals contacts between the nonpolar covers.

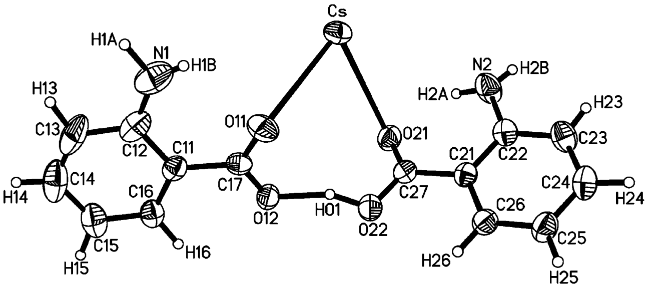

Figure 7. Asymmetric unit in the structure of Cs[H(Anth)$_2$] (ORTEP[25c] drawing with 50% probability ellipsoids and atomic numbering).

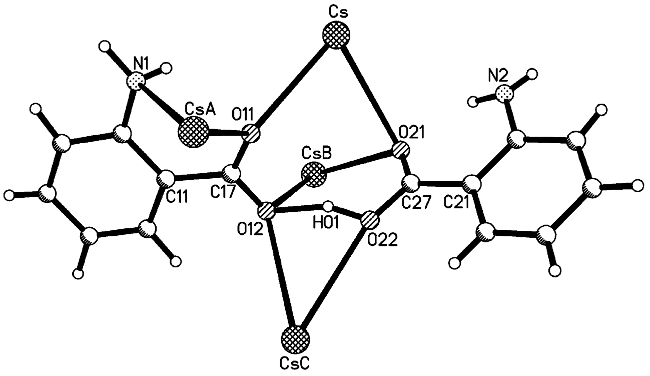

Figure 8. In Cs[H(Anth)$_2$] the complex anion chelates and bridges four different cesium atoms, resulting in the formation of six- and four-membered rings.

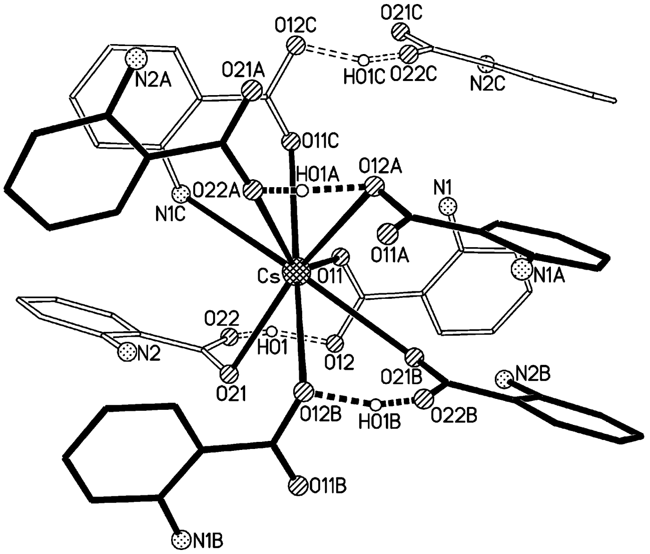

Figure 9. Eight-coordinate cesium ions in Cs[H(Anth)$_2$]. Selected bond lengths (Å), angles (deg), and symmetry transformations (indicated by superscript numbers): Cs−O11 3.025(2), Cs−O21 3.079(2), Cs−O12A^1 3.170(2), Cs−O22A^1 3.073(2), Cs−O12B^2 3.180(2), Cs−O21B^2 3.137(2), Cs−O11C^3 3.185(3), Cs−N1C^3 3.474(4); O11−Cs−O21 78.06(6), O11−Cs−O12A^1 114.49(6), O11−Cs−O22A^1 141.85(7), O11−Cs−O21B^2 73.71(6); (1) $x, -y + 1.5, z - 0.5$; (2) $-x, -y + 1, -z + 2$, (3) $-x, -y + 2, -z + 2$.

