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Volumes of Complexation of Cryptands with Mono- and Divalent Cations in Water and in Methanol

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Abstract: The volumes of complexation of the cryptands 2.2.2, 2.2.1, and 2.1.1 with the alkali-metal cations Li^+ to Cs^+ have been determined in methanol, at 298.15 K, by using a flow digital densimeter. The behavior of 2.2.2-cryptates in methanol has been compared to that previously observed in water. We have also determined the volumes of complexation of 2.2.2 with various divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Hg^{2+}, Cd^{2+}) in water, at 298.15 K. From all these results, it appears that the interactions between the solute and the solvent show a discontinuity when the radius of the complexed cation is equal to the radius of the maximum cavity of the undistorted ligand. The transfer effect from water to methanol and the charge effect in water show that the ligand does not shield totally the trapped cation from the environment.

The diazapolyoxamacrobicyclic ligands (cryptands) synthesized by Lehn and co-workers[1] form very stable complexes (cryptates) with many cations.[2,3] It is usually accepted that the most stable complexes are of the inclusive type, the cation being trapped inside the cavity of the ligand.[4] The volumes of complexation should thus bring, in this respect, valuable information. We have determined, recently, the standard volumes of complexation of alkali chlorides by cryptand 2.2.2 in water.[5] These results have shown clearly how the ligand cavity adjusts to the cation radius upon complexation. It appears that the ligand cavity varies in a continuous way with the radius of the cations as long as the cations are smaller than the maximum cavity of the undistorted ligand, in agreement with the selectivity pattern deduced from the stability constants.[2] It would be interesting to see if the volumes of complexation reflect as well the selectivity patterns observed with the cryptands 2.2.1 and 2.1.1. Such a systematic investigation cannot be performed in water because of the low stability of some of the complexes (in particular those with cryptand 2.1.1).[2] There is, however, an increase of the stability constants when going from water to methanol[2,6] large enough to permit the determination of the volumes of complexation of the whole series (except $[Cs^+2.1.1]$) of alkali-metal cations with cryptands 2.1.1, 2.2.1, and 2.2.2.

In this paper, we present the results of this systematic study in methanol. A comparison is made between these results and those previously obtained in water for cryptand 2.2.2.

The stability constants of the cryptates are not only very dependent on the size of the cations but are also extremely sensitive to the cation charge.[2] We have thus also determined the volumes of complexation of cryptand 2.2.2 with various divalent cations in water. The results presented here are relative to 2.2.2 + Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Hg^{2+}, and Cd^{2+} (and Tl^+ for comparison).

Experimental Section

Reagents. Cryptands 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Merck, Kryptofix 222), 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (Merck, Kryptofix 221), and 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (Merck, Kryptofix 211) were kept in a dessicator and used without further purification. The alkali chlorides LiCl, CsCl (Merck, pro analysi), NaCl, KCl, and RbCl (Merck, suprapur) were dried under vacuum at 425 K for many days. Particular precautions were taken with highly hygroscopic LiCl. $CaCl_2\cdot 2H_2O$, $Cd(NO_3)_2\cdot 4H_2O$, $Pb(NO_3)_2$, $SrCl_2\cdot 6H_2O$, $Hg(NO_3)_2\cdot H_2O$, $TlNO_3$ (Merck, pro analysi), and $BaCl_2\cdot 2H_2O$ (Prolabo, pro analysis) were used as such but the exact water content of each of these salts was determined by using complexometric metods.[7]

All solutions were prepared by weight either with triply distilled water partially degased prior to use or with methanol purified by two distillations (one over magnesium and iodine and one over picric acid). Karl Fisher titrations indicated water content of our distilled methanol to be less than 0.02%. It has been shown that such a small water content cannot modify the equilibrium of complexation[2] nor the volumetric properties.[16]

In a first step, each cryptand was dissolved in pure methanol; at least ten solutions were prepared such as to cover the concentration range 0.02–0.07 m (molality). Next, equimolar solutions of alkali halides and of each of the three cryptands were prepared in pure methanol for the most stable complexes and in the presence of 0.01 M tetrabutylammonium methoxide (prepared according to Cundiff and Markunas' method[8]) for $[Li^+2.2.2]$, $[K^+2.1.1]$ and $[Rb^+2.1.1]$. Equimolar solutions of each of the other salts and cryptand 2.2.2 were prepared in pure water (in water + 0.1 M HNO_3 (Prolabo, normapur) for the mercuric nitrate). The concentration range covered by all these solutions was about 0.02–0.05 m.

