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Sandwich and Mixed Sandwich Complexes of the Cesium Ion with Crown Ethers in Nitromethane

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Cesium-133 nuclear magnetic resonance was used as a probe of the interaction of the Cs^+ ion with the crown ethers 18C6, 15C5, 12C4, and with HMHCY (hexamethyl hexacyclen) in nitromethane solution with thiocyanate as the counterion. A study of the ^{133}Cs chemical shift as a function of crown to Cs^+ mole ratio showed that the complexation reactions occur stepwise. Formation of a 1:1 complex is followed by the addition of a second complexant molecule to form a sandwich cation. In the case of 18C6, there is strong evidence for the intermediate formation of a 3:2 adduct. The formation constants of sandwich complexes that contain two molecules each of 18C6, 15C5, and HMHCY and various mixed sandwiches of these complexants (and also 12C4) in solution were evaluted from the mole ratio data. The crystal structure of the mixed sandwich salts $Cs^+(18C6)(12C4)SCN^-{\cdot}2(CH_3OH)$ and $Rb^+(18C6)(12C4)I^-{\cdot}H_2O$ were also determined.

Introduction

Since the first syntheses of macrocyclic crown ethers that are capable of forming stable and selective complexes with alkali and alkaline earth metal ions were performed,[1] a number of studies have been made to understand the factors that control the thermodynamic and kinetic stability and selectivity of the resulting complexes.[2−5] Moreover, crown ethers were found to increase the solubility of alkali metals in amines and in some other polar organic solvents.[6] This permitted the study of alkali metal anions and solvated electrons in a variety of solvents[7−9] and led to the discovery and study of crystalline alkalides and electrides.[10−16] One of the interesting features of crown ethers as nearly two-dimensional macrocyclic ligands is their ability to form 2:1 (ligand to metal) sandwich complexes with metal ions that have larger ionic sizes than the the size of the hole in the crown ether. The formation of sandwich complexes in solution[17−19] and in the crystalline state,[20,21] in which both complexant molecules are the same, has already been extensively reported. We synthesized an electride, $[Cs^+(18C6)(15C5)e^-]_6{\cdot}(18C6)$,[22,23] and some alkalides,[24] K^+ $(18C6)(12C4)Na^-$, $Rb^+(18C6)(12C4)Na^-$, $Rb^+(18C6)(12C4)Rb^-$, and $Cs^+(18C6)(15C5)Na^-$, whose sandwich structures contained mixed crown ethers. These structures raised the possibility that some mixed sandwich complexes may be more stable than the "parent" complexes in which both crown ethers are the same. To examine this question more generally, we carried out the present study of the formation of mixed sandwich complexes of alkali cations in solution and in crystalline salts with more conventional anions.

In this paper we report NMR evidence for the formation of sandwich and mixed sandwich complexes of the Cs^+ ion with 18-crown-6 (18C6), hexamethyl hexacyclen (HMHCY), 15-crown-5 (15C5), and 12-crown-4 (12C4) in nitromethane solution with thiocyanate as the counterion. We also report the syntheses and structures of the crystalline salts, $Cs^+(18C6)(12C4)SCN^-{\cdot}2(CH_3OH)$ and $Rb^+(18C6)(12C4){\cdot}I^-{\cdot}H_2O$. In the course of this study we also found NMR evidence for the formation in nitromethane of an unusual 3:2 complex, $(Cs^+)_2(18C6)_3$.

Experimental Section

Chemicals used were of the highest purity available and were obtained from the following sources: 18C6, Sigma; 12C4, 15C5, HMHCY, CsI, and RbI, Aldrich; CsSCN, Pfaltz & Bauer; nitromethane, EM Science. They were further purified and dried as described elsewhere.[25−27]

Cesium-133 NMR measurements were carried out on a Varian VXR-300 instrument at 39.345 MHz and a field strength of 7.04 T. All chemical shift measurements were carried out at 25.0 ± 0.1 °C and are referenced to aqueous Cs^+ at infinite dilution.

The formation constants of the various complexes were evaluted by nonlinear least-squares fits to the observed ^{133}Cs chemical shifts at various crown/Cs^+ mole ratios (MR) with program KINFIT2, a modification of program KINFIT.[28] Both previously derived equations[29,30] and modified equations were used. These equations give the observed chemical shift as a function of the free and complexed metal ion and the formation constants. In the case of CsSCN with 18C6 it was necessary to use multiple data sets with simultaneous adjustment of the parameters.

