Unusual Ligand Coordination for Cesium

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When complexed by tetrabenzo-24-crown-8, the cesium ion can accommodate unprecedented ligation. The structures of the following complexes are presented. [Cs(tetrabenzo-24-crown-8)(η^1-NCMe)$_2$(η^2-NCMe)][NO$_3$] (**1**): triclinic $P\bar{1}$, $a = 12.0119(14)$ Å, $b = 13.3680(15)$ Å, $c = 13.7859(12)$ Å, $\alpha = 89.124(8)°$, $\beta = 66.928(9)°$, $\gamma = 71.536(10)°$, $V = 1916.7(4)$ Å^3, $Z = 2$. [Cs(tetrabenzo-24-crown-8)(η^1-NCMe)$_2$(η^2-CH$_2$Cl$_2$)][NO$_3$] (**2**): triclinic, $P\bar{1}$, $a = 12.295(3)$ Å, $b = 13.295(3)$ Å, $c = 13.782(3)$ Å, $\alpha = 89.105(17)°$, $\beta = 66.096(18)°$, $\gamma = 71.980(19)°$, $V = 1929.5(8)$ Å^3, $Z = 2$. These structures are the first reported examples of linear η^2-acetonitrile coordination to any metal ion and the first structures illustrating η^2-acetonitrile and dichloromethane ligation to an alkali metal ion. Possible steric and electronic origins of these unusual metal−ligand interactions are discussed.

The electronic component of ligand binding to alkali metal ions can generally be considered in terms of simple electrostatics. In fact, these cations may be characterized as a sphere of positive charge generally attracting donors with little regard for ligand orientation.[1] Much of the observed selectivities of particular crown ether molecules for a specific alkali metal cation derive from these facts.[2] Specifically, if a crown ether can adopt an energetically reasonable conformation with its oxygen donor atoms oriented toward the alkali metal cation, forming appropriate cation−oxygen bond lengths, favorable binding will occur.[3] Since crown ether molecules rarely complete the cation's coordination sphere, other ligands, typically anions, solvent molecules, or even parts of other crown molecules, are often observed to also bind the cation.[1] The nature of this additional binding is often overlooked, as the focus of most work is on the primary cation/crown interaction. However, once the crown ether binds the cation, the stereoelectronic environment of the cation changes dramatically. Its charge is dissipated by the donor atoms of the crown, and access to the cation is restricted by the presence of the crown. Additional ligands that can approach the crown−cation complex and interact favorably with nearby portions of the crown may exhibit unusual binding characteristics.

Because of the unique electronic topography created by the cation−crown complex, subsequent ligation may be possible for what otherwise might be a weakly binding ligand. There is mounting evidence suggesting that alkali metal ions can favorably interact with ligands containing arene or other more weakly donating groups.[4,5] This becomes increasingly common as the charge-to-size ratio decreases, with the heaviest alkali metal ions exhibiting this ligation most often.[1,5]

Our recent work on the selective extraction of the cesium ion with large crown ether molecules led us to examine the structure of the cesium ion when complexed by tetrabenzo-24-crown-8. We observed that the crown does not complete the cation's coordination sphere but leaves two U-shaped clefts available for additional ligation.[6,7] In this paper, we present two structures that exhibit unusual ligation in one of the two clefts: the first structural characterizations of an alkali metal ion

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Table 1. Summary of Crystallographic Data

	1	**2**
empirical formula	$C_{38}H_{41}CsN_4O_{11}$	$C_{37}H_{40}Cl_2CsN_3O_{11}$
a, Å	12.0119(14)	12.295(3)
b, Å	13.3680(15)	13.295(3)
c, Å	13.7859(12)	13.782(3)
α, deg	89.124(8)	89.105(17)
β, deg	66.928(9)	66.096(18)
γ, deg	71.536(10)	70.980(19)
V, Å^3	1916.7(4)	1929.5(8)
Z	2	2
fw	862.7	906.5
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
T, K	100	100
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.50	1.56
μ, cm^{-1}	10.3	11.6
R1^a	0.046	0.053
wR2^b	0.128	0.144