Apparatus. Using a Picker flow digital densimeter,[9] we have measured the densities with a precision of about 5×10^{-6} g cm^{-3}. This densimeter being a differential instrument, we have performed the measurements relative to the following reference solvents: methanol + 0.01 M Bu_4NOCH_3 for $[Li^+2.2.2]$, $[K^+2.1.1]$, and $[Rb^+2.1.1]$ and pure methanol for all the other alkali-metal cryptates in methanol; water + 0.1 M HNO_3 for $[Hg^{2+}2.2.2]$ and pure water for all the other 2.2.2-cryptates in water, respectively. All the measurements were carried out at 298.15 ± 0.01 K.

Results and Discussion

From the measured densities of the solvent, ρ_0, and of the solution, ρ, we can calculate the apparent molar volume ϕ_v from eq 1 with M_r being the solute molecular weight (which for the equimolar solutions of salt and cryptand is equal to the sum of the molecular weights of both species) and m being the molality.

$$\phi_v = M_r/\rho + 1000(\rho_0 - \rho)/m\rho\rho_0 \qquad (1)$$

The standard molar volume of an electrolyte (at infinite dilution), $\phi_v^\ominus$ or $V^\ominus$, can be evaluated from[10] eq 2 with S_v being the theoretical Debye–Hückel limiting slope and b_v being an empirical constant which for the solutions studied here is very close to zero.

$$\phi_v = \phi_v^\ominus + S_v(m\rho_0)^{1/2} + b_v m \qquad (2)$$

At 298.15 K, S_v is equal to 1.868 and to 9.706 cm^3 mol$^{-3/2}$ L$^{1/2}$ for 1:1 and for 2:1 electrolytes in water[10] and to 15.77 cm^3 mol$^{-3/2}$ L$^{1/2}$ for 1:1 electrolytes in methanol.[11] It is usually accepted that a standard volume is the sum of two main contributions: a cavity term which corresponds to the creation in the solvent of a cavity of suitable size to accommodate the solute molecule and a term

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Table I. Standard Partial Molar Volumes of Free Ligands in Water and in Methanol

cryptand	solvent	$V^\ominus$, cm^3 mol^{-1}
2.2.2	H_2O	315.$_5$^{a}
2.2.2	CH_3OH	320.$_6$
2.2.1	CH_3OH	283.$_9$
2.1.1	CH_3OH	244

^{a} From ref 5.

which corresponds to the interaction of the solute with the neighboring molecules.[12] The accurate calculation of the cavity terms can only be done, at present, for rigid and spherical solutes of very well-defined molecular diameters, through the equations of scaled particle theory.[13] Accordingly, it does not seem possible to resolve the standard volumes of the flexible cryptands and of the cryptates into their cavity and interaction contributions. We must then rely on the sole observation of the global effects which, nevertheless, are characteristic of the intrinsic volume of the species since there is always a correlation between the cavity and the interaction contributions for a homologous series.

The complete set of measured densities and calculated ϕ_v is available as supplementary material.

Cryptands in Methanol. The macroheterobicyclic diamines are protonated when dissolved in pure methanol. From the protonation constants of 2.2.2, 2.2.1, 2.1.1,[14] and the ionic product of methanol[15] the fraction α of the ligand which is monoprotonated at a given concentration is easily estimated. It appears that, for the concentration range covered by our solutions, an average of about 0.5% of 2.2.2, 1.5% of 2.2.1, and 5% of 2.1.1 is monoprotonated. This can be considered negligible for ligands 2.2.2 and 2.2.1: the actual experimental data are effectively concentration independent. The α relative to 2.1.1 is, on the other hand, comparable to that observed previously for 2.2.2 in pure water.[5] We have shown in ref 5 that the standard molar volume of the free ligand tends toward the high concentration limit of the ϕ_v of the ligand in pure solvent. It thus seems accurate enough, considering all the other uncertainties that will affect our volumes of complexation, to simply deduce the $V^\ominus$ of free 2.1.1 from our experimental data in pure methanol.

We have reported in Table I the standard partial molar volumes $V^\ominus(L)$ of free ligands in methanol and, for comparison, the volume of free 2.2.2 in water. We see that the volume of transfer of 2.2.2 from water to methanol, $\Delta V_{tr}^\ominus(2.2.2)$, is positive and equal to 5 cm^3 mol^{-1}.

