

Solvent Effects in the Complexation of [2]-Cryptands and Related Monocycles with Transition- and Heavy-Metal Cations

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Abstract: Potentiometric and spectrophotometric results on the complexation of transition- and heavy-metal cations by the bicyclic cryptands 211, 221, and 222 and the related monocycles 21 and 22 in water, methanol (MeOH), dimethyl sulfoxide (Me₂SO), and propylene carbonate (PC) are discussed. The complexes formed in solution are strongly influenced by the solvent: the mononuclear 1:1 complexes are in some cases accompanied by dinuclear 2:1 and/or protonated mononuclear 1:1:1 complexes. With 1:1 complexes, it is shown that (i) for a given complex the stability sequence is Me₂SO < H₂O < MeOH < PC, (ii) for a given cation the variation of the stability with the cryptand cavity size is parallel in all solvents, and (iii) a strong macrobicyclic effect is displayed in all solvents by the larger Pb²⁺ and Ag⁺ cryptates whereas no significant cryptate effect is found with transition cations. The generalized extrathermodynamic assumption involving cryptates recently proposed in the literature appears to be generally not consistent with the Ph₄As⁺/Ph₄B⁻ assumption, with divalent as well as with monovalent cations. The transfer activity coefficients of divalent cryptates are calculated from the present data by using the literature values of the transfer activity coefficients of the uncomplexed cryptands and of the free cations.

The diazapolyoxamacrobicycles, or [2]-cryptands, first synthesized by Dietrich, Lehn, and Sauvage in 1969 and represented in Figure 1, are well-known for their ability to form 1:1 inclusion complexes, or cryptates, with metallic cations.¹⁻⁴

The thermodynamics of complexation in solution of 211, 221, and 222 has been mainly studied with alkali and alkaline-earth cations in water and in various nonaqueous solvents. The main potentiometric and calorimetric studies are due to Lehn et al.,^{5,6} Schneider et al.,⁷⁻⁹ Kolthoff et al.,^{10,11} Bessiere et al.,^{12,13} and Abraham et al.¹⁴⁻¹⁷ The complexation of Ag⁺ and Tl⁺ has been investigated by Anderegg in aqueous medium¹⁸ and by most of the previous authors both in water and in some nonaqueous solvents.^{7,8,11,12,16-19} However, no systematic investigation of the complexation of transition- and heavy-metal cations by [2]-cryptands in various solvents had been undertaken before our own studies²⁰⁻²⁴ of the complexation of the bicyclic ligands 211, 221,

and 222 and the related monocycles 21 and 22 (Figure 1) in water,²⁰ methanol,^{21,22} Me₂SO,²⁴ and PC.^{23,24}

We report here some new results concerning water and Me₂SO media and discuss the complete set of our potentiometric and spectrophotometric results.²⁰⁻²⁴ As each of the monocyclic ligands is one of the cycles of the bicyclic [2]-cryptands, our results allow a comparison of the complexing properties of both class of macrocycles, which is of special interest when two ligands of comparable cavity sizes are compared, such as 221 and 21 or 222 and 22 (see caption of Table II). Before our work, the complexation of 21 and/or 22 with transition- and heavy-metal cations had only been studied in aqueous medium with Cu²⁺,²⁶ Cd²⁺,^{18,26} Ag⁺, and Hg²⁺¹⁸ and more recently in 95/5 methanol with Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, and Cd²⁺.¹⁹

Results

The overall stability constants $\beta_{xy,z}$ for the general equilibrium 1 between a cation Mⁿ⁺, a macrocycle L, and protons is given by



eq 2. $\beta_{xy,z}$, which is a concentration ratio, is an apparent overall

$$\beta_{xy,z} = [M_xH_yL_z^{(nx+y)+}] / [M^{n+}]^x [H^+]^y [L]^z \quad (2)$$

stability constant. But in the particular case of the formation of 1:1 macrocyclic complexes ($x = z = 1, y = 0$), as already pointed out by Popov and Lehn,⁴ the value of the apparent stability constant can be assimilated to the thermodynamic stability constant, provided that the ionic strength is not too high, i.e., that the activity factors of the cations do not depend upon their ionic radius. In fact, Popov has shown that the ionic strength I does not modify the stability constants of the complex of crown ethers in methanol up to $I = 0.05$.²⁸

The technique employed in water was pH measurement (complexation of Hg²⁺ by 211, 221, and 21 and Ag⁺ by 221). In Me₂SO, potentiometric methods were mainly used with a copper-selective electrode for the copper complexes and a silver