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, based on $F_o^2 > 2\sigma(F_o^2)$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Cs^+(B_424C8)(\eta^1\text{-NCMe})_2L$ ($L = \eta^2\text{-NCMe}, \eta^2\text{-CH}_2\text{Cl}_2$)

	1	**2**
Cs−O$_{crown}$ range	3.190(3)−3.424(3)	3.213(3)−3.438(3)
Cs−O$_{crown}$ av^a	3.32(7)	3.33(7)
Cs−N$_{\eta^1-NCMe}$	3.159(5), 3.172(5)	3.176(4), 3.182(5)
C≡N$_{\eta^1-NCMe}$	1.123(7), 1.135(7)	1.138(7), 1.148(7)
N−C−C$_{\eta^1-NCMe}$	178.7(7), 179.5(6)	175.4(7), 179.2(6)
Cs−N$_{\eta^2-NCMe}$^{b}	3.44(3)	
Cs−C$_{\eta^2-NCMe}$^{b}	3.471(14)	
C≡N$_{\eta^2-NCMe}$^{b}	1.11(2)	
N−C−C$_{\eta^2-NCMe}$^{b}	175(2)	
Cs−Cl		3.602(2), 3.684(2)

^{a} Uncertainties quoted for M$^+$−O av are *σ* values based on the statistical distribution of M$^+$−O$_{crown}$ values observed in the structures reported here. ^{b} Only values for the major disordered component are presented.

complex containing an η^2-acetonitrile ligand or an η^2-dichloromethane ligand.

Experimental Section

Materials. All chemicals were used as supplied. Tetrabenzo-24-crown-8 was prepared as described elsewhere.[8] All other chemicals were of the best AR grade available.

X-ray Crystallography. General Details. A summary of crystallographic data is given in Table 1, and selected bond lengths and angles are listed in Table 2. Complete crystallographic information is available as Supporting Information. Data were obtained using a Nonius CAD4 diffractometer fitted with a 1.1 mm collimator. Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied on the basis of a set of *ψ* scans. Calculations were carried out using XCAD4[9] (data reduction), SHELXTL[10] (absorption correction, structure solution/refinement, and molecular graphics), and PLATON[11] (structure analysis). Each H atom was placed in a calculated position, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 (CH, CH$_2$) or 1.5 (CH$_3$) times the equivalent isotropic displacement parameter of the atom to which it was attached. When warranted, methyl H atomic positions were allowed to rotate about the adjacent C−C bond. Full-matrix least-squares refinement against $|F|^2$ of the quantity $\sum w(F_o^2 - F_c^2)^2$ was used to adjust the positions and anisotropic thermal parameters of all non-hydrogen atoms.

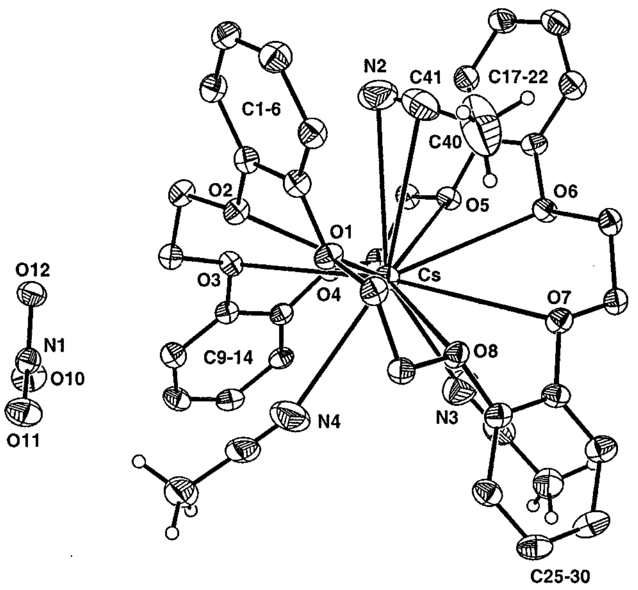

Figure 1. ORTEP representation (50% probability ellipsoids) of **1**. Hydrogen atoms, except those on the acetonitrile ligands, and the minor disorder component are omitted for clarity.