Alkali Cryptates in Methanol. For a solution of alkali chloride and ligand, we have the equilibrium

$$M^+Cl^- + L \rightleftarrows [M^+L] + Cl^- \qquad (3)$$

We may then write for the equimolar solution

$$\phi_v = \alpha V^\ominus([M^+L]) + (1-\alpha)V^\ominus(L) + (1-\alpha)V^\ominus(M^+) + V^\ominus(Cl^-) \qquad (4)$$

where the partial molar volume of each species is assumed equal to the corresponding standard partial molar volume at infinite dilution, the concentration of the involved species being low enough to permit such an approximation.

The standard molar volume change upon complexation is then given by the average over the studied concentrations of

$$\Delta V_c^\ominus = V^\ominus([M^+L]) - V^\ominus(L) - V^\ominus(M^+) \qquad (5a)$$

$$\Delta V_c^\ominus = [\phi_v - S_v(m\rho_0)^{1/2} - V^\ominus(L) - V^\ominus(MCl)]/\alpha \qquad (5b)$$

with α, the fraction of ligand complexed at a given concentration, being calculated from the stability constants of the complexes in methanol[6] and $V^\ominus(MCl)$ being given by Kkawaizumi and Zana.[16]

Table II. Standard Molar Volumes of the Ions and Standard Molar Volumes of Complexation in Methanol

cation	$V^\ominus(M^+)$,^{a} cm^3 mol^{-1}	$\Delta V_c^\ominus$, cm^3 mol^{-1} 2.2.2	 2.2.1	 2.1.1
Li$^+$	−17.9	3	4	7
Na$^+$	−17.1	11	13	9
K$^+$	−7.3	16	9	6
Rb$^+$	−1.7	15	5	3
Cs$^+$	4.8	7	1	

^{a} From ref 16.

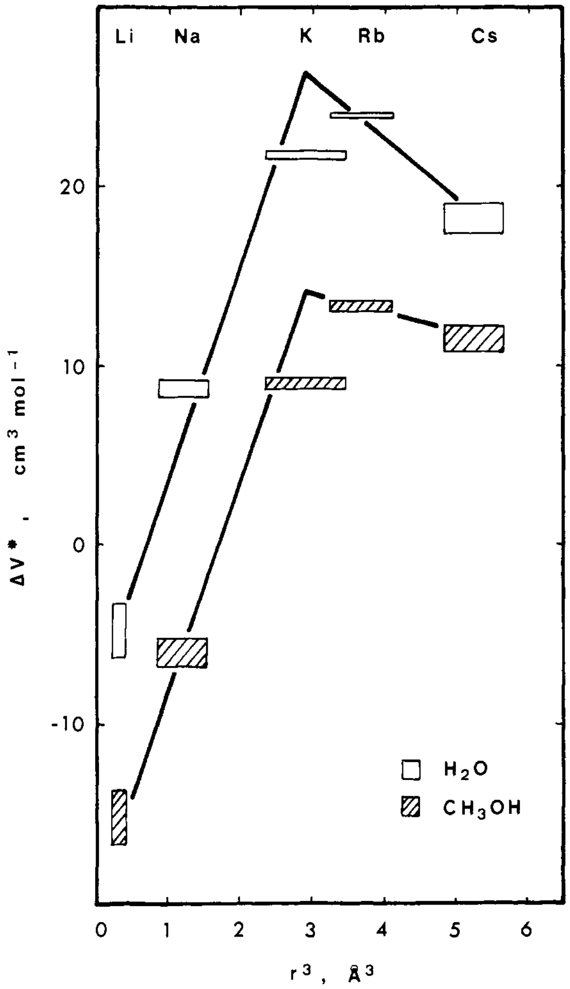

Figure 1. ΔV^* of 2.2.2 with the alkali-metal cations in water[5] and in methanol vs. the cation's radius.

We have reported in Table II the standard molar volumes of complexation of the series Li$^+$ to Cs$^+$ with the three cryptands in methanol.