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Table I. Logarithms of the Overall Stability Constants β_{xyz} in Water and Me_2SO , $I = 0.1 \text{ M Et}_4\text{NClO}_4$, at 25 °C

solvent	cations	$\log \beta_{xyz}$	211	221	222	21	22
H_2O	Ag^+	$\log \beta_{101}$		12.43 ± 0.01^a			
	Hg^{2+}	$\log \beta_{101}$	15.97 ± 0.04^a	19.97 ± 0.18^a		16.65 ± 0.13^a	
		$\log \beta_{111}$	18.71 ± 0.18^a				
Me_2SO	Cu^{2+}	$\log \beta_{101}$	4.08 ± 0.03^b	3.77 ± 0.06^b	2.68 ± 0.10^b	4.37 ± 0.10^b	3.00 ± 0.10^b
		$\log \beta_{111}$				4.49 ± 0.10^c	3.30 ± 0.09^c
	Pb^{2+}	$\log \beta_{101}$	3.68 ± 0.10^d	8.37 ± 0.05^d	7.23 ± 0.01^d	3.57 ± 0.05^d	4.22 ± 0.02^d

^a pH measurement. ^b Potentiometry with a copper-selective electrode. ^c Visible and near-IR spectrophotometry. ^d Potentiometry with a silver electrode, competition with Ag^+ .

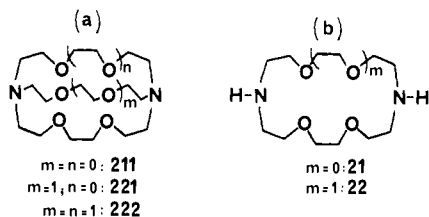


Figure 1. The [2]-cryptands (a) and the related monocycles (b) studied in this work.

electrode for the lead complexes. Some of the results obtained with copper were also confirmed by visible-near-IR spectrophotometry. More experimental details are given in the Experimental Section.

Our potentiometric data have been refined by the computer programs SCOGS²⁹ or MINQUAD.³⁰ The spectrophotometric data collected at various wavelengths were analyzed by the matrix-rank treatment of Hugus and El-Awady,³¹ which provides the minimum number of species to take into account for the interpretation of the whole set of data. The stability constants and the electronic spectra of the various species in solution have been calculated by the general program LETAGROP-SPEFO.³² Figure 2 summarizes some of our previously published results concerning the 1:1 complexes given in this paper. The newly determined overall stability constants are listed in Table I with their 95% confidence interval $\pm 2\sigma$, and some of them are visualized in Figure 2.

Our previous and new results show that in all cases studied we find 1:1 mononuclear species, sometimes accompanied in the protic solvents by protonated 1:1:1 species (Cu^{2+} and Zn^{2+}). More unexpected is the evidence for binuclear 2:1 complexes found in some cases, i.e., in methanol, with all studied cations except Zn^{2+} , and in PC, with Pb^{2+} . Obviously, these binuclear complexes cannot be real inclusion bimetallic complexes as, for instance, the so-called "bis-tren" complexes synthesized by Lehn³³ and studied in solution by Martell et al.³⁴ the cavities of the ligands studied in this work are too small to encapsulate two cations, even the smallest transition cations. Consequently, either both cations are bound outside the cavity or one is inside and the other outside the cavity.

If we now focus our interest on the 1:1 mononuclear complexes, the following questions may be answered: (i) what are the medium effects upon the stability constants, (ii) is any size effect observable, as in the case of alkali and alkaline-earth cations,⁵ and (iii) is there evidence for any macrobicyclic effect, i.e., any enhancement of stability of the complexes of bicyclic ligands, compared to the analogue complexes of monocyclic ligands of comparable cavity sizes?

(i) Figure 2 clearly demonstrates that with the five cations Ag^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} , the stability sequence for a given complex increases in the order $\text{Me}_2\text{SO} < \text{H}_2\text{O} < \text{MeOH} < \text{PC}$. It is of interest to point out that in their recent study of alkali