Crystalline salts with mixed sandwich complexants were prepared as follows: equivalent amounts of the crown ethers and the alkali salt (1 mmol) were dissolved in about 25 mL absolute methanol (Baker) and set aside in the dark to allow the slow evaporation of the solvent. After several days, the colorless crystals of the corresponding mixed sandwich complexes were obtained. In the case of $Cs^+(18C6)(12C4)SCN^-{\cdot}2(CH_3OH)$, the methanol solution was slowly cooled from −5 to −10 °C. A Nicolet P3F X-ray diffractometer was used to collect data for $Rb^+(18C6)(12C4){\cdot}I^-{\cdot}H_2O$, and a Bruker-

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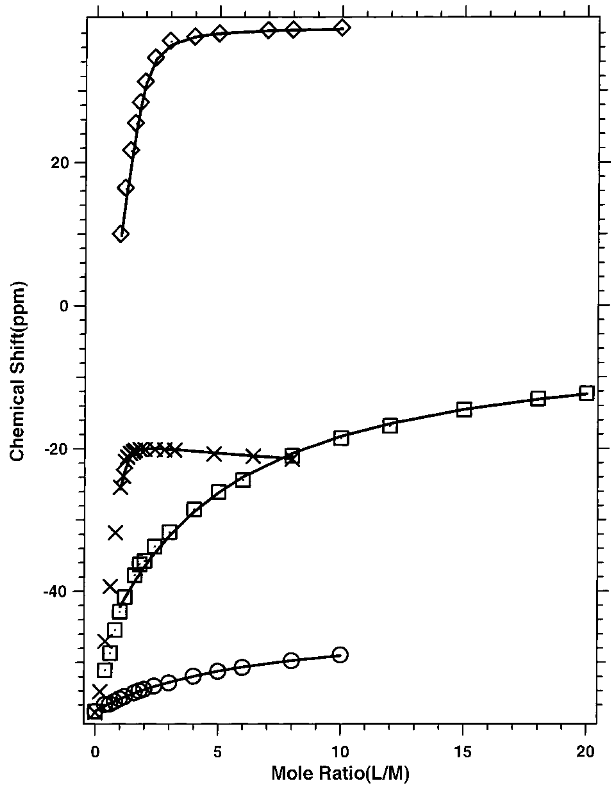

Figure 1. Variation of the chemical shift with complexant/cesium mole ratio (MR) for a total Cs^+ concentration of 0.005 M. Complexants are diamonds, HMHCY; crosses, 18C6; squares, 15C5; circles, 12C4. In all cases, the solid lines are least-squares fits of the appropriate equations.

Siemens CCD diffractometer was used for $Cs^+(18C6)(12C4)SCN^-{\cdot}2(CH_3OH)$.

Results and Discussion

Complexes in Solution with a Single Crown Ether. Since, in the complexation reactions, the ligand must compete with solvent molecules for cations, the use of solvents of low solvating ability is expected to lead to greater stability. Because of the low stabilities (especially the low K_2 values of 2:1 complexes) in water and other high donicity solvents,[2-5] we chose to study crown ether complexation of the cesium ion in nitromethane, a solvent with a moderate dielectric constant (35.9) but a very low Gutmann donor number (2.7).[31]

Cesium-133 chemical shifts were measured as a function of the mole ratio of complexant to cesium ion. In all cases (except with HMHCY up to MR = 1) only one population-averaged resonance was observed, showing that the exchange rate of the cation between the bulk solution and the complexed sites is fast on the NMR time scale. The resulting mole ratio data for the crown ethers and for HMHCY are shown in Figure 1. With 18C6 there is a linear chemical shift of the ^{133}Cs resonance in the expected (paramagnetic) direction until a $18C6/Cs^+$ mole ratio of 1.0 is reached. This implies that K_1 is large ($>10^5$ M^{-1}). The behavior beyond MR = 1.0 shown in Figure 2 for two concentrations of CsSCN is complex and is not compatible with simple formation of a 2:1 complex upon the addition of more 18C6. The chemical shift changes rapidly at first and levels off after MR $\cong$ 1.5. Beyond MR = 2.0 the chemical shift decreases slightly with an increase of the 18C6 concentration, requiring the presence of at least two species in addition to the 1:1 complex. The formation of 2:1 complexes in various nonaqueous solvents has been reported previously, but in this solvent an intermediate complex is also formed with 18C6. As described later, the chemical shift behavior over the whole range with MR > 1.0 can be quantitatively fit by assuming the formation of a strong 3:2 complex in solution in addition to a weaker 2:1 complex.

