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Unusual Two-Dimensional Sheet Structure of the Solvent-Free Cesium Aryloxide Complex $CsO-2,6-i-Pr_2C_6H_3$

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Introduction

There is considerable current interest in understanding both the solid-state and solution structures of simple alkali metal salts such as alkyls,[2] amides,[2e,3] and alkoxides,[4] in an attempt to correlate the chemical behavior of these species with a knowledge of the degree of aggregation and solvation of the complex. The majority of interest to date has been focused upon complexes of the lighter alkali metals, principally lithium, and much less attention has been paid to the corresponding derivatives of the heavier alkali metals. Only recently have theoretical calculations of the structures of organopotassium, -rubidium, and -cesium complexes appeared.[2i,5] These calculations, involving delocalized carbanions, showed that the larger, more polarizable cations (K, Rb, and Cs) preferred multihapto interactions with ring carbons, while the smaller alkali metals tended to interact with the center of highest charge. Collateral interactions with additional carbanions were also found to be preferred for the heavier alkali metals, in contrast to findings for lithium and sodium cations, which favored interactions with heteroatoms such as nitrogen and oxygen. In a related series of studies, the interactions of both alkali metal and alkylammonium cations with neutral arene rings (so-called "cation−π interactions") have received considerable attention, since such interactions are thought to play an important role in a variety of proteins that bind cationic ligands or substrates.[6]

During recent investigations into the structure and reactivity of lanthanide aryloxide derivatives, we have isolated a number of salt or "ate" complexes of the stoichiometry $M'[Ln(OAr)_4]$ ($M' = K$,[7] Cs[8]) and $Cs_2[La(OAr)_5]$[9] ($Ar = 2,6-i-Pr_2C_6H_3$) in which the coordination sphere of the alkali metal cations consists exclusively of multihapto η-arene interactions with aryloxide ligands from adjacent $[Ln(OAr)_4]^-$ or $[Ln(OAr)_5]^{2-}$ units. Following our preparation and utilization of the parent alkali metal aryloxide complex $Cs(O-2,6-i-Pr_2C_6H_3)$ during the synthesis of the lanthanum salts, we became aware of the dearth of structural data concerning heavy alkali metal aryloxide species. Although many complexes of both the lighter[10] and heavier[11] alkali metal aryloxides have been structurally characterized in which a crown ether is employed to encapsulate the cation, very few solvent-ligated or solvent-free aryloxide salts containing sodium,[12,13] potassium,[12h,14] rubidium,[12h] or cesium[12h,15] have been subjected to X-ray diffraction studies. In the case of cesium, we have found only one example of a structurally characterized solvent-free aryloxide complex, namely cesium picrate $Cs[O-2,4,6-(NO_2)_3C_6H_2]$, which has been subjected to X-ray diffraction studies by two independent groups.[12h,15] In addition, very recent high-resolution powder X-ray diffraction data for cesium phenoxide (CsOPh) revealed a chain structure with both six-coordinate and three-coordinate metal ions and a

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very weak interaction (Cs−C, 3.6(2) Å) between the cesium cation and an adjacent arene ring.[16]

Here, we report upon the unusual two-dimensional infinite-sheet structure of the solvent-free cesium aryloxide complex Cs(O-2,6-*i*-$Pr_2C_6H_3$). To the best of our knowledge, this work represents the first structural characterization of an alkyl-substituted solvent-free aryloxide complex of the heavier alkali metals.

Experimental Section

General Procedures and Techniques. All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres glovebox. 2,6-Di-*iso*-propylphenol was purchased from Aldrich and degassed before use. Cesium metal was obtained from Aldrich and stored in the drybox. Solvents were degassed and distilled from sodium benzophenone ketyl under nitrogen. THF-d_8 was degassed, dried over Na−K alloy, and then trap-to-trap distilled before use.