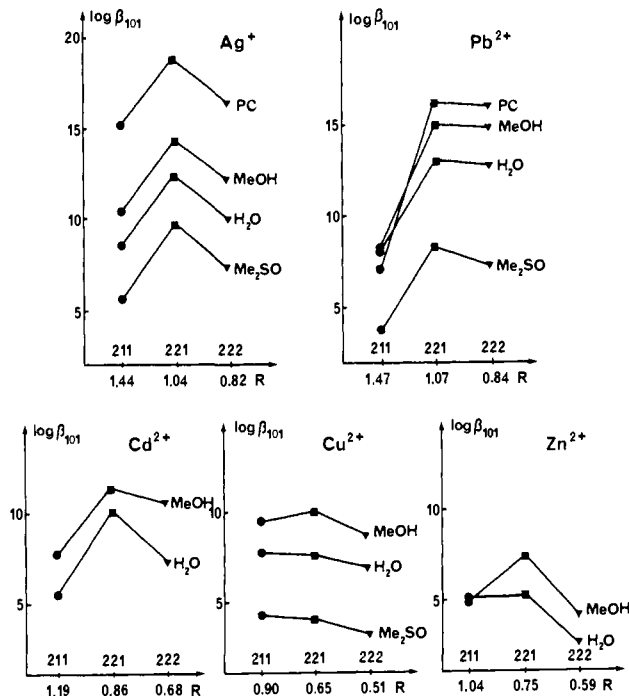


Figure 2. Logarithms of the stability constants for Ag^+ , Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} 1:1 cryptates vs. the ratio R of the cation ionic radius to the ligand cavity radius.

cation cryptates, Cox et al.,⁹ Kolthoff and Chantooni,¹⁰ Yee et al.,²⁵ and Bessiere et al.¹³ also find that the stability sequence is identical for all alkali cations but that the stability in water is always lower than in Me_2SO . Thus the stability sequence depends on the type of the cation and is not the same for alkali cation cryptates as for transition- or heavy-metal cation cryptates.

(ii) Concerning size effects, Figure 2 shows evidence of two facts: for a given cation the variation of the stability with the cavity size of the ligand is parallel in all solvents. This conclusion was also reached by Cox et al.⁹ with the monovalent alkali cations, for which they find a selectivity pattern independent of the solvent. A pronounced stability maximum is displayed in all cases by the cryptand 221 except for Cu^{2+} in water and Me_2SO , where $\text{Cu}(211)^{2+}$ is the most stable complex. Such a situation is quite understandable for the larger Ag^+ and Pb^{2+} cations, which fit best inside the cavity of 221, as can be seen on Figure 2 from the ratio R of the cation ionic radius to the cavity radius. But for the smaller cations Cu^{2+} and Zn^{2+} , one could have expected on the basis of size considerations, a stability maximum to be reached with the cryptand 211. When this is not observed it can be due to the partially covalent character of the bonds between the transition cations and the ligands heteroatoms.

(iii) As shown in Table II, in which 221 is compared to 21 and 222 to 22, a strong bicyclic or cryptate effect is displayed in all solvents by the larger cations Pb^{2+} and Ag^+ , and the effect is always more important with 221 than with 222. For both cations, the smallest effect is observed in Me_2SO . On the contrary, with the smaller copper cation, the macrobicyclic effect is nearly negligible, and even reversed in Me_2SO . No significant macrobicyclic effect was found with the other transition cations.

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Table II. The Macrobicyclic Effect

cations	ligands	water	methanol	Me ₂ SO	PC
Pb ²⁺	221/21 ^a	7.27	7.24	4.80	7.70
	222/22	5.82	5.36	3.01	4.36
Ag ⁺	221/21	6.58	6.69	4.56	
	222/22	1.95	1.82	0.94	
Cu ²⁺	221/21	0.39	0.63	-0.60	
	222/22	0.63	0.11	-0.32	

^a 221/21 = log β₁₀₁(M(221)ⁿ⁺) - log β₁₀₁(M(21)ⁿ⁺) and 222/22 = log β₁₀₁(M(222)ⁿ⁺) - log β₁₀₁(M(22)ⁿ⁺). Cavity sizes from CPK molecular models:²⁰ 221 (1.10 Å), 21 (1.0 Å), 222 (1.40 Å), 22 (1.40 Å).

Discussion

The stability constants of 1:1 alkali cryptates in various solvents have been used in the past 3 years to test the validity of the new extrathermodynamic assumption involving cryptates proposed by Bessiere et al.^{12,13} in which a cryptand L and a cryptate MLⁿ⁺ undergo the same solvation changes upon transfer from a reference solvent S₀ to a solvent S provided that MLⁿ⁺ is a real inclusion complex.

