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Crystal Structure of a CsF–Uranyl–Salen Complex. An Unusual Cesium–Chlorine Coordination

Massimo Cametti,[†,‡] Maija Nissinen,*[,†] Antonella Dalla Cort,*[,‡] Kari Rissanen,[†] and Luigi Mandolini[‡]

Nanoscience Center, Department of Chemistry, University of Jyväskylä, P.O. Box 35, 40014 JYU, Finland, and Dipartimento di Chimica and IMC-CNR, Università La Sapienza, Box 34, Roma 62, 00185 Roma, Italy

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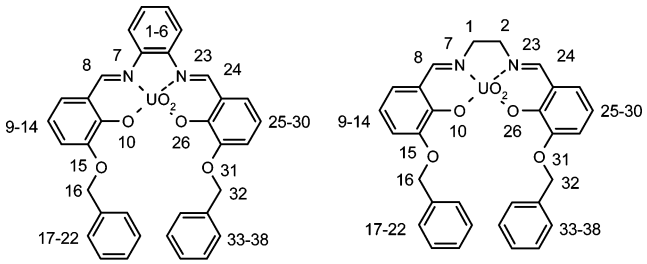
Complexation of CsF with the ditopic uranyl–salen receptor results in a solid-state structure, in which the coordination sphere of cesium is filled by ligation to one of the chlorine atoms of the solvent chloroform. This X-ray structure is the first example of chloroform ligation to an alkali-metal ion.

Investigation of synthetic ditopic receptors capable of simultaneous recognition of both counterions of organic and inorganic salts has attracted much attention in recent years.[1,2] We recently reported that uranyl−salophen receptor **1** (Chart 1) forms strong complexes with alkali-metal halides, in which anion recognition is ensured by binding to the Lewis acidic uranyl center, and cation−π interactions are established between the aromatic pendants and the counterion.[3] As a further development of such an investigation, we have prepared the CsF complex of the uranyl−salen receptor **2** (Chart 1) and determined its X-ray crystal structure to investigate whether and to what extent the less rigid salen influences the structure of the receptor−salt complex. To our surprise, we found that in this complex the cesium cation can accommodate unusual organochlorine coordination. Herein we report on the preparation and crystal structure of **2**·CsF·$CHCl_3$ as the first structural characterization of a complex with a molecule of chloroform ligated to an alkali-metal ion.

Chart 1. Chemical Formula of Uranyl Complexes Showing the Crystallographic Numbering



Crystals of **2**·CsF·$CHCl_3$ were obtained by slow evaporation of a solution of receptor **2**[4] and CsF in a mixture of $CHCl_3$, CH_3CN, and CH_3OH in a 8:1:1 ratio. The crystal structure[5] (Figure 1, upper) reveals that two uranyl−salen complexes form a dimeric 2:2 arrangement mediated by the

* To whom correspondence should be addressed. E-mail: majoni@cc.jyu.fi (M.N.), antonella.dallacort@uniroma1.it (A.D.C.).
† University of Jyväskylä.
‡ Università La Sapienza.

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(4) Synthesis of **2**: 1,2-Ethylenediamine (73 μL, 1.085 mmol) was added dropwise to a refluxing solution of 2-hydroxy-3-(phenylmethoxy)-benzaldehyde (0.3 g, 2.17 mmol) in methanol (30 mL). After 1.5 h, $UO_2(OAc)_2$·$2H_2O$ (0.46 g, 1.085 mmol) was added and reflux maintained for 15 min. The mixture was kept at room temperature overnight. The precipitated deep-red solid was filtered and dried in vacuo. Yield: 75%. Elem anal. Calcd for $C_{30}H_{26}O_6N_2U$·H_2O: C, 47.00; H, 3.68; N, 3.65. Found: C, 47.36; H, 3.49; N, 3.43. MS (ESI). Calcd for $C_{30}H_{27}O_6N_2U$ $[M + H]^+$ *m*/*z* 749.57. Found: *m*/*z* 749.4. Calcd for $C_{31}H_{30}O_7N_2UNa$ $[M + MeOH + Na]^+$ *m*/*z* 803.60. Found: *m*/*z* 803.5. Calcd for $C_{31}H_{30}O_7N_2UK$ $[M + MeOH + K]^+$ *m*/*z* 819.71. Found: *m*/*z* 819.8. ^{1}H NMR (500 MHz, DMSO): δ 9.459 (s, 2H), 7.594 (d, 4H, J = 7.4 Hz), 7.418 (t, 4H, J = 7.7 Hz), 7.353 (t, 2H, J = 7.2), 7.27−7.21 (m, 4H), 6.576 (t, 2H, J = 7.7 Hz), 5.354 (s, 4H), 4.493 (s, 4H). ^{13}C NMR (500 MHz, DMSO): δ 169.022, 160.456, 150.117, 138.079, 128.801, 128.543, 128.209, 127, 103, 124.313, 119.386, 115.869, 70.766, 64.11.