X-ray Structure Determination for [Cs(tetrabenzo-24-crown-8)(η^1-NCMe)$_2$(η^2-NCMe)][NO$_3$] (1). Suitable crystals were grown from slow evaporation of tetrabenzo-24-crown-8 (50 mg, 0.092 mmol) and CsNO$_3$ (0.18 mL, 0.51 M aqueous solution) in 10 mL of acetonitrile. The crystals are sensitive to solvent loss and were therefore quickly transferred to the diffractometer's cold stream. A crystal measuring 0.65 × 0.36 × 0.20 mm^3 was mounted on a glass fiber. Unit-cell dimensions were refined by using the settings of 25 reflections in the range $20 < 2\theta < 31°$. Intensities were measured by $\omega - 2\theta$ scans. A total of 9943 reflections were collected ($2\theta \le 38°$, $\pm h,\pm k,\pm l$; $38° \le 2\theta \le 50°$, $\pm h,\pm k,+l$). The data were averaged over $\bar{1}$ symmetry (R_{int} = 3.1%). The structure was solved using direct methods. The η^2-acetonitrile ligand was disordered over two sites (67:33). The U_{ij} components of disordered, bonded atoms or disordered atoms within 0.7 Å of each other were restrained to be similar. A total of 517 parameters, with 18 restraints, refined to final residuals R1 = 0.046 (based on $I > 2\sigma_I$) and wR2 = 0.128, with the eight highest residual peaks (2.71−0.66 e Å^{-3}) within 2.7 Å of Cs.

X-ray Structure Determination for [Cs(tetrabenzo-24-crown-8)(NCMe)$_2$(η^2-CH$_2$Cl$_2$)][NO$_3$] (2). Crystals were prepared by mixing 8 mg (0.02 mmol) of CsBPh$_4$, 10 mg (0.02 mmol) of tetrabenzo-24-crown-8, and 6 mg (0.02 mmol) of [*n*-Bu$_4$N][NO$_3$] in 4 mL of CH$_2$Cl$_2$/CH$_3$CN/pentane (5:1:5), followed by cooling to −5 °C. The crystals are sensitive to solvent loss and were therefore quickly transferred to the diffractometer's cold stream. A crystal measuring 0.72 × 0.33 × 0.26 mm^3 was mounted on a glass fiber. Unit-cell dimensions were refined by using the settings of 25 reflections in the range $20 < 2\theta < 26°$. Intensities were measured by $\omega - 2\theta$ scans. A total of 9288 reflections were collected ($2\theta \le 22°$, $\pm h,\pm k,\pm l$; $22° \le 2\theta \le 54°$, $\pm h,\pm k,+l$). The data were averaged over $\bar{1}$ symmetry (R_{int} = 3.2%). The structure was solved using direct methods. A total of 484 parameters refined to final residuals R1 = 0.053 (based on $I > 2\sigma_I$) and wR2 = 0.144. The two highest peaks in the final difference electron density map (2.6 and 2.5 e Å^{-3}) were located within 1 Å of cesium; the only other peak greater than 0.82 e Å^{-3} (1.2 e Å^{-3}) was 1.2 Å from N2 and 3.6 Å away from Cs.

Results

The structures of (tetrabenzo-24-crown-8)bis(η^1-acetonitrile)-(η^2-acetonitrile)cesium nitrate (**1**) and (tetrabenzo-24-crown-8)-bis(η^1-acetonitrile)(η^2-dichloromethane)cesium nitrate (**2**) are illustrated in Figures 1 and 2, with selected bond distances and

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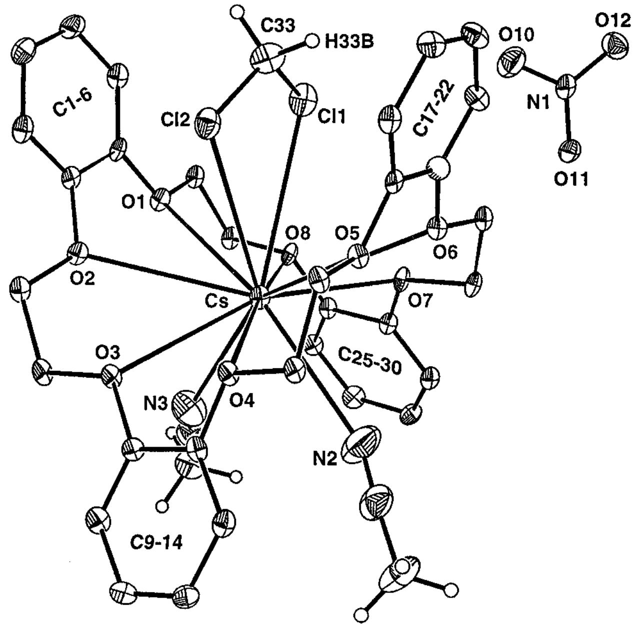