If γ_{S₀}^S(i) is the transfer activity coefficient of the species i when transferred from S₀ to S, Bessiere's generalized assumption may be written

$$\gamma_{S_0}^S(ML^{n+}) = \gamma_{S_0}^S(L) \quad (3)$$

Quite rigorously, and independent of any extrathermodynamic assumption, the difference between the logarithms of the formation constants of a cryptate MLⁿ⁺ in the solvents S and S₀ is equal to the logarithm of the transfer activity coefficient of the cation Mⁿ⁺ plus the difference δ_{S₀}^S between the transfer activity coefficients of the cryptand and the cryptate:

$$\Delta_{S_0}^S = \log \beta(S) - \log \beta(S_0) = \log \gamma_{S_0}^S(M^{n+}) + \delta_{S_0}^S \quad (4)$$

$$\delta_{S_0}^S = \log \gamma_{S_0}^S(L) - \log \gamma_{S_0}^S(ML^{n+}) \quad (5)$$

According to Bessiere's proposal, δ_{S₀}^S should be equal to 0, and the experimental value of Δ_{S₀}^S should be equal to the transfer activity coefficient of the cation Mⁿ⁺, regardless of the solvents S₀ and S used. Thus, if valid, the assumption should have the great advantage of providing a new method for the determination of transfer activity coefficients of cations. This method would find its most interesting application with divalent cations, as the measurement of their transfer activity coefficients based upon other extrathermodynamic assumptions is often subject to serious restrictions.³⁵

Of course, one cannot prove whether an extrathermodynamic assumption is right or not, but one can compare the results derived from two different extrathermodynamic assumptions and analyze whether they are self-consistent or not.

In this respect, all conclusions concerning the transfer properties of the cryptates of the *monovalent* alkali, Ag⁺ and Tl⁺, cations imply the well-known and widely used tetraphenylarsonium tetraphenylborate assumption: γ_{S₀}^S(Ph₄As⁺) = γ_{S₀}^S(Ph₄B⁻)³⁶ for the estimation of γ_{S₀}^S(M⁺).

The first conclusions were established with the ligand 222 and the cations K⁺, Ag⁺, and Tl⁺, which fit closely inside the cavity of the cryptand. The quantity δ_{S₀}^S was found to be equal to 0 *only* if S₀ and S are two dipolar aprotic solvents.^{7,10} If the reference solvent S₀ is water and S is a dipolar aprotic solvent, δ_{H₂O}^S is found to be approximately constant for these cations, whatever S (δ = 3.75 according to ref 7), whereas a slightly different value was found for the smaller Na⁺ cation.¹⁰ If the transfer occurs between water and methanol, no constancy of δ_{H₂O}^{MeOH} was observed, probably due, as suggested by Kolthoff et al.¹⁰ and by Abraham et al.,¹⁴⁻¹⁸ to the hydrophobic solvation of LMⁿ⁺ in water and to a lesser extent to the fact that methanol is an H-bonding solvent. The detailed investigations of Abraham and co-workers, all devoted

to the transfer of monovalent 222 cryptates from water to methanol, confirm that for this case Bessiere's assumption is not consistent with the Ph₄As⁺/Ph₄B⁻ assumption: strong deviations are observed for the small Li⁺ cation and for the large Cs⁺ cation.

Further studies concerning the complete series of alkali cations and the other cryptands 221 and 211^{8,9,11} are in agreement with the above conclusions and point out the fact that the constancy of δ_{S₀}^S only applies to the real *inclusive* cryptates defined by Popov and Lehn.⁴

The transfer properties of *divalent* cation cryptates have been much less studied. Only transfers from water to PC and DMF (dimethylformamide) of CaL²⁺ (L = 211, 221, and 222)⁹ and transfer of BaL²⁺ (L = 222 and dibenzo-222) from water to methanol¹¹ have been investigated very recently. Both studies suggest large differences between the solvation of cryptates of monovalent and divalent cations.

In the present state of investigations about the extrathermodynamic assumption involving cryptates, our results bring forth the following new contributions: (i) they concern more cryptates of divalent cations (Pb²⁺, Cu²⁺, Cd²⁺) and (ii) they enable a comparison between the transfer properties of bicyclic and monocyclic diazapolyoxamacrocyclic complexes. This latter point is of particular interest for testing the validity of Bessiere's assumption, as there is no obvious reason why it should also apply to complexes of monocyclic ligands where the cation is certainly much less shielded from the solvent than in cryptates.

Table III gives our experimental Δ values for the transfers from water to methanol, PC, and Me₂SO.

(a) At first sight, the Δ values concerning the *bicyclic* ligands seem, in most cases, to be roughly independent of the nature of the cryptand. The only exceptions concern Pb(211)²⁺, which has a very different behavior than Pb(221)²⁺ and Pb(222)²⁺, and the cadmium cryptates of 221 and 222, for which no constancy of Δ_{H₂O}^{MeOH} is observed. One could be tempted to explain the particular behavior of Pb(211)²⁺ by the fact that it is not an inclusive complex, but the same could also be said for Ag(211)⁺, which however does not display any singular behavior. Other factors probably have to be considered to explain the particular behavior of Pb(211)²⁺. The relative constancy of Δ displayed by most of the bicyclic systems investigated in this work enables the definition of mean Δ values for bicyclic systems, noted Δ_B, which can be calculated with their experimental uncertainty (see Table III).