(5) Crystal data for $C_{30}H_{26}N_2O_6U$·CsF·$CHCl_3$: M = 1019.85, monoclinic, space group $P2_1/n$ (No. 14), a = 11.3318(2) Å, b = 17.9194(4) Å, c = 16.0631(4) Å, β = 94.0485(8)°, V = 3253.6(1) Å^3, T = 173.0(2) K, Z = 4, μ(Mo Kα) = 6.389 mm^{-1}, 19 071 reflections collected, 5724 unique reflections, final R_1 = 0.037, R_w = 0.071 for $I > 2\sigma(I)$. The corresponding values for all data are R_1 = 0.066 and R_w = 0.084.

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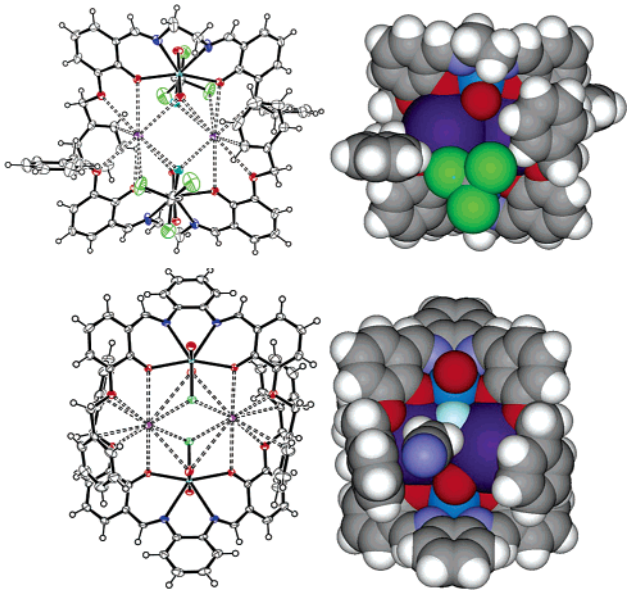

Figure 1. Upper: crystal structure of the dimeric assembly of **2**·CsF·$CHCl_3$. The coordination sphere of the cesium is filled by electrostatic interactions to the oxygens of the receptor, to fluoride anions, to solvent chloroform, and by cation···π interactions to one aromatic side arm. Lower: crystal structure of the dimeric assembly of **1**·CsF·CH_3CN.[3] Acetonitrile is excluded from the ORTEP plot for clarity. Both complexes were obtained by slow evaporation of the same $CHCl_3/CH_3CN/CH_3OH$ solvent mixture.

coordination of two cesium cations to two receptors. The fluoride anions are bound in the equatorial plane of the uranyl centers, and the negatively charged receptor−fluoride units are connected via coordination to metal cations situated in close proximity to the aromatic side arms.

Similar dimeric arrangements were found to be of general occurrence in the complexation of receptor **1** with alkali-metal halides (KCl, RbCl, CsCl, and CsF).[3] Whereas the size of the cation has practically no effect on the structure of dimeric complexes, the size of the anion causes differences. The smaller fluoride leaves more space inside the dimeric assembly of the CsF complex of **1**, and inclusion of a molecule of solvent acetonitrile via CH···F hydrogen bonding to electronegative fluoride is possible (Figure 1, lower).