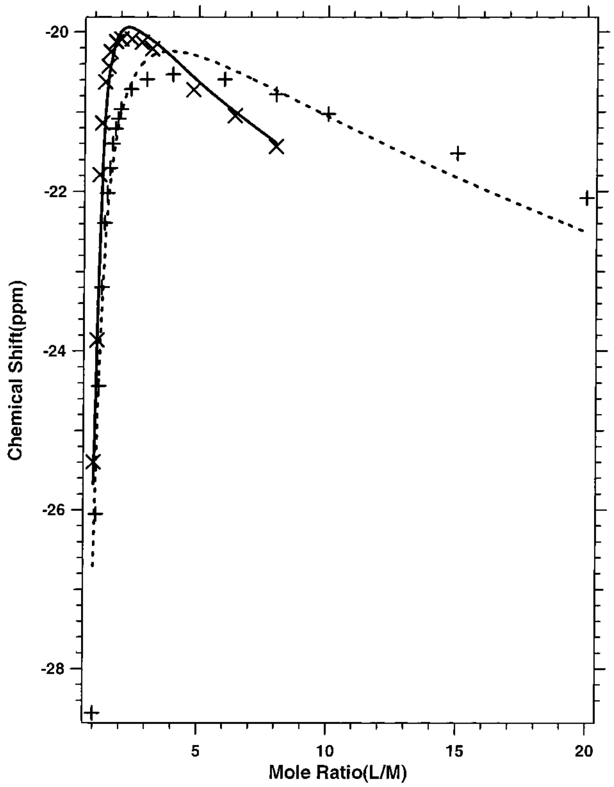

Figure 2. Chemical shift vs overall MR for $Cs^+(18C6) + 18C6$: plus signs, concentration = 0.002 M; crosses, concentration = 0.005 M. Solid and dashed lines are least-squares fits.

In the cases of 15C5 and 12C4, the addition of ligand to the Cs^+ solution produces a paramagnetic shift of the ^{133}Cs resonance that does not require other complexes than those with 1:1 and 2:1 stoichiometry. The dependence of the chemical shift on mole ratio in the case of 15C5 clearly requires the formation of both a strong 1:1 complex and a 2:1 complex, although formation of the latter complex is incomplete even at MR = 10. If intermediate complexes form, their presence is not evident from the chemical shift data. The variation with mole ratio in the case of 12C4 is so gradual that the formation of complexes other than 1:1 cannot be verified, although a 2:1 complex could be present.

Computer fitting of the data utilized the KINFIT2 program.[28] The approach used for a single complexant that forms both 1:1 and 2:1 complexes has been described in detail previously.[17,29] In a solvent with donicity as low as that of nitromethane, ion pair formation cannot be ignored, nor can unit activity coefficients be assumed. However, except for the formation of the 3:2 complex, activity coefficient effects cancel out upon addition of a neutral complexant. Ion pair formation was studied in separate experiments in which the chemical shifts of solutions of Cs^+SCN^- and $Cs^+(18C6)SCN^-$ were studied as a function of concentration. The resulting species chemical shifts and ion pair formation constants are given in Table 1. Activity corrections used the Debye–Hückel equation with a size parameter, *a*, of 6 Å. The situation is more complicated at higher mole ratios because of the simultaneous presence of 1:1, 3:2, and 2:1 complexes. Changes in the overall concentration in regions with MR > 1 therefore changed not only the relative concentra-

TABLE 1: Equilibrium Constants and ^{133}Cs NMR Chemical Shifts for Various Complexes of Cs^+ in Nitromethane[a]

		equilibrium constants	
reactants and chemical shifts[b]	products and chemical shifts	designation	value
$Cs^+[-59.0(2)] + SCN^-$	Cs^+SCN^- [−22(7)]	K_{0ip}	25(8)
Cs^+(18C6) [−31.5(7)] + SCN^-	Cs^+(18C6) SCN^- [−11.7(7)]	K_{1ip}	$2.3(5) \times 10^2$
Cs^+ + 12C4	Cs^+(12C4) [−44.5(3)]	K_4	37(2)
Cs^+ + 15C5	Cs^+(15C5) [−42.2(3)]	K_5	$>10^4$
Cs^+(0.002M) + 18C6	Cs^+(18C6) [−26.7(3)]	K_6	$>10^5$
Cs^+(0.005M) + 18C6	Cs^+(18C6) [−25.7(9)]	K_6	$>10^5$
$2Cs^+$(18C6) (0.002M) + 18C6	$(Cs^+)_2(18C6)_3$ [−15.3(4)]	$K_{6(23)}$	$6.2(8) \times 10^5$
$2Cs^+$(18C6) (0.005M) + 18C6	$(Cs^+)_2(18C6)_3$ [−17.2(2)]	$K_{6(23)}$	$6.2(8) \times 10^5$
Cs^+(18C6) + 18C6	$Cs^+(18C6)_2$ [−48.3] [c]	K_{66}	57(4)
Cs^+(15C5) + 15C5	$Cs^+(15C5)_2$ [−4.5(6)]	K_{55}	42(2)
Cs^+(18C6) + 12C4	Cs^+(18C6)(12C4) [−12(4)]	K_{64}	15(7)
Cs^+(18C6) + 15C5	Cs^+(18C6) (15C5) [−10.9(1)]	K_{65}	64(5)
Cs^+ + HMHCY	Cs^+(HMHCY) [+9.7(3)]	K_H	$>10^5$
Cs^+(HMHCY) + HMHCY	$Cs^+(HMHCY)_2$ [+38.9(1)]	K_{HH}	$2.0(2) \times 10^3$
Cs^+(HMHCY) + 12C4	Cs^+(HMHCY) (12C4) [−3.4(1)]	K_{H4}	$7(2) \times 10^3$
Cs^+(HMHCY) + 15C5	Cs^+(HMHCY) (15C5) [−17.4(1)]	K_{H5}	$8(2) \times 10^3$