The results concerning the *monocyclic* systems are interesting in two respects. First, as with bicyclic ligands, for a given transfer and a given cation, Δ is often independent of the nature of the ligand, except for lead complexes transferred from water to PC (Δ_{H₂O}^{PC} being respectively equal to 2.8 and 4.7 for 21 and 22) and for silver complexes transferred from water to Me₂SO (Δ_{H₂O}^{Me₂SO} being respectively -0.7 and -1.7 for 21 and 22). When possible, the mean Δ_M values for the monocyclic systems are also given in Table III. Second, for the transfers from water to methanol, the Δ_M values are not significantly different from the corresponding Δ_B values, whereas both sets of values are significantly different for transfers from water to Me₂SO. This observation confirms that Bessiere's assumption is more justified for transfers to dipolar aprotic solvents than to methanol and extends this conclusion to divalent cations. Our Δ_M values for transfers from H₂O to Me₂SO are less negative than the corresponding Δ_B values (see Table III). According to eq 4 and 5, if Δ_M > Δ_B, the quantity log γ_{H₂O}^{Me₂SO}(L) - log γ_{H₂O}^{Me₂SO}(MLⁿ⁺) is greater for the monocyclic systems than for the bicyclic ones. Consequently, with L_B and L_M being respectively the bicyclic and the monocyclic diazapolyoxamacrocyclics,

$$\log \gamma_{H_2O}^{Me_2SO}(L_B) - \log \gamma_{H_2O}^{Me_2SO}(L_M) < \log \gamma_{H_2O}^{Me_2SO}(ML_B^{n+}) - \log \gamma_{H_2O}^{Me_2SO}(ML_M^{n+}) \quad (6)$$

Thus upon transfer from water to Me₂SO, the difference in the solvation changes undergone by the free mono- and bicyclic diazapolyoxamacrocyclics is less important than for corresponding complexes.

Table IV shows a comparison between the mean Δ_B values and

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Table III. Log β_{101} , Δ , and Mean $\bar{\Delta}_B$ and $\bar{\Delta}_M$ Values

cations	ligands	log β_{101} (H ₂ O) ^c	log β_{101} (MeOH)	Δ (H ₂ O → MeOH)	log β_{101} (PC)	Δ (H ₂ O → PC)	log β_{101} (Me ₂ SO)	Δ (H ₂ O → Me ₂ SO)
Ag ⁺ (<i>r</i> = 1.15 Å) ⁱ	211	8.52	10.30 ^d	1.8	15.00 ^f	6.5	5.45 ^f	-3.1
	221	12.43	14.30 ^d	1.9	18.80 ^f	6.4	9.73 ^f	-2.7
	222	9.85	12.00 ^d	2.1,	16.33 ^f	6.5,	7.15 ^f	-2.7,
				$\bar{\Delta}_B = 1.9 \pm 0.2$			$\bar{\Delta}_B = 6.5 \pm 0.1$	$\bar{\Delta}_B = -2.8 \pm 0.2$
	21	5.85	7.61 ^d	1.8			5.17 ^f	-0.7
	22	7.90	10.18 ^d	2.3,			6.21 ^f	-1.7
			$\bar{\Delta}_M = 2.0 \pm 0.3$					
Cu ²⁺ (<i>r</i> = 0.72 Å) ^b	211	7.78	9.51 ^e	1.8			4.08 ^h	-3.7
	221	7.56	10.08 ^e	2.5			3.77 ^h	-3.8
	222	6.81	8.59 ^e	1.8,			2.68 ^h	-4.1,
				$\bar{\Delta}_B = 2.0 \pm 0.4$				$\bar{\Delta}_B = -3.9 \pm 0.2$
	21	7.17	9.45	2.3			4.37 ^h	-2.8
	22	6.18	8.48 ^e	2.3,			3.00 ^h	-3.2,
			$\bar{\Delta}_M = 2.3 \pm 0.0$				$\bar{\Delta}_M = -3.0 \pm 0.2$	
Pb ²⁺ (<i>r</i> = 1.18 Å) ⁱ	211	7.93	8.18 ^d	0.2	7.01 ^g	-0.9	3.68 ^h	-4.2
	221	13.12	15.11 ^d	2.0	16.34 ^g	3.2	8.37 ^h	-4.8
	222	12.72	14.84 ^d	2.1,	16.00 ^g	3.3,	7.23 ^h	-5.5,
				$\bar{\Delta}_B = 2.0 \pm 0.1^a$			$\bar{\Delta}_B = 3.2 \pm 0.1$	$\bar{\Delta}_B = -5.1 \pm 0.4^a$
	21	5.85	7.87 ^d	2.0	8.64 ^g	2.8	3.57 ^h	-2.3
	22	6.90	9.48 ^d	2.6,	11.64 ^g	4.7	4.22 ^h	-2.7,
			$\bar{\Delta}_M = 2.3 \pm 0.3$				$\bar{\Delta}_M = -2.5 \pm 0.2$	
Cd ²⁺ (<i>r</i> = 0.95 Å) ⁱ	221	10.04	11.30 ^d	1.3				
	222	7.10	10.41 ^d	3.3				
	21	6.46	8.72 ^d	2.3				
	22	5.31	7.83 ^d	2.5,				
			$\bar{\Delta}_M = 2.4 \pm 0.1$					