NMR spectra were recorded at 22 °C on a Brüker WM300 spectrometer. ^{1}H NMR chemical shifts are reported in parts per million relative to the ^{1}H impurity in THF-d_8 set at δ 3.58. Elemental analysis was performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Table 1. Summary of Crystal Data for CsO-2,6-*i*-$Pr_2C_6H_3$ (**1**)

empirical formula	$C_{12}H_{17}CsO$
space group	*Pbca*
a, Å	18.755(4)
b, Å	7.267(2)
c, Å	18.812(5)
temp (K)	198
Z	8
V (Å^3)	2563.9(11)
d_{calc}, (g cm^{-3})	1.607
λ (Å)	0.71073
fw	310.17
μ, cm^{-1}	28.58
R1 [$I > 2\sigma(I)$]^a	0.0402
wR2[$I > 2\sigma(I)$]^a	0.0959

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Cs(O-2,6-*i*-$Pr_2C_6H_3$) (1). In the drybox, 2.00 g (15.0 mmol) of cesium metal was added to a rapidly stirring solution of 2.68 g (15.0 mmol) of 2,6-di-*iso*-propylphenol dissolved in 50 mL of THF in a Schlenk reaction vessel. Vigorous stirring was continued for 72 h at room temperature. The resulting purple solution was filtered through a Celite pad, and all solvent was removed from the filtrate in vacuo to yield a purple solid, which was found to be free from contaminants by ^{1}H NMR spectroscopy; yield, 3.038 g (65%). X-ray quality crystals were obtained by slow evaporation of a THF solution in the drybox atmosphere. ^{1}H NMR (300 MHz, THF-d_8): δ 6.68 (d, J = 7 Hz, 2 H, meta OAr), 6.00 (t, J = 7 Hz, 1 H, para OAr), 3.46 (septet, J = 7 Hz, 2 H, C*H*Me$_2$), 1.13 (d, J = 7 Hz, 12 H, CH*Me*$_2$). Anal. Found: C, 47.52; H, 5.76. Calcd for $C_{12}H_{17}CsO$: C, 46.47; H, 5.52.

Crystallographic Studies. Cs(O-2,6-*i*-$Pr_2C_6H_3$) (1). A colorless rectangular block was attached to a thin glass fiber using silicone grease. The crystal, which was mounted from a pool of mineral oil bathed in argon, was then immediately placed under a nitrogen cold-stream on a Siemens P4/PC diffractometer utilizing graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 1.0° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS version 2.10b software. All data reduction, including Lorentz and polarization corrections, structure solution, and graphics were performed using SHELXTL PC version 4.2/360 software. The structure refinement was performed using SHELX 93 software.[17] All data were corrected for absorption using the ellipsoidal option in the XEMP facility of SHELXTL PC. Data collection parameters are given in Table 1.

The structure was solved in space group *Pbca* using direct methods and difference Fourier techniques. This solution yielded all non-hydrogen atom positions. The hydrogen atoms were fixed in positions of ideal geometry, with a C−H distance of 0.93 Å for benzyl hydrogens, 0.96 Å for methyl hydrogens, and 0.98 Å for methine hydrogen atoms. The hydrogens were refined using the riding model in the HFIX facility in SHELXL 93. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 times (benzyl and methine) or 1.5 times (methyl) the equivalent isotropic U of the carbon atom to which they were bonded. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms and converged to R1 = 0.0402 and wR2 = 0.0959.[18]

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(18) $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0610P)^2 + 16.6319P]$, with $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for CsO-2,6-*i*-Pr$_2$C$_6$H$_3$ (**1**)[a]

Cs(1)−O(1)#1	2.875(4)	Cs(1)−O(1)#2	2.898(5)
Cs(1)−C(1)	3.711(7)	Cs(1)−C(2)	3.630(7)
Cs(1)−C(3)	3.479(6)	Cs(1)−C(4)	3.375(6)
Cs(1)−C(5)	3.468(6)	Cs(1)−C(6)	3.622(6)
Cs(1)−C(1)#1	3.750(5)	Cs(1)−C(1)#2	3.589(7)
Cs(1)−C(4)#3	3.716(6)	O(1)−C(1)	1.304(7)
O(1)#1−Cs(1)−O(1)#2	94.12(9)		
Cs(1)#4−O(1)−Cs(1)#5	119.3(2)		
Cs(1)#4−O(1)−C(1)	123.1(4)		
Cs(1)#5−O(1)−C(1)	111.6(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*, *y* + 1/2, −*z* + 1/2; #2 *x*, *y* + 1, *z*; #3 −*x* + 1/2, *y* + 1/2, *z;* #4 −*x*, *y* −1/2, −*z* + 1/2; #5 *x*, *y* − 1, *z*; #6 − *x* + 1/2, *y* − 1/2, *z*.