[a] Except as designated, all complexation reactions have a total Cs^+ concentration of 0.005M. [b] Chemical shifts in brackets, estimated standard deviation of the last digit in parentheses. [c] Dimer chemical shift fixed at average value in other solvents (see text).

tions of ion pairs and free ions but also the relative concentrations of the three species. Therefore, it was not possible to make ion-pair and activity coefficient corrections in these cases. The concentration dependence was studied at MR = 1.5 and MR = 4.0, but we were unable to fit the complex variations in species concentrations that occur as the overall concentration was changed. However, at concentrations and mole ratios that coincided with those in the mole ratio studies described above, the observed chemical shifts agreed within ± 1 ppm.

The behavior of the chemical shift of ^{133}Cs upon addition of 15C5 or 12C4 to 0.005M CsSCN in nitromethane was "conventional", in that the shifts with the former could be quantitatively described by the formation of a strong 1:1 complex and a weaker 2:1 complex while those with the latter complexant could be satisfactorily fit by assuming formation of only the 1:1 complex. Attempts to fit the 12C4 data with two equilibria resulted in standard deviation estimates larger than the parameters. The data are given in Table 1 and shown in Figure 1.

Because of the complexity of the 18C6 data, repeated runs were made at CsSCN concentrations of 0.005M and 0.002M. The reproducible rapid increase in the chemical shift between MR 1.0 and 1.5 and the gradual decrease at higher mole ratios could be accounted for by the inclusion of a 3:2 complex. Thus, the equilibria required above MR = 1.0 are

$$2\,Cs^+(18C6) + 18C6 \xrightleftharpoons{K_{6(23)}} (Cs^+)_2(18C6)_3 \qquad (1)$$

$$Cs^+(18C6) + 18C6 \xrightleftharpoons{K_{66}} Cs^+(18C6)_2 \qquad (2)$$

As indicated above, it was not possible to correct for ion pair formation or activity coefficient variation, so only an apparent value of $K_{6(23)}$ could be obtained. The decrease in the chemical shift (δ) at higher mole ratios shows that $\delta_{2:1}$ is more negative than $\delta_{3:2}$. However, the former could not be used as an adjustable parameter because it is strongly coupled to K_{66} and its standard deviation estimate is larger than its value when both parameters are adjusted.

Chemical shifts are most sensitive to the immediate environment of Cs^+ and much less dependent on "second sphere" influences.[32] As a result, the chemical shift of Cs^+ in the sandwich complex $Cs^+(18C6)_2$ with a variety of counterions is remarkably constant at −50 ± 5 ppm in various solvents and in the solid state.[17] In fitting the data here, we assumed a value of −48.3 ppm for $\delta_{2:1}$, which is the weighted average value in other solvents. This permitted determination of K_{66}, $K_{6(32)}$, $\delta_{1:1}$ and $\delta_{3:2}$ as given in Table 1. Because of the formation of ion pairs, the "effective chemical shifts" of the complexes were separately adjusted at the two Cs^+ SCN^- concentrations. The fits of the data are shown by the lines in Figure 2. Note that the data at 0.005M CsSCN could only be obtained to MR = 7.0 because of the limited solubility of 18C6 in nitromethane. Figure 3 shows the relative concentrations of the three complexes as a function of mole ratio for 0.005 M. CsSCN. The behavior with 0.002 M.CsSCN is similar.