Cesium hydrogen dianthranilate, Cs[H(Anth)$_2$], is anhydrous and crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. The asymmetric unit thus contains one cesium cation and two hydrogen-bridged anthranilate anions (Figure 7). Taking a larger domain of the crystal lattice, it appears that the [H(Anth)$_2$]$^-$ anion is linked to four cesium cations (Figure 8), while each cesium cation has contacts to four of the anions and reaches coordination number 8 (Figure 9). The inner coordination sphere accommodates seven oxygen atoms (O11, O21, O12A, O22A, O12B, O21B, and O11C), together with one nitrogen atom (N1C). The Cs−O distances are in the narrow range from 3.025(2) Å for O11 to 3.185(3) Å for O11C, but the Cs−N contact is much longer at 3.474(4) Å for N1C. The geometry is rather distorted and not related to any of the eight-vertex regular polyhedra.

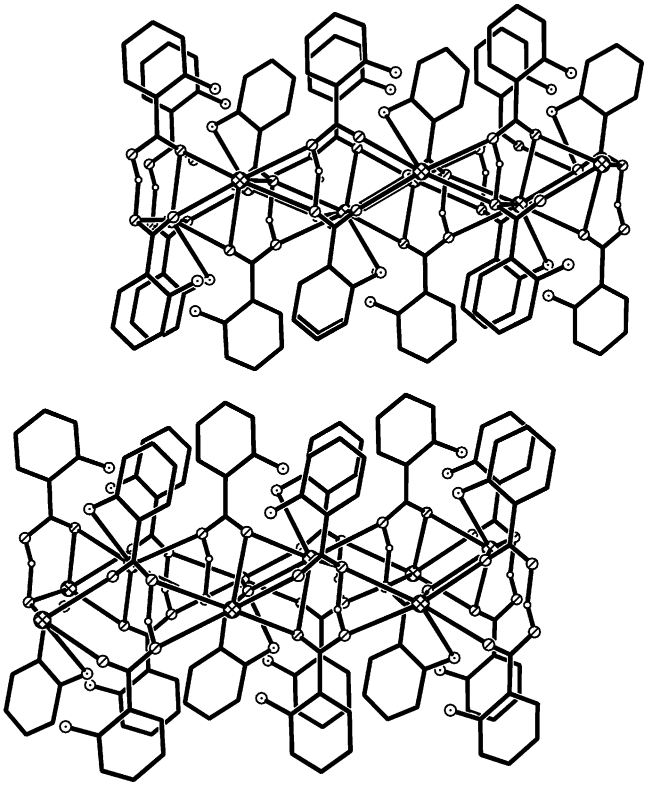

Figure 10. Formation of layers in crystals of Cs[H(Anth)$_2$]. All amino substituents point in the direction of the polar domains, yet only every second nitrogen atom is engaged in weak metal coordination.

The assembly of layers of the polar and nonpolar groups again leads to a stacking of sandwiches with the cesium cations, the carboxylate groups, and half of the amino groups forming the core structure. The aromatic rings, half of which have amino groups not engaged in coordination, protrude above and below the layers (Figure 10). Both amino groups (N1, N2) entertain hydrogen bonds with carboxylate oxygen atoms of the same anion (O11 and O21, respectively). The shortest hydrogen bond is established between O12 and O22 (Table 2).

Although Cs(Sal)(H$_2$O) and Cs[H(Anth)$_2$] have different ligands in a different stoichiometry, their crystal structures are found to follow the same principle based on electrostatic forces and steric requirement of the components. No directional effects are discernible, and the structures therefore have great flexibility. $\pi-\pi$-Stacking of arenes can be ruled out owing to excessively long distances ($d > 4$ Å). While the details of ion packing (coordination number, coordination geometry) are variable, the bulk *layer* structure is always preserved.

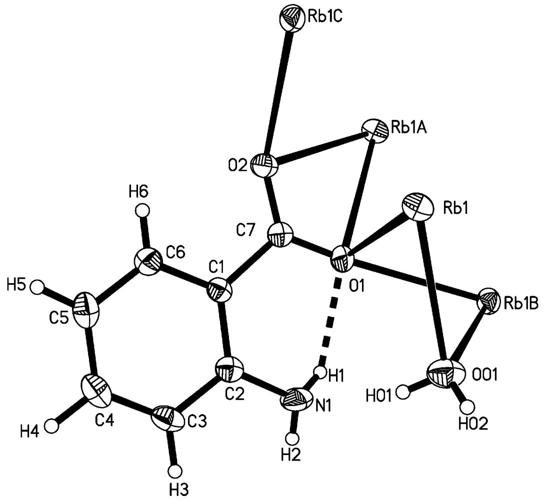

Figure 11. Coordination modes of the anthranilate anions toward rubidium cations (ORTEP[25c] drawing with 50% probability ellipsoids and atomic numbering).