Figure 2. ORTEP representation (50% probability ellipsoids) of **2**. Hydrogen atoms, except those on the acetonitrile and dichloromethane ligands, are omitted for clarity.

angles given in Table 2. The crown conformation in both structures is very similar to that of previously reported (tetrabenzo-24-crown-8)cesium complexes.[6,7] It approximates S_4 symmetry, reminiscent of K^+ structures with nonactin[12] and dibenzo-30-crown-10,[13] and can be described as similar to the seam on a baseball. As the crown wraps around cesium, benzo rings from opposite sides of the crown ring are moved toward each other. The only space available for additional ligation to cesium is two clefts, formed by the opposing pairs of crown benzo groups.

The structures presented here are generally comparable to similar structures containing 1,4-dioxane,[6] water,[6] and 1,2-dichloroethane[7] in the clefts. However, while the two clefts were roughly equivalent in shape in the previously reported complexes, they are significantly different in **1** and **2**. Here, the clefts occupied by the two η^1-acetonitrile ligands are larger than the clefts containing a single solvent molecule. Specifically, the centroid−centroid distances between rings C1−C6 and C17−C22 are 7.20 Å (**1**) and 7.13 Å (**2**), while between rings C9−C14 and C25−C30 they are 8.13 Å (**1**) and 7.99 Å (**2**). The corresponding distances in the 1,4-dioxane complex are 7.55 and 7.63 Å, for example.[6] Additionally, the structures reported here exhibit a broader range of Cs−O_{crown} distances (Table 2) than was observed in the 1,4-dioxane complex (3.264(3)−3.352(3) Å)[6] or the 1,2-dichloroethane complex (3.245(4)−3.375(4) Å).[7] However, they remain well within the broad range of values previously observed for cesium−crown ether complexes,[4a,6,7,14,15] and the average Cs−O_{crown} distances are essentially the same for all four structures (Table 2; 3.31(3) Å and 3.29(5) Å were reported for the 1,4-dioxane[6] and 1,2-dichloroethane[7] complexes).

The η^1-acetonitrile ligands in the structures of both **1** and **2** exhibit Cs−N bond lengths ranging from 3.159(5) to 3.182(5) Å (Table 2), which is consistent with known structures.[4d,g,16] The short C≡N bond lengths and linear N−C−C bond angles for these ligands are also consistent with known structures of acetonitrile complexes with alkali metal ions and are essentially unperturbed from those of uncomplexed acetonitrile.[14,17]

The structure of **1** features three acetonitrile ligands filling the two clefts. Two η^1 ligands occupy the "lower" (as pictured in Figure 1) cleft, and an η^2 ligand fills the "upper" cleft. While the η^2-acetonitrile ligand is disordered over two sites (67:33), the bonding conformations and parameters are similar for both components. As might be expected, the standard uncertainties for the minor component are significantly higher than those for the major component. Because of the large uncertainties and small occupancy factor for the minor disorder component, it is not pictured in Figure 1 nor are its bond lengths and angles presented in Table 2. The Cs−N2 bond length for the major component of the η^2-acetonitrile ligand is considerably longer (3.44(3) Å) than the Cs−N bond lengths on the other side of the cation. The Cs−C41 distance of 3.471(14) Å is significantly smaller than the sum of the van der Waals radii for cesium (2.15 Å)[18] and carbon (1.70 Å).[19] Within standard uncertainties, the C41≡N2 bond is unperturbed relative to that of free acetonitrile and the N2−C41−C40 angle is linear for the η^2-acetonitrile ligand (Table 2).