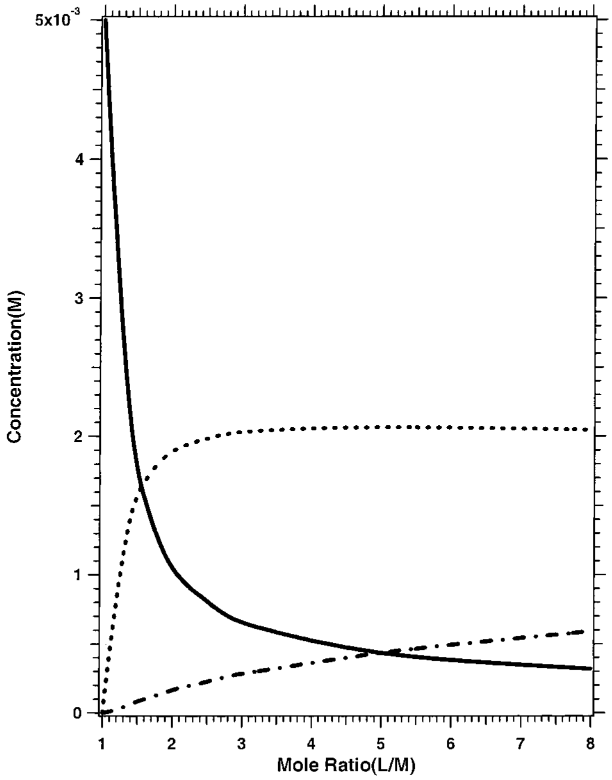

Figure 3. Concentrations of various species vs MR for $(Cs^+)_{total}$ = 0.005 M.: solid line, Cs^+(18C6); dashed line, $(Cs^+)_2(18C6)_3$; dash−dot line, $Cs^+(18C6)_2$. Concentrations represent the sum of free ion and ion pair concentrations of each species.

It is surprising that such a strong 3:2 complex is formed with 18C6, since there is no hint of it with the other crown ethers or with 18C6 in other solvents. The most likely configuration is a "club sandwich" with two cesium cations on the axis of the three crown ether molecules as in the crystal structure of Domasevitch, et al.[33] Also, it is known that 18C6 forms a crystalline solid with nitromethane[34] in which hydrogen-bonding between the methyl hydrogens and the oxygens in the ring is important. Such an interaction of the solvent with the two exterior 18C6 molecules in the club sandwich may be important in stabilizing this complex. Other geometries cannot be ruled out, however. For example, crystal structures with stoichiometries $(Na^+)_2(15C5)_3$[35] and $(K^+)_2(18C6)_3$[36] are known in which each metal cation is coordinated in normal fashion by all the oxygens of one crown ether molecule but by only two oxygen atoms on the central crown ether.

Because of the extreme resistance of HMHCY to reductive decomposition,[37,38] we have used this ligand for the synthesis of some thermally stable sodides.[39] To the best of our knowledge, there is no report on the study of HMHCY complexes with alkali ions in solution. However, it has been shown that the parent unmethylated compound, hexacyclen, can complex metal ions, including Sr^{2+}, Ca^{2+}, and K^+ in aqueous solution.[40] According to the previous studies, the substitution of some oxygen atoms of the 18C6 ring by nitrogen atoms significantly decreases the stability of the corresponding complexes with alkali[4,41] and alkaline earth cations[42] because of the weaker interactions between the cations as hard acids and nitrogen atoms as soft bases. On the other hand, it was reported that substitution of the somewhat acidic amino protons of diaza-18-crown-6 with electron donating groups such as $-CH_3$ causes an increase in the stability of the resulting alkali and alkaline earth complexes.[43] Thus, we expected to observe the formation of fairly stable complexes between the Cs^+ ion and HMHCY (compared with hexacyclen), especially in a low donicity solvent such as nitromethane.

The variation of the ^{133}Cs chemical shift as a function of the HMHCY/Cs^+ mole ratio in nitromethane solution is shown in Figure 1. It is interesting to note that, for MR between 0.0 and 1.0, two broad ^{133}Cs resonances for the cation were observed. This indicates both the formation of a stable 1:1 complex and the slow exchange of the Cs^+ ion between the free and complexed sites. However, above MR = 1.0 only one population-averaged broad signal was observed, which showed a paramagnetic shift upon further addition of the ligand. As can be seen from Figure 1, above MR = 1.0 the ^{133}Cs chemical shift varies gradually with the mole ratio and begins to level off at MR > 2.0. This behavior is clearly indicative of the formation of a stable $Cs^+(HMHCY)_2$ sandwich complex in solution. The chemical shifts and formation constants are given in Table 1.

Mixed Sandwich Complexes. The formation of the mixed sandwich complexes $Cs^+(18C6)(15C5)$ and $Cs^+(18C6)(12C4)$ was studied in separate experiments, in which either 15C5 or 12C4 was added to solutions with an 18C6/Cs^+ mole ratio of 1.0. The results are shown in Figure 4. The gradual paramagnetic shift upon the addition of the second ligand clearly demonstrates the formation of mixed sandwich complexes in solution such as $Cs^+(18C6)(15C5)$ and $Cs^+(18C6)(12C4)$. The chemical shifts of these complexes and the formation constants are given in Table 1.

Reproducibility of the data and the competition between the formation of $Cs^+(18C6)(15C5)$ and $Cs^+(18C6)_2$ or $Cs^+(15C5)_2$ were studied by the addition of a 1:1 mixture of 18C6 and 15C5 to 0.005M CsSCN, by the addition of 15C5 to a 2:1 mixture of 18C6 and Cs^+SCN^- and by the addition of 18C6 to solutions with a 15C5/Cs^+ mole ratio of 1.0. The data are shown in Figure 5. As in the concentration studies, the chemical shifts observed in various experiments agree at points of identical overall composition. The addition of 18C6 to $Cs^+(15C5)$ shows an initial increase in the chemical shift followed by a decrease. This indicates probable formation of mixed dimers, complexes of 3:2 stoichiometry and finally $Cs^+(18C6)_2$. The many equilibria that can be involved in such a complex system prevented quantitative fits of the data.