^a Mean for 221 and 222 complexes. ^b Reference 38. ^c Reference 20. ^d Reference 21. ^e Reference 22. ^f Reference 24. ^g Reference 23. ^h This work. ⁱ Reference 37.

Table IV. Comparison Between $\bar{\Delta}_B$ and the Logarithms of the Transfer Activity Coefficients of the Cations according to the Ph₄As⁺/Ph₄B⁻ Assumption

cations	S	$\bar{\Delta}_B$	log $\gamma_{H_2O}^S(M^{n+})$
Ag ⁺	Monovalent		
	MeOH	1.9	1.3 ^a
	PC	6.5	2.9 ^a
	Me ₂ SO	-2.8	-5.9 ^a
Cu ²⁺	Divalent		
	MeOH	2.0	4.4 ^a
	Me ₂ SO	-3.9	-8.8 ^a
Cd ²⁺	Divalent		
	MeOH	1.3 ^b	8 ^a
		3.3 ^b	
Pb ²⁺	MeOH	2.0	
	PC	3.2	
	Me ₂ SO	-5.1	
Ba ²⁺	MeOH	3.4 ^c	3.2 ^d
Ca ²⁺	PC	6.3 ^e	
	DMF	-0.7 ^e	

^a Reference 35. ^b Single Δ values for 221 and 222. ^c Value for Ba(222)²⁺ from ref 11. ^d Reference 39. ^e Values for Ca(222)²⁺ from ref 9.

the most reliable literature values for log $\gamma_{H_2O}^S(M^{n+})$ derived from the Ph₄As⁺/Ph₄B⁻ assumption. In the few cases in which both quantities are known, two remarks can be made: (i) $\bar{\Delta}_B$ and log $\gamma_{H_2O}^S(M^{n+})$ are always the same sign and (ii) they are not of equal magnitude. This confirms the conclusion previously established for the transfer from water to a solvent S of monovalent cryptates ($\delta_{H_2O}^S \neq 0$) and extends it to the divalent copper cryptates. It is regrettable that no value for $\gamma_{H_2O}^S(Pb^{2+})$ based upon the Ph₄As⁺/Ph₄B⁻ assumption can be found in the literature and that, consequently, our data on lead complexes cannot be further discussed. The only case for which we find a $\bar{\Delta}_B$ value not very different from log $\gamma_{S_0}^S(M^{n+})$ concerns silver cryptates transferred from water to methanol. A similar agreement between both quantities has also been found recently by Kolthoff and Chantooni for the transfer of Ba(222)²⁺ from water to methanol (see Table IV). As this transfer is precisely the case in which Bessiere's assumption seems to be less applicable, the observed agreement is probably fortuitous.¹¹

Table V. Values of log $\gamma_{H_2O}^S(L)$ and log $\gamma_{H_2O}^S(ML^{n+})$ using Values of log $\gamma_{H_2O}^S(M^{n+})$ Derived from the Ph₄As⁺/Ph₄B⁻ Assumption