As indicated in ref 5, by correcting the volume of complexation for the standard molar volume of the cation, we get a volume term ΔV^* which, in some measure, reflects the modification of the ligand upon complexation.

$$\Delta V^* = V^\ominus([M^+L]) - V^\ominus(L) = \Delta V_c^\ominus + V^\ominus(M^+) \qquad (6)$$

The single ion volumes $V^\ominus(M^+)$ are determined either by a direct experimental method using an ultrasonic technique[17] or by various empirical methods based on extrathermodynamic assumptions.[10] The situation is simple in water since the ionic volumes determined by various of these methods are in satisfactory agreement;[10,18] the compilation of Millero[10] is generally adopted. On the other hand,

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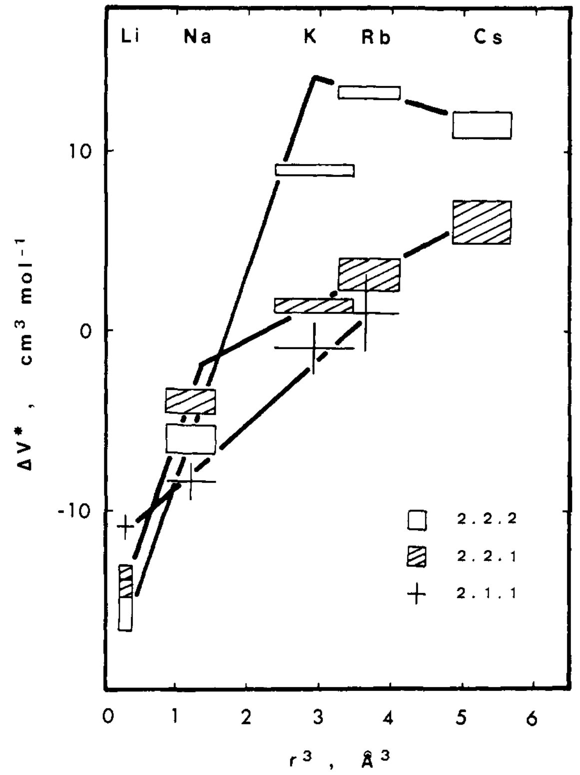

Figure 2. ΔV^* of 2.2.2, 2.2.1, and 2.1.1 with the alkali-metal cations in methanol vs. the cation's radius.

a close examination of the fewer studies performed in methanol[16,19,20] obviously reveals that the sole acceptable ionic volumes in this solvent are those which have been determined by the direct experimental ultrasonic method.[16] Using Kawaizumi and Zana's ionic volumes,[16] we have thus calculated the ΔV^* terms and have reported them in Figures 1 and 2 vs. the cationic radii r to the cubic power. Any error in the single-ion values will result in a solvent-dependent translation of these curves but the relative positions of the three curves of Figure 2 will remain unchanged. The width of the rectangles used to represent each point on the graphs is due to the use of Shannon and Prewitt's effective ionic radii[21] for a coordination number of both 6 and 8 (4 with the small cations). The height of these rectangles corresponds to the estimated uncertainty of the calculated ΔV^*.

In Figure 1, the results for 2.2.2-cryptates in water[5] and in methanol are compared. The behavior of ΔV^* is similar in both solvents: the straight line is broken at a radius value equal to the radius of the internal cavity of 2.2.2,[2] implying that different types of interactions are involved depending on whether the cation radius is smaller or larger than 1.4 Å. The left-hand part of the curves shows that for the small cations the ΔV^* of transfer from water (W) to methanol (M) is negative and almost constant ($\sim$−12 cm³ mol⁻¹). If it is corrected for the transfer of the cryptand itself, we get

$$\begin{aligned}\Delta V_{\mathrm{tr}}^{\ominus}([\mathrm{M}^+2.2.2]) &= V^{\ominus}([\mathrm{M}^+2.2.2])_{\mathrm{M}} - V^{\ominus}([\mathrm{M}^+2.2.2])_{\mathrm{W}} \\ &= \Delta V_{\mathrm{tr}}^* + \Delta V_{\mathrm{tr}}^{\ominus}(2.2.2) \\ &\simeq -7 \text{ cm}^3 \text{ mol}^{-1}\end{aligned} \qquad (7)$$