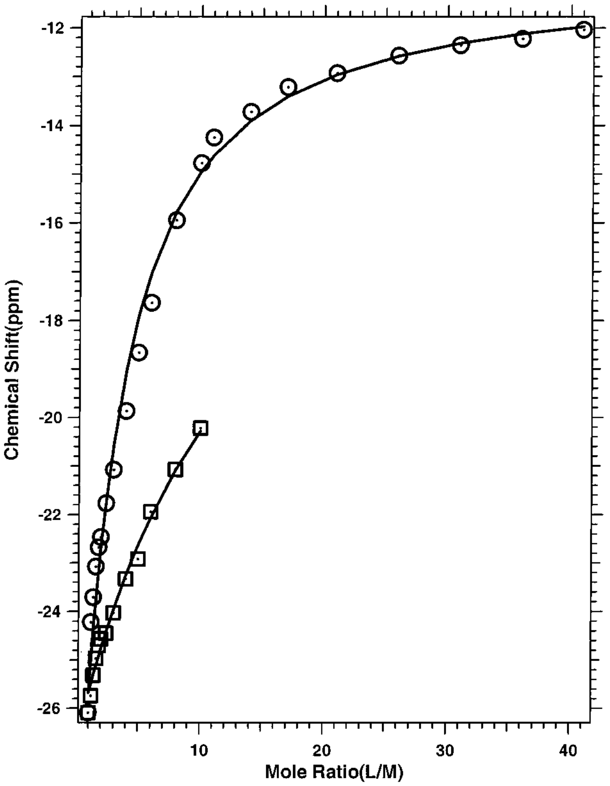

Figure 4. Chemical shift vs MR for mixed sandwich dimer formation with $(Cs^+)_{total} = 0.005$ M; circles, $Cs^+(18C6) + 15C5$; squares, $Cs^+(18C6) + 12C4$. Solid lines are least-squares fits.

Both 18C6 and 15C5 form strong 1:1 complexes with Cs^+. When a 1:1 mixture of the two complexants is added to 0.005 M.Cs SCN, the chemical shift varies linearly with the *overall* ratio of ligand to metal (*R*) up to *R* = 1.0 (not shown in Figure 5). The chemical shift over this range is given quantitatively by

$$\delta_{obs} = (1 - R)\delta_{Cs^+} + \frac{R}{2}\delta_{Cs^+(15C5)} + \frac{R}{2}\delta_{Cs^+(18C6)} \qquad (3)$$

as expected for strong 1:1 complex formation with both complexants. Beyond R = 1 the chemical shift continues to increase but the behavior cannot be quantitatively fit because of the formation of various species and the likely displacement of 15C5 by 18C6.

Although the formation constants of the two 1:1 complexes, $Cs^+(18C6)$ and $Cs^+(15C5)$, are too large to measure, it is likely that $K_6 > K_5$. This is indicated by the displacement of $Cs^+(15C5)(18C6)$ by $Cs^+(18C6)_2$ when 18C6 is added to a solution of $Cs^+(15C5)SCN^-$.

The formation of mixed complexes of Cs^+ with HMHCY and other ligands was studied by the addition of either 15C5 or 12C4 to nitromethane solutions with a HMHCY/ Cs^+ mole ratio of 1.0. In these cases, the resulting ^{133}Cs broad signals shifted *diamagnetically* upon addition of the second ligand and tended