S	cations	log $\gamma_{H_2O}^S(M^{n+})$	ligands	log $\gamma_{H_2O}^S(L)$	log $\gamma_{H_2O}^S(ML^{n+})$	$\delta_{H_2O}^S$	
MeOH	Cu ²⁺	4.4 ^d	211	0.4 ^a	3.0	-2.6	
			221	0.4 ^a	2.3	-1.9	
			222	0.8 ^c	3.4	-2.6	
	Cd ²⁺	8.0 ^d	221	0.4	7.1	-6.7	
			222	0.8	5.5	-4.7	
	Ba ²⁺	3.2 ^b	222	0.8	0.8 ^b	0	
Ag ⁺		1.3 ^d	211	0.4	-0.1	0.5	
			221	0.4	-0.2	0.6	
		222	0.8	0.0	0.8		
Me ₂ SO	Na ⁺	1.5 ^b	222	0.8	-1.7 ^b	2.5	
		K ⁺	1.8 ^b	222	0.8	-2.6 ^b	3.4
			0.7 ^b	222	0.8	-2.3 ^b	3.1
PC	Cu ²⁺	-8.8 ^d	222	1.1 ^a	-3.6	4.7	
		Ag ⁺	-5.9 ^d	222	1.1	-2.1	3.1
			2.9 ^d	222	0.9 ^a	-2.7	3.6

^a From ref 9. ^b Data from ref 11. ^c Mean value of the data from ref 15, 9, and 11. ^d Data from ref 35.

The constant value $\delta_{H_2O}^S = 3.75$ proposed by Gutknecht and co-workers⁷ for the transfer of monovalent cryptates from water to a dipolar aprotic solvent applies very well to our results, as it provides, for Ag⁺, a value of ($\bar{\Delta}_B - 3.75$) close to log $\gamma_{H_2O}^S(Ag^+)$ (with S = PC or Me₂SO). For the transfer from water to Me₂SO of copper cryptates, we find a positive value of $\delta_{H_2O}^{Me_2SO} = -3.9 + 8.8 = 4.9$, which is significantly larger than 3.75. But no further information about the magnitude of $\delta_{H_2O}^S$ for divalent cations cryptates (S being a dipolar aprotic solvent) can be obtained for the moment, as the transfer activity coefficients $\gamma_{H_2O}^S$ of Pb²⁺ and Ca²⁺, for which stability constants of the cryptates in various solvents are available, have not yet been determined on the basis of the Ph₄As⁺/Ph₄B⁻ assumption.

(b) A sharper analysis of the individual Δ values for each complex (listed in Table III) can be attempted by taking into account the determinations of the transfer activity coefficients of the free cryptands, recently performed by Abraham et al.,¹⁵

Cox et al.,⁹ and Kolthoff et al.¹¹ (see Table V). The knowledge of $\log \gamma_{\text{H}_2\text{O}}^{\text{S}}(\text{M}^{n+})$, according to the $\text{Ph}_4\text{As}^+/\text{Ph}_4\text{B}^-$ assumption, and of $\log \gamma_{\text{H}_2\text{O}}^{\text{S}}(\text{L})$ enables the calculation of $\log \gamma_{\text{H}_2\text{O}}^{\text{S}}(\text{ML}^{n+})$ from eq 4 and 5. Table V gives the calculated values of $\log \gamma_{\text{H}_2\text{O}}^{\text{S}}(\text{ML}^{n+})$ for the cryptates of Ag^+ and of the divalent cations Cu^{2+} and Cd^{2+} . Literature values for the 222 cryptates of Ba^{2+} , Na^+ , K^+ , and Tl^+ are listed in Table V for comparison purposes.

For the *transfer from water to methanol*, $\log \gamma_{\text{H}_2\text{O}}^{\text{MeOH}}(\text{ML}^+)$ is found to be negative for alkali cations cryptates,¹¹ the monocharged cryptates being more solvated in methanol than in water. We find a positive and quite large $\log \gamma_{\text{H}_2\text{O}}^{\text{MeOH}}(\text{ML}^{2+})$ value for Cu^{2+} and Cd^{2+} cryptates, respectively about 3 and 5–7. Thus, on the basis of the $\text{Ph}_4\text{As}^+/\text{Ph}_4\text{B}^-$ assumption, the cryptates of Cu^{2+} and Cd^{2+} are more solvated in water than in methanol, as also found for the free ligands and the free divalent cations. The difference $\delta = \log \gamma(\text{L}) - \log \gamma(\text{ML}^{n+})$, which measures the deviation from Bessiere's proposal, is negative for cryptates of Cu^{2+} and Cd^{2+} and is positive for the monovalent cryptates. The absolute value of δ , though, is not higher for Cu^{2+} cryptates than for some alkali cation cryptates, and in both cases, Bessiere's assumption is not consistent with the tetraphenylarsonium assumption.