The structure of **2** is nearly identical to that of **1** except that the η^2-acetonitrile ligand is replaced by an η^2-dichloromethane ligand. The Cs−Cl distances of 3.602(2) Å (Cl2) and 3.684(2) Å (Cl1) are consistent with a closely related structure, recently determined in our laboratories, (tetrabenzo-24-crown-8)bis(η^2-1,2-dichloroethane)cesium nitrate. The 1,2-dichloroethane ligands were disordered in the previously determined structure, giving a broad range of Cs−Cl distances (2.98(2)−3.83(2) Å).[7] Because the dichloromethane ligand in **2** is well ordered, it provides more reliable values for the Cs−Cl distances, which are comparable to close cesium−inorganic chlorine contacts (as short as 3.4 Å).[20] Other than the structures of these two complexes, no other crystal structure of an alkali metal ion with an organochlorine ligand has been reported, to the best of our knowledge.[14] The dichloromethane is tilted in the cavity so that one of its electropositive hydrogen atoms is oriented toward one of the arene rings. The distance between this hydrogen atom (H33B) and the ring centroid (for the C17−C22 ring) is 2.63 Å, with a C−H−centroid angle of 137°.

Discussion

The structure of **1** is the first example of η^2-coordination of a simple nitrile to an alkali metal ion.[21] In contrast, there are dozens of structures reporting η^1-nitrile coordination to alkali metal ions,[14] although only a few involve the Cs^+ ion.[4d,g,16] Why then is η^2 bonding exhibited in **1**, especially when η^1 bonding exists on the other side of the cation in what appears to be a nearly identical environment? As is usually the case, steric and electronic factors apparently conspire to bring about this unusual bonding configuration.

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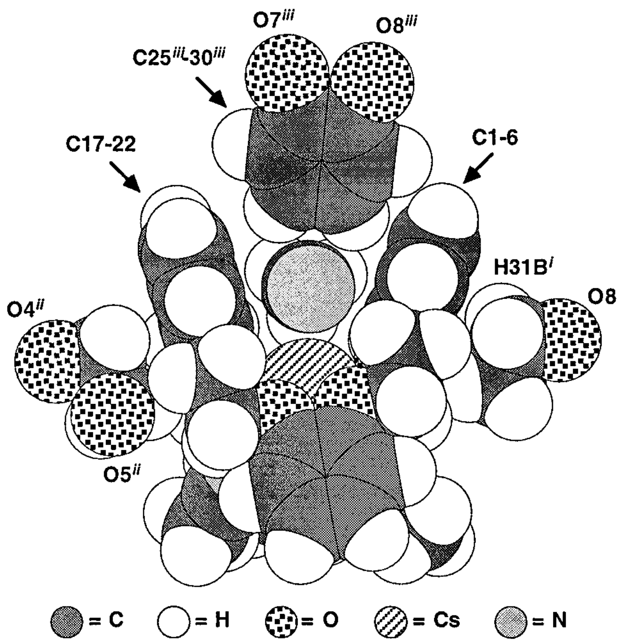

Figure 3. Space-filling partial crystal packing diagram for **1**. The minor disorder component, the nitrate anion, and hydrogen atoms are omitted for clarity. Symmetry codes: (*i*) $-x$, $-y$, $1 - z$; (*ii*) $-x$, $1 - y$, $-z$; (*iii*) $x - 1$, y, z.

First, we shall consider the favorable steric environment created by the cesium−crown complex and its packing in the crystal lattice. The narrowing of the top cleft may be a result of the arene groups being “pushed” together by crown CH_2 groups on their outside faces (Figure 3). For example, the distance between $H31B^{i}$ and the centroid of C1−C6 is 2.74 Å. These intermolecular interactions represent C−H···π-arene interactions with the outer walls.[22] Figure 3 also reveals that an arene group from an adjacent complex ($C25^{iii}$−$C30^{iii}$) is positioned directly above the cleft containing the η^2-nitrile (rings C1−C6 and C17−C22). If it can be assumed that the packing in this crystal lattice is primarily determined by the large (tetrabenzo-24-crown-8)bis(η^1-acetonitrile)cesium complex, the positioning of $C25^{iii}$−$C30^{iii}$ may inhibit η^1 bonding of acetonitrile in the top cleft.