Although there are analogies between the CsF complexes of receptors **1** and **2**, there are also significant differences. In both cases, each cesium is coordinated to six oxygens, creating a pseudo crown ether environment, and to two fluorides. The coordinative distances in **2**·CsF are in agreement with typical Cs^+···O and Cs^+···F^- ranges, being 3.009(5)−3.980(5) Å for coordination to oxygen and 2.911(4)−2.925(4) Å for coordination to fluoride (Table 1). Whereas both side arms of **1** establish cation-π interactions with cesium,[3] only one side arm of **2** is in contact with cesium, with the closest coordinative distance Cs^+···C of 3.448(8) Å. This indicates η^1 binding because distances to other aromatic carbons are significantly longer [3.744(7)−4.787(8) Å]. The second side arm is bent outward from the interior of the dimer, and the chloroform is CH···F hydrogen bonded to fluoride (C90/C90B···F ∼ 3.1 Å). This hydrogen bonding orients the chloroform toward the interior of the dimeric assembly and keeps it in close proximity to the

Table 1. Closest and Coordinative Distances (Å) between the Alkali-Metal Cation and Uranyl−Salen Receptor **2**[a]

	2·CsF distance (Å)
aromatic side arm 1[b]	
C17	3.744(7)
C18	*3.448(8)*
C19	3.905(8)
C20	4.542(8)
C21	4.787(8)
C22	4.422(2)
centroid 1	B: 3.931(8)
aromatic side arm 2	no connection
fluoride A[b]	*2.911(4)*
fluoride B[b]	*2.925(4)*
O1(A)[b]	*3.980(5)*
O1(B)[b]	*3.580(5)*
O10(B)[b]	*3.121(4)*
O15(B)[b]	*3.119(4)*
O26(A)[b]	*3.153(5)*
O31(A)[b]	*3.009(5)*
$CHCl_3$[c]	*3.47(1)/3.73(1)*

[a] Clearly coordinative bonds are shown in italics. [b] A and B denote the aromatic side arms, halides, and oxygens from different asymmetric units. [c] Disordered chloroform. The two figures refer to different components of the disorder.

cesium cation, to which it is coordinated via chlorine in a η^1 fashion [3.47(1) or 3.73(1) Å depending on which part of the disordered chlorine is investigated]. This unusual solvent ligation completes the coordination sphere of the cation, which in the case of the CsF complex of **1** is filled by cation−π interactions to two aromatic side arms.

Differences between the two complexes arise from the replacement of the flat and rigid *o*-phenylenediamine moiety in **1** with the bent, more flexible ethylenediamine moiety in **2**. It is likely that the more important role of cation−π interactions in the complex with **1** reflects a higher degree of preorganization of the salophen receptor. The contribution of the side arms in the complex with the less preorganized salen receptor **2** is significantly lessened, which renders the cesium ion accessible to ligation of a competing donor, even as weak as chloroform.

The less ordered structure of **2** compared to **1** is evidenced in the crystal structures of their salt-free methanol complexes (Figure 2, upper), in which the methanol is coordinated to the uranyl center.[3,6] The side arms of **1** are turned inward in a quasimacrocyclic arrangement that encloses the methanol guest, whose C−H bonds are engaged in CH···π interactions with the side arms.[3] Because a very similar isomorphous structure was obtained when **1** was crystallized from acetonitrile[3] and because the shape of the salophen moiety is also very similar in the CsF complex (Figure 1, lower), it is clear that the uranyl−salophen receptor **1** is rigid enough to retain essentially the same concave shape in different complexes, regardless of the guest coordinated to the uranyl center. In contrast, as a consequence of the distortion imposed by the

(6) Crystallized by slow evaporation from a MeOH/acetone mixture. Crystal data for $C_{30}H_{26}N_2O_6U\cdot CH_3OH\cdot 0.5(CH_3)_2CO$: $M = 809.64$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.0159(5)$ Å, $b = 10.4519(4)$ Å, $c = 15.2798(7)$ Å, $\alpha = 103.338(2)°$, $\beta = 95.853(2)°$, $\gamma = 104.600(3)°$, $V = 1484.2(1)$, $T = 173.0(2)$ K, $Z = 2$, μ(Mo Kα) = 5.522 mm^{-1}, 7938 reflections collected, 4987 unique reflections, final $R_1 = 0.045$, $R_w = 0.119$ for $I > 2\sigma(I)$. The corresponding values for all data are $R_1 = 0.051$ and $R_w = 0.122$.