The volume of transfer of the complex and the volume of transfer of the ligand are thus of opposite sign. As far as the volumes are concerned, this seems to indicate that the inclusive cryptate behaves more like a charged species than like the neutral cryptand. It thus looks as if the surrounding ligand does not prevent the central cation from interacting with the solvent, this being in agreement with the interpretation given by Abraham et al.[22] of the enthalpies and free energies of transfer of these cryptates. When the cation radius is larger than 1.4 Å, the complexation process can be different: evidence has been given by ^{133}Cs NMR studies[23] of the existence of a temperature- and solvent-dependent equilibrium between an inclusive and an exclusive complex. This could explain the sudden drop of ΔV^* when r becomes larger than 1.4 Å: the actual ΔV^* (Cs$^+$) is very much smaller than the ΔV^* (Cs$^+$) which could be extrapolated from the extension of the left-hand part of the curves (drop of −37 cm³ mol⁻¹ in water and −32 cm³ mol⁻¹ in methanol). The fact that the drop of ΔV^* is less pronounced in methanol than in water can be partially due to the difference of the solvation of Cs$^+$ in each solvent, but as soon as an exclusive complex can be involved and that there is possibility for some distortion of the ligand, the exact interpretation of the ΔV^* values becomes extremely difficult.

Table III. Standard Molar Volumes of the Ions and Standard Molar Volumes of Complexation of 2.2.2 with Monovalent and Divalent Cations in Water

cation	$V^{\ominus}(\mathrm{M})$,[a] cm³ mol⁻¹	$\Delta V_{\mathrm{c}}^{\ominus}$, cm³ mol⁻¹
Li$^+$	−6.3	2[b]
Na$^+$	−6.6	15[b]
K$^+$	3.6	18[b]
Rb$^+$	8.7	15[b]
Cs$^+$	15.9	2[b]
Tl$^+$	5.2	17
Ca^{2+}	−28.6	26
Sr^{2+}	−29.0	24
Ba^{2+}	−23.3	19
Pb^{2+}	−26.3	28
Hg^{2+}	−30.1	23
Cd^{2+}	−30.8	20

[a] From ref 10. [b] From ref 5.

In Figure 2, we have reported the results for 2.2.2-, and 2.2.1-, and 2.1.1-cryptates in methanol. According to Lehn and Sauvage[2] the radius of the internal cavity is 0.8 Å for 2.1.1, 1.1 Å for 2.2.1, and 1.4 Å for 2.2.2. We observe for 2.2.2- and 2.2.1-cryptates a drastic slope change of the plots ΔV^* vs. r^3 when r is equal to the internal cavity radius whereas our results do not show, on the other hand, any discernible slope change for 2.1.1-cryptates. These discontinuities of ΔV^* reflect some modification of the nature of the interactions between the complexed cation and the solvent. The cations of radius larger than the radius of the cavity seem more accessible to the solvent. This may be due to some interaction through the faces of the macrobicyclic ligand (18-membered ring)[24] or to a distortion of the cryptand itself[25] or, at the limit, to the existence of an exclusive form of the complex.

Divalent Cryptates in Water. We know that the stability of the complexes is also very dependent on the cation charge.

We have reported in Table III our volumes of complexation of 2.2.2 with various monovalent and divalent cations along with the ionic volumes of the cations in water. The corresponding ΔV^* results plotted on Figure 3 show that the increase of the charge of the cation corresponds to a decrease of the volume of the cryptate. We have assumed that the ΔV^* results of the divalent cryptates fall on a straight line which is almost parallel to that of the monovalent cryptates. For confirmation of this behavior, however, further results would be necessary, especially for smaller cations. Unfortunately, the 2.2.2-cryptates of small cations like Mg^{2+} and Cu^{2+} (which are of the size of Li$^+$) are not stable enough in water[3,26] to avoid precipitation of the hydroxide. When going from a monovalent to a divalent cation of the same size, the volume

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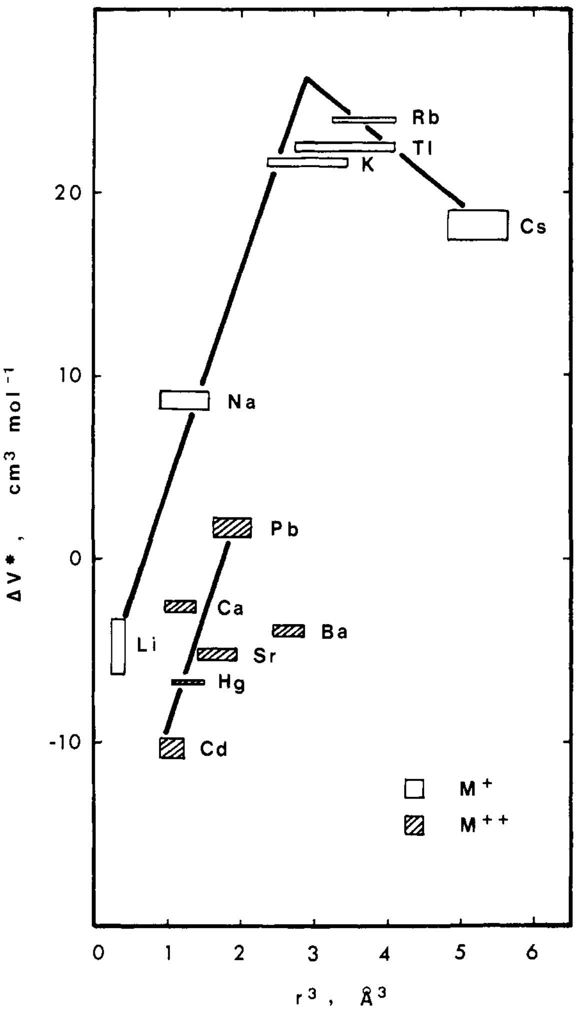