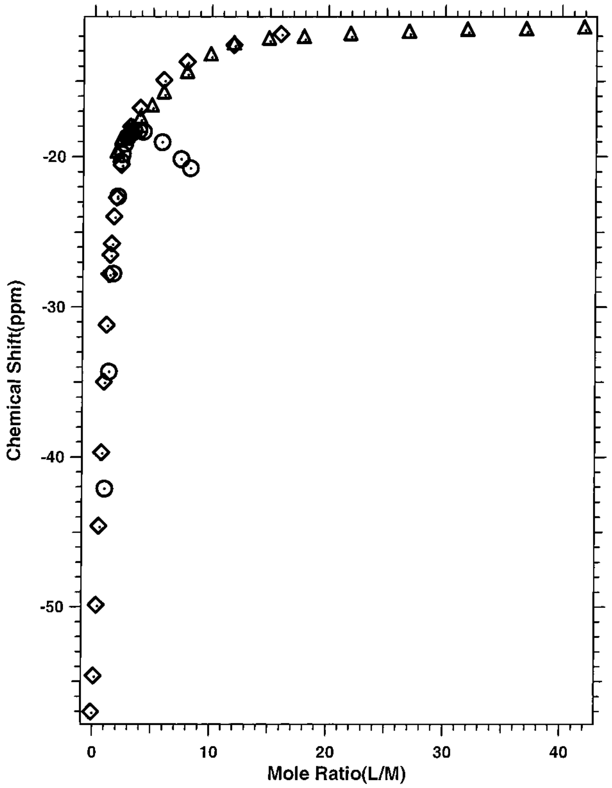

Figure 5. Chemical shift vs MR for $(Cs^+)_{total} = 0.005$ M; circles, $Cs^+(15C5) + 18C6$; diamonds, Cs^+ + 1:1 (18C6)/(15C5); triangles, Cs^+ with 2(18C6) + 15C5. Because of the complexity of these systems, the data could not be fit by equations (see text).

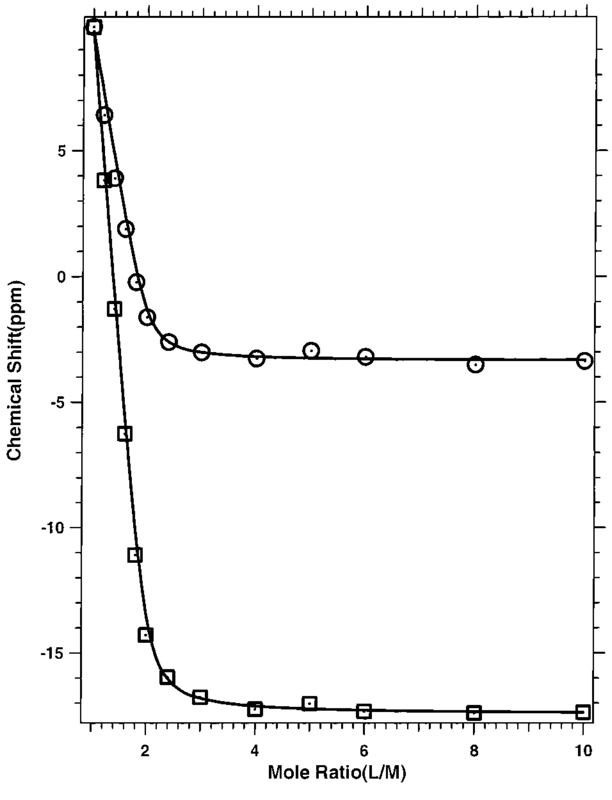

Figure 6. Chemical shift vs MR for mixed dimer fomation involving HMHCY at $(Cs^+)_{total} = 0.005$ M; circles, $Cs^+(HMHCY) + 12C4$; squares, $Cs^+(HMHCY) + 15C5$. Solid lines are least-squares fits.

to level off at mole ratios >2.0 (Figure 6) indicating the formation of the mixed sandwich complexes Cs^+(HMHCY)(15C5) and Cs^+(HMHCY)(12C4), respectively. The mole ratio data were used to obtain the formation constants of the resulting 2:1 mixed complexes given in Table 1. The K_{H5}, K_{H4}, and K_{HH} values vary in the order Cs^+(HMHCY)(15C5) > Cs^+(HMHCY)(12C4) > $Cs^+(HMHCY)_2$. It is interesting to note that, in contrast to the case of 18C6 sandwich complexes, the homosandwich $Cs^+(HMHCY)_2$ forms the least stable 2:1 complex in this series. The presence of the six bulky $-CH_3$ groups on the nitrogen atoms of the macrocyclic ring probably inhibits the close approach of another ligand to a previously complexed cesium ion. On the other hand, the smaller molecule 15C5 seems to have the best size to "cap" the previously formed bowl shaped 1:1 complex of the Cs^+ ion with HMHCY. The complexant 12C4, with smaller size and fewer donating oxygen atoms, forms a weaker sandwich complex than Cs^+(HMHCY)(15C5) but stronger than $Cs^+(HMHCY)_2$.

TABLE 2: Crystallographic and Refinement Data for $Cs^+(18C6)(12C4)SCN^-\cdot 2(CH_3OH)$ and $Rb^+((18C6)(12C4)I^-\cdot H_2O$

	$Cs^+(18C6)(12C4)SCN^-\cdot$ $2(CH_3OH)$	$Rb^+((18C6)(12C4)I^-\cdot$ H_2O
space group	*P*21/*c*	*P*21/*c*
cell parameters		
a, Å	11.6292(23)	10.487(8)
b, Å	19.1484(38)	20.013(12)
c, Å	14.7266(29)	14.326(11)
α	90	90
β	92.771(30)	109.02(5)
γ	90	90
z	4	4
crystal dimensions, mm	0.6 × 0.6 × 0.5	0.4 × 0.9 × 1.2
scan type	*ω*	*ω*
maximum 2*θ*		50°
temperature, *K*	100	200
no. of reflections collected	20118	3320
no. of unique reflections	7544	1690
no. of reflections used in refinement with $F_0^2 > 3\sigma(F_0^2)$	6730	1690
no. of variables	307	143
R	0.060	0.065
high peak in final difference map, e/Å^3	0.18	1.7