Support for the hypothesis that packing is determined by the Cs^+−crown complex may be found by examination of both structures presented here. The similarity of the unit-cell parameters (Table 1) for **1** and **2** is remarkable, and examination of packing diagrams shows that they are virtually identical except for the ligand in the top cleft. In fact, the atomic coordinates for the cation, crown, and η^1-acetonitrile ligands, as well as the nitrate anion, are very much the same for the two structures. As a result, the dichloromethane structure (**2**) also experiences intermolecular C−H···π-arene interactions with the outer walls of the top cleft. An arene group (like $C25^{iii}$−$C30^{iii}$ in Figure 3) also occupies the space above the dichloromethane ligand, limiting the space directly above the cleft. These similarities suggest that crystallization is largely determined by the Cs^+−crown complex and that the ligand in the top cleft fills the remaining void.

A favorable electronic environment is also created by the cesium−crown complex. The cesium ion is known to bind acetonitrile in an η^1 fashion, as illustrated in the lower cleft of **1** and **2**, as well as in previously reported Cs^+-acetonitrile structures;[4d,g,16] however, Cs^+ has a very low charge-to-size ratio and is well-known to accept soft donors, sometimes in preference to harder donors.[4f−h,5a,c−e,7] It is also quite plausible that the donor atoms of the crown ether and η^1-acetonitrile ligands lower the effective charge on the cesium ion. It is therefore possible that the difference in binding energies between an η^1-nitrile structure and an η^2-nitrile structure may be relatively small in the top cleft.

Additional electronic stabilization of the η^2-binding mode in **1** possibly results from the smaller inter-arene distance observed in the top cleft. Namely, the η^2-nitrile ligand is stabilized by π-stacking interactions between the C≡N bond and the arene π clouds. The distances between the centroid of the C≡N bond and the arene centroids are ~3.6 Å, roughly equal to the interlayer distance in graphite.[23] The fact that the arene rings are almost 1 Å further apart in the bottom cleft, where η^1 binding is observed, suggests that cleft size may be a key factor in determining the hapticity of acetonitrile on Cs^+.

Complex **1** contains the first linear η^2-nitrile ligand to be structurally characterized for any metal.[21,24] The rare examples of structurally characterized η^2-nitrile ligands all involve electron-rich transition metals strongly back-bonding ($d \rightarrow \pi^*$) to the nitrile triple bond.[25] This results in significant lengthening of the C≡N bond (1.22−1.27 Å) and bending of the N−C−C angle (128−141°).[24] On the basis of this record, one might be tempted to assume that this would be the only electronic environment conducive to an η^2-nitrile ligand. This is clearly not the case with **1**, since the C≡N bond is unperturbed[17] and the N−C−C angle is linear for the η^2-acetonitrile ligand (Table 2). This is not surprising because the filled d orbitals of the cesium ion are unlikely to be able to significantly overlap with ligand π^* orbitals.

The structure of **2** shows the first example of dichloromethane acting as a ligand toward an alkali metal ion and a rare example of it behaving as a ligand.[26] While dichloromethane was present in excess over acetonitrile during the crystallization of **2**, there was clearly a choice of ligands to fill the top cleft. The observation of dichloromethane in the cleft suggests that it is a better ligand for this cleft.

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Finally it is interesting to note that, in both structures, the nitrate anion is excluded from cesium's inner coordination sphere in deference to weakly binding ligands. As discussed in a related paper,[7] this may have more to do with nitrate's incompatibility with the cleft than it does with the ability of these ligands to bind Cs^+ strongly.

Conclusion

The two structures presented here are remarkably similar, differing only in the unusual ligation observed in one of two similar clefts formed by (tetrabenzo-24-crown-8)cesium. The unprecedented linear η^2-nitrile and η^2-dichloromethane ligands are both observed to bind to the cesium ion in this cleft. The origins of these interactions appear to be a combination of a limiting steric environment enforced by the crystal packing and a favorable electronic environment created by the relatively soft cesium ion at the base and the π clouds making up the walls of the cleft.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of [Cs(tetrabenzo-24-crown-8)(η^1-NCMe)$_2$(η^2-NCMe)][NO_3] (**1**) and [Cs(tetrabenzo-24-crown-8)(NCMe)$_2$(η^2-CH_2Cl_2)][NO_3] (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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