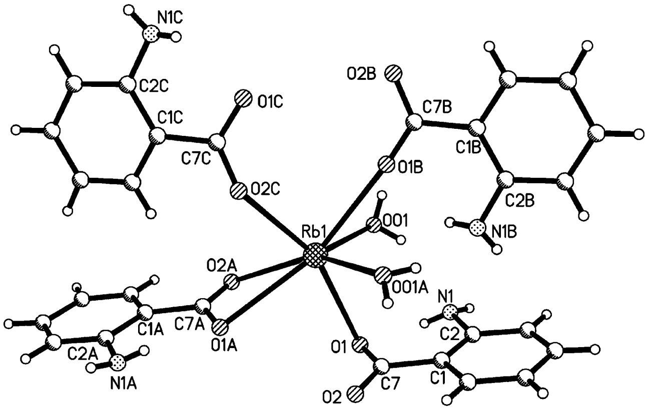

Figure 12. Coordination sphere of the metal ions in Rb(Anth)(H$_2$O). Selected bond lengths (Å), angles (deg), and symmetry operations (indicated by superscript numbers): Rb−O1 3.067(2), Rb−O01 2.923(2), Rb−O01A^1 2.952(2), Rb−O1A^2 2.942(2), Rb−O2A^2 2.928(2), Rb−O1B^1 2.886(2), Rb−O2C^3 2.822(2); O01−Rb−O2C^3 18.66(5), O01−Rb−O1B^1 71.27(5), O01−Rb−O2A^2 86.90(5); (1) $-x + 0.5$, $y + 0.5$, z, (2) $-x$, $-y$, $-z$, (3) $x + 0.5$, $-y + 0.5$, $-z$.

Rubidium anthranilate hydrate, Rb(Anth)(H$_2$O), crystallizes in the orthorhombic space group *Pbca* with $Z = 8$ formula units in the unit cell. The asymmetric unit contains one rubidium cation, one anthranilate anion, and one water molecule. The anion has short contacts to three rubidium atoms in a very unusual arrangement: The two carboxylate oxygen atoms O1 and O2 are attached to four rubidium atoms (Rb1, Rb1A, Rb1B, and Rb1C). The oxygen atoms are both in bridgehead positions over metal atoms. The water molecule also bridges rubidium atoms with distances O01−Rb1 = 2.923(2) Å and O01−Rb1B = 2.952(2) Å (Figure 11). The rubidium cations are seven-coordinate exclusively by oxygen contact atoms with distances in the range from 2.923(2) Å for O01 to 3.067(2) Å for O1 (Figure 12). In this count the longer distances to O2 (3.532(2) Å) and O01 (3.608(2) Å) of a symmetry-related water molecule omitted in Figure 12 are ignored. The water molecules and the amino groups are engaged in hydrogen bonding as identified in Table 2 and illustrated in Figure 13.

The bulk structure of the compound is again a stacking of sandwiches in which the core layer contains all polar units while the periphery is made up of the aromatic rings (Figure 14). This structure is very similar to that of the cesium hydrogen bis(anthranilate) (Figure 11).

Discussion and Conclusions

The results of the present studies demonstrate that salicylic and anthranilic acid form stable salts with the largest alkali metals. These salts obtained from neutralization reactions with a 1:1 stoichiometry are soluble in water. Only two of

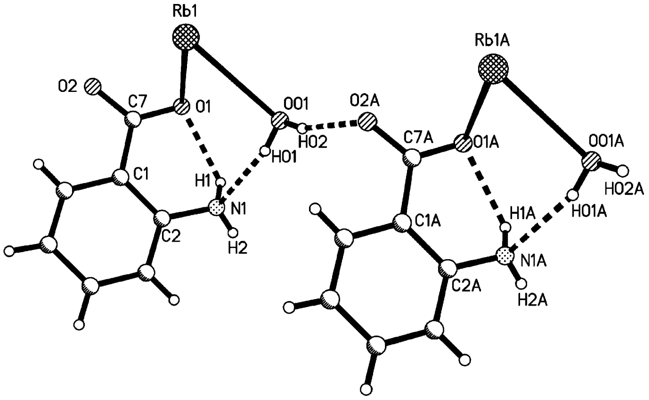

Figure 13. Hydrogen bonding in Rb(Anth)(H_2O). The water molecules are in a bridging position between two anions.