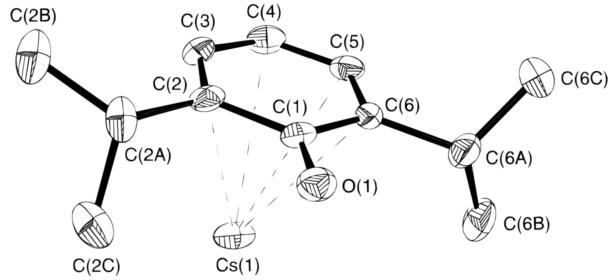

Figure 1. ORTEP plot (50% probability ellipsoids) of the Cs(O-2,6-*i*-Pr$_2$C$_6$H$_3$) unit, giving the atom numbering scheme used in the table.

Results and Discussion

Synthesis and Characterization. The reaction of cesium metal with 1 equiv of 2,6-di-*iso*-propylphenol in THF, followed by crystallization from the same solvent, allows the isolation of the solvent-free cesium salt CsO-2,6-*i*-Pr$_2$C$_6$H$_3$ (**1**) as a light-purple solid in 65% yield (eq 1). The aryloxide salt is found

$$\text{HO-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3 \xrightarrow[\text{THF}]{\text{Cs}} \underset{\mathbf{1}}{\text{CsO-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3} + \frac{1}{2}\text{H}_2 \qquad (1)$$

to be insoluble in hydrocarbon solvents but may be conveniently recrystallized from THF.

Ambient temperature ^{1}H NMR spectra of **1** in THF-d_8, together with microanalytical data, support the formulation of **1** without any solvent molecules within the coordination sphere of the cesium cation. In addition, the ^{1}H NMR resonances of the meta and para protons of the aromatic ring were noticeably upfield shifted as compared to their chemical shift in typical transition metal complexes. Similar upfield shifting of resonances has been observed previously for arene rings coordinated to cesium cations.[8,11h] This observation, together with the lack of solvent molecules within the formulation of **1**, led us to undertake an X-ray diffraction study in order to determine the nature of the coordination environment about the cesium metal center.

Solid State and Molecular Structure. CsO-2,6-*i*-Pr$_2$C$_6$H$_3$ (1). Single crystals of **1** suitable for an X-ray diffraction study were grown by slow evaporation of a concentrated THF solution in the drybox atmosphere at ambient temperature. A summary of crystal data and processing parameters is given in Table 1, while selected bond lengths and angles are presented in Table 2. An ORTEP plot of a single CsOAr unit in **1**, giving the atom numbering scheme used in the tables, is shown in Figure 1. A view of the extended structure of **1**, showing the formation of the chain and sheet structure is shown in Figure 2. The overall solid-state structure of **1** can be seen to comprise Cs(O-2,6-*i*-Pr$_2$C$_6$H$_3$) units, which form pseudo-one-dimensional infinite chains by means of both Cs−O and Cs−π-arene interactions with the neighboring unit. The one-dimensional chains are further held together into two-dimensional sheets by means of Cs−C interactions between a carbon atom in the para position of the arene ring and a cesium cation from an adjacent chain (Figure 2). It is notable that no solvent molecules are present within the solid-state structure, despite the fact that the aryloxide salt was crystallized from THF.

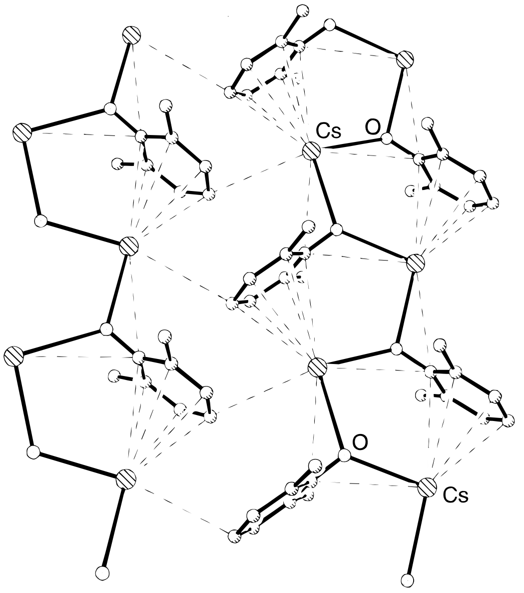

Figure 2. Ball-and-stick drawing of the extended solid-state structure of CsO-2,6-*i*-Pr$_2$C$_6$H$_3$ (**1**). Methyl carbon atoms of the isopropyl groups are omitted for clarity.