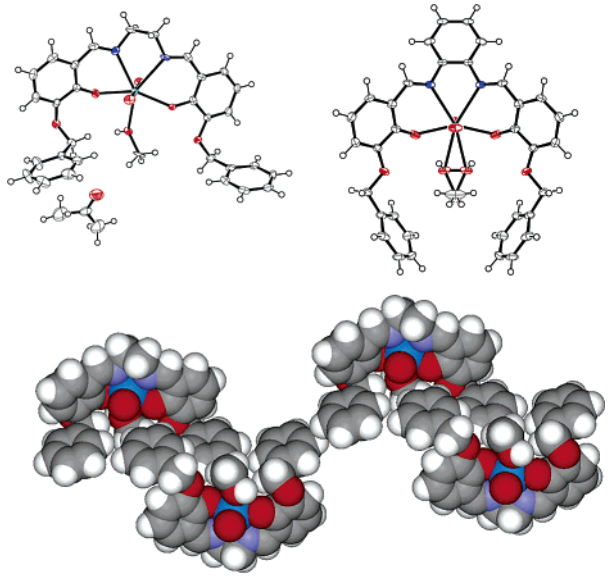

Figure 2. Upper left: crystal structure of receptor **2** crystallized from MeOH/acetone. The cocrystallized acetone shows some CH···π interactions with one of the side arms. Upper right: crystal structure of **1**·MeOH.[3] Lower: van der Waals representation of the crystal packing of **2**, showing π stacking between the side arms of adjacent receptors. Acetone is excluded from the van der Waals picture.

nonplanar geometry of the ethylendiamine moiety, the salen unit in the methanol complex of **2** is forced to adopt a less regular, more open conformation, in which the side arms are completely turned away from the core of the receptor. No CH···π connection is observed between the side arms and the complexed methanol. The crystal packing (Figure 2, lower) reveals the existence of π stacking of the aromatic side arms of adjacent receptors, indicating that packing effects including π stacking are in a more governing role than CH···π interactions with methanol.

Organochlorine ligation to an alkali-metal ion is extremely rare. Previous examples, the only ones available to our knowledge, have been reported by Bryan et al., who found that in complexes of $CsNO_3$ with tetrabenzo-24-crown-8 the cesium cation can accommodate ligation to either dichloromethane[7] or 1,2-dichloroethane,[8] both with η^2 binding. Acetonitrile was found to behave in a similar way.[7] The origin of such ligation was assigned to steric reasons and crystal packing as well as to the favorable electronic environment of the relatively soft cesium cation. These considerations also apply to our complexes. However, there are some differences, the most significant being the role of the anion for ligation and complexation. In uranyl−salen and −salophen receptors, there is, by design, an anion binding site at the uranyl center, which is proximal to the cation binding site. This enables a tight cation−anion interaction, which reinforces the binding. Because of the lack of an anion binding site in the tetrabenzo-24-crown-8 ligand, the nitrate counteranion is excluded from the cation coordination sphere and located in the interstice of the crystal lattice. In both **1**·CsF and **2**·CsF, the strong hydrogen-bonding ability of fluoride affects the position of the included solvent molecule by orienting the C−H bond toward the anion and, hence, the interior of the assembly. Furthermore, the hydrogen bonding to fluoride prevents the acetonitrile in **1**·CsF from ligation to the metal ion, as was found to be the case in the complex of tetrabenzo-24-crown-8. Interestingly, ligation to chlorine in **2**·CsF occurs in a η^1 fashion, instead of the η^2 fashion found in Bryan's complexes, presumably as a consequence of the orientation imposed to the bound chloroform by hydrogen bonding to fluoride.

In conclusion, the structure of the CsF complex of the salen receptor **2** has been described in detail and compared with the structure of the corresponding complex of the salophen analogue **1**. In the complex with **2** but not in that with **1**, the cesium ion can accommodate unusual ligation to a chloroform solvent molecule. The structure of **2**·CsF·$CHCl_3$ is a rare example of a situation in which the steric and electronic environment created in the surroundings of an alkali-metal ion, upon complexation with a receptor, allows subsequent ligation even for a ligand with extremely weak binding properties such as chloroform.

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Supporting Information Available: Presentation of the coordination of the individual cesium cation by receptors **1** and **2** and crystallographic data in CIF format for **2**·CsF and **2**·MeOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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