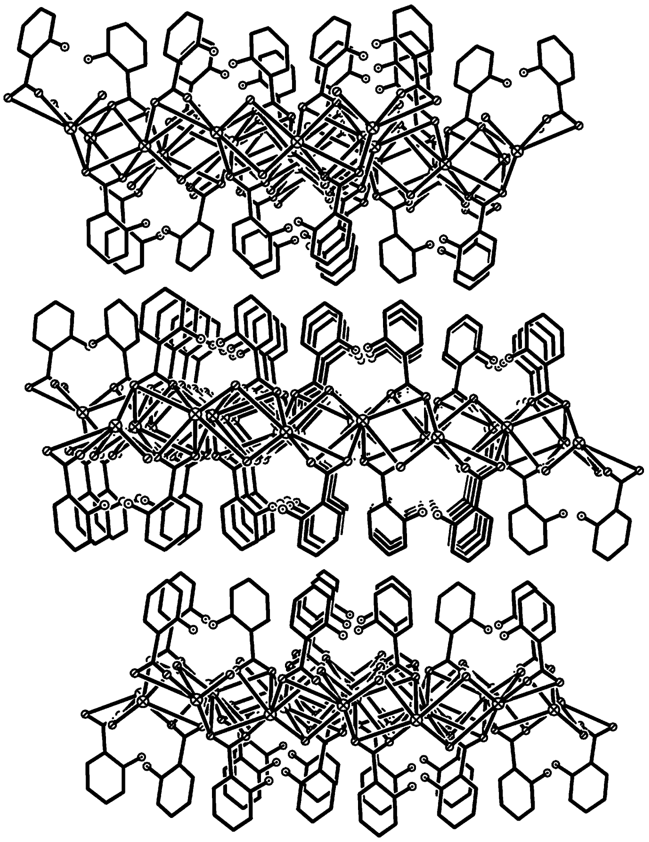

Figure 14. Cell plot of Rb(Sal)(H_2O). Although the amino groups are directed toward the rubidium ions, there is no short metal−nitrogen contact discernible.

the four compounds with this stoichiometry could be crystallized and were found to be the monohydrates Cs(Sal)(H_2O) and Rb(Anth)(H_2O). 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 carboxylate groups and the water molecules are all in bridging positions between the metal atoms. The hydroxy group of the salicylate and the amino group of the anthranilate are only involved in hydrogen bonding. The coordination sphere around the metal atoms is quite irregular and appears to be governed solely by electrostatic and steric effects. The coordination number for cesium is eight; for rubidium it is seven.

Aqueous solutions of cesium anthranilate, Cs(Anth), were found to absorb carbon dioxide to give cesium bicarbonate and cesium hydrogen bis(anthranilate) (eq 2), both of which could be crystallized. The structure of Cs(HCO_3) was redetermined, and the data of one of the two previous investigations[26,27] were confirmed and refined. The structure of the anhydrous Cs[H(Anth)$_2$] follows a pattern very similar to that of Rb(Anth)(H_2O) and Cs(Sal)(H_2O), but the cesium atoms are eight-coordinate involving one long Cs−N contact.

From the details of the new structures it is obvious that the 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 nonpolar organic groups. The most prominent difference from salts with the smaller alkali or alkaline-earth metals is the strict conservation of a certain coordination number and a more regular polyhedral geometry for the smaller cations such as magnesium with its strict octahedral hexacoordination toward oxygen donor atoms. Rubidium and cesium therefore are among the least amenable to play a template role in biological systems, and therefore were discarded in the evolutionary processes. 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 different from the structural characteristics recently found for the corresponding thallium(I) compounds.[23,24] Contrary to Rb^+ and Cs^+, Tl^+ clearly has a marked template effect in that it directs the donor atoms of the ligands to only half of its coordination sphere, the remainder of the hemisphere being shielded by the $6s^2$ lone pair of electrons. This effect is of great influence to the physiological properties as particularly obvious from the high toxicity of thallium compounds.

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