Cs−O distances to the aryloxide ligands are 2.875(4) and 2.898(5) Å. These Cs−O distances are comparable to those observed in cesium picrate complexes,[11h,j,12h,15] and also to the Cs−O distance in tetrameric [Cs(O-*t*-Bu)]$_4$ (2.924 Å).[19] The Cs−arene interaction is quite asymmetric, with the cesium metal center being offset toward the para carbon (C(4)), away from the sterically demanding isopropyl groups in the 2,6-positions. Thus, a vector from the cesium atom passing perpendicular to the ring plane intersects the plane at a point that is offset 0.39 Å from the ring center toward C(4). Cs−C distances within the primary cesium−η^6-arene interaction lie in the range 3.375(6)−3.622(6) Å, while interchain Cs−C contacts of 3.716(6) Å are made by the para carbon atoms of the aryloxide ring. These Cs−C distances lie within the range of 3.35(4)−4.12(1) Å found in other structurally characterized complexes containing Cs−arene interactions.[2g,5a,8,9,11h,i,20] The Cs−ring$_{\text{centroid}}$ distance of 3.24 Å in **1** is among the shortest yet reported, being comparable to the Cs−ring$_{\text{centroid}}$ distances of 3.21−3.34 Å found

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for the multiple Cs−η^6-arene interactions in $Cs_2[La(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_5]$[9] and to the 3.24 Å observed in the cesium alkyl complex $[Cs(MeOCH_2CH_2OCH_2CH_2OMe)]_2[Ph_2CCPh_2]$.[2g] This strong Cs−$\pi$-arene interaction presumably reflects the partial anionic character of the arene ring, since the Cs−ring$_{centroid}$ distance is considerably shorter than interactions that have been reported between cesium cations and neutral arene solvent molecules.[20g−i]

Concluding Remarks

The solid-state structure of **1** provides a marked contrast to that of the only other structurally characterized example of an unsolvated cesium aryloxide complex, namely cesium picrate $CsO\text{-}2,4,6\text{-}(NO_2)_3C_6H_2$,[12h,15] briefly described above. In the solid-state structure of the picrate derivative, cesium cations are coordinated in a tricapped trigonal prismatic fashion by nine oxygen atoms from seven different picrate anions and only one Cs−C contact of 3.695(4) Å to the ipso ring carbon atom is observed. Thus, it would appear that the six donor oxygen atoms within the nitro groups effectively saturate the coordination sphere of the cesium cation and prevent the formation of multiple cesium−π-arene interactions.

The structure of **1** thus expands upon the extremely limited number of crystallographic studies of heavy alkali metal aryloxides and begins to reveal a disparity in structural types between the earlier and later alkali metal salts similar to that observed for alkyl complexes. Lithium and, to a lesser extent, sodium aryloxide salts tend to oligomerize into discrete clusters in the solid state (typically dimers,[21] cubane-like tetramers,[12b,c,i,13e,22] and hexamers[4c]) with solvent molecules completing the coordination sphere of the alkali metal cations. The considerably larger ionic radii of potassium, rubidium, and cesium, however, together with their weaker affinity for donor solvents such as THF, allow them to enter into multihapto coordination with more than one arene ring, leading to the formation of extended chain, sheet, or network structures. Although such extended structures have been frequently reported for heavier alkali metal alkyl complexes,[2i,5a] a similar body of knowledge is only just beginning to be accumulated for aryloxide species. We do note, however, that no definitive structural dividing line can be drawn between sodium and potassium aryloxides, since the solvent-free sodium aryloxide complex $[Na(O\text{-}4\text{-}MeC_6H_4)]_n$ has been found to exist in the solid state as a one-dimensional chain containing sodium−arene interactions,[12b] whereas potassium 2,4,6-tris(trifluoromethyl)-phenoxide displays a discrete THF-solvated dimeric structure.[12c]

Previous mention has been made in the literature of the unusually large affinity of cesium cations for arene moieties.[11h,23] The crystallization of **1** from THF as a solvent-free complex, together with our isolation of solvent-free $Cs[La(OAr)_4]$[8] and $Cs_2[La(OAr)_5]$[9] ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$) complexes, appears to reinforce this assertion. In addition, we note that the ^1H NMR resonances of the arene rings in **1** are upfield shifted in THF-d_8 solution, suggesting that the cesium−π-arene interactions are maintained even in donor solvents.

Further investigations into the solid-state structures of anionic lanthanide aryloxide complexes with heavy alkali metal cations are currently in progress.

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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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