The formation constants for Cs^+(HMHCY)(15C5) and Cs^+(HMHCY)(12C4) complexes from Cs^+(HMHCY) are much larger than those for Cs^+(18C6)(15C5) and Cs^+(18C6)(12C4). CPK models and crystal structures[39] show that the most stable configuration for the HMHCY molecule in a 1:1 complex with Cs^+ has a rigid bowl-shaped structure in which more than half of the Cs^+ is surrounded by the HMHCY molecule. The cesium ion, which is partially inside this bowl, can interact strongly with the six nitrogen atoms of the macrocycle. Models show that a 15C5 molecule can easily cover the open side of the bowl to form a three-dimensional cavity, of appropriate size for Cs^+, which can bind more or less strongly to all 11 donating atoms available (including the 5 oxygens of the 15C5 ring).

Crystalline Mixed Sandwich Complexes. The crystalline iodide and thiocyanate salts of Cs^+(18C6)(15C5), Cs^+(18C6)(12C4), Rb^+(18C6)(15C5), and Cs^+(18C6)(12C4) mixed sandwich complexes were prepared according to the procedure mentioned in the experimental part. The crystal structures of $Cs^+(18C6)(12C4)SCN^-\cdot 2(CH_3OH)$ and $Rb^+(18C6)(12C4)I^-\cdot H_2O$ (which gave the best crystals in the series) were determined.

The salt $Cs^+(18C6)(12C4)SCN^-\cdot 2(CH_3OH)$ crystallizes in the space group *P*21/*c*. The crystal data are given in Table 2.

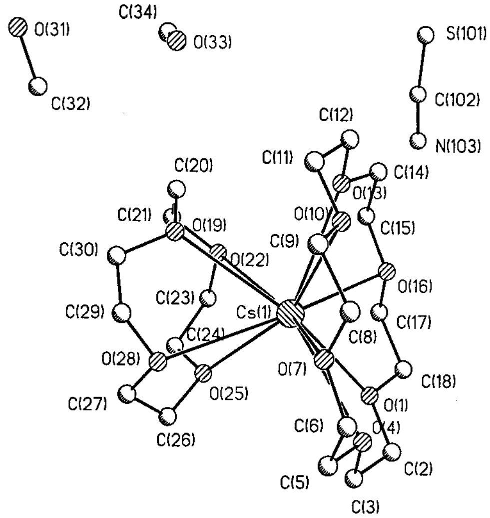

Figure 7. Structure of the mixed sandwich compound, $Cs^+(18C6)(12C4)SCN^- \cdot 2(CH_3OH)$. Hydrogens are not shown.

Two methanol molecules are present for each sandwich molecule. All non-hydrogen atoms were refined anisotropically without any major problem. The cesium cation is coordinated to the 10 oxygen atoms of the two crown ether molecules with normal Cs−O distances that range from 3.087 to 3.284 Å. Somewhat surprisingly in view of the incommensurate symmetry of the 18C6 ring and that of 12C4, both complexant molecules have well-determined positions with normal thermal parameters. The single molecule drawing is shown in Figure 7.

The salt $Rb^+(18C6)(12C4)I^- \cdot H_2O$ also crystallizes in the space group $P21/c$. The crystal data are given in Table 2. The structure confirms that the Rb^+ cation is complexed by one 18C6 and one 12C4 molecule. The atoms of 18C6 were well-determined with reasonable bond distances and bond angles. The atoms of 12C4, however, were found having higher temperature factors and some of the bond distances and bond angles deviated significantly from the normal values. Rb^+ and I^- were refined anisotropically while the carbon and oxygen atoms were refined isotropically. The 10 Rb−O distances for the complexed cation range from 2.93 to 3.17 Å. The cation position is similar to that in the $Rb^+(18C6)(12C4)Na^-$ structure.[24] The structure contains one water molecule for each $Rb^+(18C6)(12C4)I^-$ unit. The single molecule drawing in the Supporting Information (Figure S1) shows the mixed sandwich structure, but the water molecule and the hydrogen atoms are not shown.

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Supporting Information Available: Structural Data for $Rb^+(18C6)(12C4)I^- \cdot H_2O$ (with ORTEP drawing) and $Cs^+(18C6)(12C4)SCN^- \cdot 2(CH_3OH)$. Positional and thermal parameters, bond distances and angles, and general temperature factor expressions included. This material is available free of charge via the Internet at http://pubs.acs.org.

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