Figure 3. ΔV^* of 2.2.2 with various monovalent[5] and divalent cations in water vs. the cation's radius.

of complexation decreases by about 13 $cm^3\ mol^{-1}$; this decrease, which is almost independent of the radius of the cation, thus seems to be due to a negative contribution to the volume of interaction related to the charge increase. The case of Ba^{2+}-cryptate is interesting: this cation is of the size of K^+ which is almost of the size of the internal cavity of 2.2.2. Thus we would normally expect Ba^{2+} to fill completely the cavity of the ligand without distorting the bonds. The solid-state structure of barium-cryptate shows, however, that the ligand takes the shape of a distorted trigonal prism, the trapped cation being still partially hydrated and in interaction with the anion.[27] These cation-solvent interactions may explain why our ΔV^* result for barium is much lower than what was estimated from the extrapolation of the straight line of Figure 3. In some measure, the behavior of Ca^{2+}- and Sr^{2+}-cryptates is also peculiar. Of course, the interactions involved with the alkaline-earth cations are very different from those involved with Pb^{2+}, Hg^{2+}, and Cd^{2+}, and it may not be surprising that both sets of divalent cryptates behave slightly differently. Our results are too close together, however, and the uncertainties too important to give, at present, a clearer description of the situation.

It would have been interesting to complete this study of the charge effect by adding some results for trivalent cryptates. Unfortunately, it has been shown that the 2.2.2-cryptate of Eu^{3+} (which is of the size of Na^+ and Ca^{2+}) has a formation constant 10^7 smaller than for the corresponding divalent cryptate and that, in addition, it has a strong tendency to complex small anions.[28]

Conclusion

From the volumes of complexation of 2.2.2, 2.2.1, and 2.1.1 with alkali-metal and divalent cations in water and in methanol, we can draw the following conclusions.

The cryptate-solvent interactions show some discontinuity when the radius of the complexed cation is equal to the radius of the internal cavity of the ligand. This modification of the nature of the interactions is likely to be due to a greater accessibility of the solvent to the large cations.

The transfer effect from water to methanol as well as the charge effect in water shows that the cryptates behave like charged species. Thus, we cannot consider that the cation in the cavity of the ligand is totally shielded from the environment.

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Supplementary Material Available: Tables of measured densities and calculated apparent molar volumes (5 pages). Ordering information is given on any current masthead page.

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Elimination, Fragmentation, and Proton Transfer in 1,3-Dithianes and 1,3-Dithiolanes in the Gas Phase

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Abstract: The gas-phase negative ion-molecule chemistry of 1,3-dithianes and 1,3-dithiolanes differs considerably from that in solution. When treated with anionic bases, 1,3-dithiane undergoes successive elimination reactions giving thiolates, in competition with deprotonation at the 2 carbon, which is the sole solution phase reaction channel. The appearance of the various product ions with changing base strength agrees with their calculated thermochemical onset. The gas-phase acidity of 1,3-dithiane is measurable if the elimination reaction is blocked by *gem*-dimethyl substitution at the 5 carbon. For 1,3-dithiolane, no deprotonation product is observed; even at thermochemical threshold, cycloreversion to RCS_2^- and ethylene occurs. This competes with successive eliminations to thiolates, as with the six-membered ring. The differences between the gas phase and solution reactivities are rationalized in terms of counterion effects.

The use of 2-lithio-1,3-dithianes **2** as acyl anion equivalents has since its inception[2] become an important technique in synthetic organic chemistry.[3] These species are equally intriguing to physical organic chemists, due to the considerable stabilization

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