The values of $\log \gamma_{\text{H}_2\text{O}}^{\text{MeOH}}(\text{ML}^{n+})$ obtained by Kolthoff and Chantooni¹¹ and by us for barium and silver cryptates, respectively, are intermediate between the results for alkali cation cryptates and for Cu^{2+} and Cd^{2+} cryptates, $\log \gamma_{\text{H}_2\text{O}}^{\text{MeOH}}(\text{ML}^{n+}) \neq 0$, and the apparent agreement with Bessiere's assumption observed in these cases is probably fortuitous.

Our data for the *transfer from water to dimethyl sulfoxide* show that $\log \gamma_{\text{H}_2\text{O}}^{\text{MeSO}}(\text{M}(222)^{n+})$ is negative for Ag^+ and Cu^{2+} cryptates, as it is for the free cations. Both the free cations and the cryptates are more solvated in Me_2SO than in water, whereas the free 222 is more solvated in water than in Me_2SO . Nevertheless, the solvation changes are more important for the free cations than for the cryptates.

The situation is different for the *transfer of silver cryptates from water to PC*, as $\log \gamma_{\text{H}_2\text{O}}^{\text{PC}}(\text{Ag}(222)^+)$ and $\log \gamma_{\text{H}_2\text{O}}^{\text{PC}}(\text{Ag}^+)$ are of opposite sign: the free silver cation, as uncomplexed 222 is more solvated in water, whereas the cryptate $\text{Ag}(222)^+$ is more solvated in PC than in water. This last result is surprising, considering that PC is ordinarily a poor solvating solvent for cations. From the results of Cox et al.,⁹ the same conclusion can be reached for $\text{Na}(222)^+$: $\log \gamma_{\text{H}_2\text{O}}^{\text{PC}}(\text{Na}(222)^+) = -3.8$ with $\log \gamma_{\text{H}_2\text{O}}^{\text{PC}}(\text{Na}^+) = 2.64$ (ref 40).

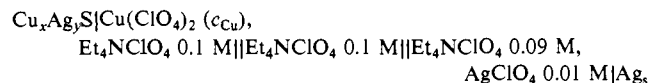
(37) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **26**, 1076 (1970).

Experimental Section

The preparation and purification of the chemicals and solvents as well as the experimental techniques used for all studies in water, methanol, and propylene carbonate and for the study of Ag^+ complexes in Me_2SO have been described in our earlier papers.^{20–24}

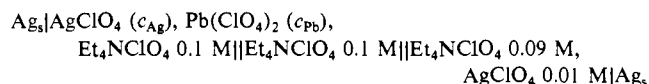
The copper perchlorate solvate in Me_2SO was prepared from $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Alfa-Ventron p a) that had been dried at 70 °C under reduced pressure for 12 h before being dissolved in Me_2SO . The solution thus obtained was concentrated by evaporation under 15 mmHg at 80 °C. The solvate, which precipitated on cooling, was recrystallized three times and dried under 1 mmHg for 12 h. The carbon and hydrogen content (respectively 16.62 and 4.14%) correspond to the tetrasolvate $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{Me}_2\text{SO}$ (theoretical composition: C, 16.69; H, 4.17).

The copper complexes in Me_2SO were studied with a copper cation selective electrode, in the following electrochemical cell:



In the range $10^{-5} \text{ M} < \text{Cu}^{2+} < 10^{-2} \text{ M}$, the slope of the linear plot $E = f(\log[\text{Cu}^{2+}])$ was found to equal 0.0290 V instead of the theoretical slope 0.0296 V, as already noticed by Coetzee and Istone.³⁵ The stability constants thus determined are in good agreement with those obtained by spectrophotometry.

The lead complexes in Me_2SO were determined by a competition method with Ag^+ by using a silver electrode in the following electrochemical cell:



After calibration of the silver electrode in the range $5 \times 10^{-5} \text{ M} < \text{Ag}^+ < 10^{-2} \text{ M}$, the ligand solution (about $5 \times 10^{-2} \text{ M}$) was added stepwise with a 1-mL "Manostat" microburet to a solution of anhydrous silver perchlorate ($2 \times 10^{-3} \text{ M}$) and lead nitrate (10^{-3} M). After each addition, the system was stabilized within less than 1 min.

All experiments were performed in 40-mL thermostated quartz cells at 25 °C under argon flushing, and with a total ionic strength of 10^{-1} M adjusted by Et_4NClO_4 .

(38) V. M. Goldschmidt, *Skr. Nor. Vidensk.-Akad., [Kl.] 1: Mat.-Naturvidensk. Kl.* 1.2, 1926.

(39) G. Hedwig, D. Owensby, and A. J. Parker, *J. Am. Chem. Soc.*, **97**, 3888 (1975).

(40) B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477, (1974).