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Cryptate Formation in $(CH_3)_2SO$. Lanthanide and Alkaline Earth Cryptates[1]

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Stability constants for lanthanide and alkaline earth cryptate formation have been measured in $(CH_3)_2SO$ by visible spectroscopic techniques using murexide as a metal ion indicator. Three cryptands (222, 221, and 211) were examined with five lanthanide ions (Pr^{3+}, Nd^{3+}, Gd^{3+}, Ho^{3+}, and Yb^{3+}) and three alkaline earth ions (Ca^{2+}, Sr^{2+}, and Ba^{2+}). Lanthanide complexes with 211 are more stable than those of the larger ligands. No appreciable metal ion specificity is observed in the formation of lanthanide cryptates, but the alkaline earth ions display metal ion specificity similar to that observed in water. The stability constants in $(CH_3)_2SO$ are less than those measured in H_2O by at least 2 orders of magnitude for all of the ions studied. Also, addition of $(CH_3)_4NCl$ leads to lower apparent stability constants in the case of lanthanide cryptates but has little effect on the formation of alkaline earth cryptates. Reasons for these results are presented.

Cryptands are macrobicyclic ligands that form inclusive complexes with various metal ions.[2-7] Interest in these ligands remains high in part because the formation of cryptate complexes proceeds with considerable metal ion specificity, the best fit of metal ion to ligand cavity being a prime requisite for complex stability. The fact that the trivalent lanthanide ions have radii comparable to Na^+ and Ca^{2+} leads to the expectation that lanthanide ions would also form stable cryptates. The preparation of such lanthanide cryptates was first reported[8] in 1977. This initial work has been considerably extended,[9] and crystal structures of some lanthanide cryptates[10-12] have appeared recently as well as a determination[13] of some lanthanide cryptate stability constants. Two striking conclusions of the electrochemical studies[8,9] of lanthanide cryptates are that the reduced (divalent) lanthanide cryptates are more stable than the trivalent cryptates and that trivalent cryptates interact with small anions in solution (notably F^- and OH^-) to an extent comparable to or greater than the uncomplexed hydrated ion. Support for the idea that the divalent lanthanide ions may form more stable complexes than the trivalent ions with macrocyclic ligands is found in electrochemical studies by other groups[14,15] of lanthanide complex formation with some macrocyclic polyethers. This result is particularly surprising since noncyclic ligands always form more stable complexes with trivalent lanthanides.[16]

Recent stability constant determinations for trivalent cryptates by pH titration methods[13] differ from the earlier electrochemical results[9] in two respects. The pH titration data show no appreciable metal ion specificity while the electrochemical measurements indicate that $[Eu^{3+}\subset 221]$ is more stable than $[Eu^{3+}\subset 222]$ by more than 2 orders of magnitude. The pH titration results also yield higher values for the stability constants. These two studies were carried out in aqueous solution with different supporting electrolytes. The pH titrations were carried out in 0.25 M $(CH_3)_4NCl$ and the electrochemical studies in 0.5 M $NaClO_4$.

The question of metal ion specificity is obviously one of considerable significance in cryptate chemistry. In order to ascertain whether such specificity exists for lanthanide cryptates, we carried out the determination of the stability constants by visible spectroscopic methods using murexide as a metal ion indicator. This technique has been used by us previously[17] in the determination of stability constants of Ca^{2+} cryptates in basic aqueous solution. In addition, we chose reaction conditions that would minimize problems associated with the measurement of the constants. Using dimethyl sulfoxide as the solvent removes difficulties associated with metal ion hydrolysis. Since concentrations of ionic species could be kept quite low by using this technique ($\lesssim 10^{-4}$ M), the experiments were carried out with no added electrolyte.[18] Possible complications[8,9] due to the interaction of trivalent lanthanide cryptates with anions are thus avoided. Alkaline earth cryptate formation was also studied by the same technique in $(CH_3)_2SO$ both as a test of the general applicability of the method and as an additional probe of the effect of $(CH_3)_2SO$ on cryptate formation.

Experimental Section

The lanthanide salts ($PrCl_3{\cdot}6H_2O$, $NdCl_3{\cdot}6H_2O$, $GdCl_3{\cdot}6H_2O$, $HoCl_3{\cdot}6H_2O$, and $YbCl_3{\cdot}6H_2O$) (Alfa) and group 2A salts ($CaCl_2{\cdot}2H_2O$, $SrCl_2{\cdot}6H_2O$, and $BaCl_2{\cdot}2H_2O$) (Fisher) were treated in vacuo over P_2O_5 for 24 h to remove excess water. $(CH_3)_2SO$ (Eastman) was distilled over CaH_2 under reduced pressure. Stock solutions of the metal ions in $(CH_3)_2SO$ were standardized by the ion-exchange technique.[19] Thus, 20 mL of solution was passed through a 2 cm × 10 cm column of Dowex 50 in the H^+ form, an approximately 50% aqueous medium being maintained by simultaneously introducing deionized water. The column was washed with 7 × 10 mL of deionized water, and the combined eluates were titrated with standard base to a phenolphthalein end point.

Murexide and $(CH_3)_4NCl$ (Fisher) and the three cryptands (222, 221, and 211) (PCR, Inc.) were dried over P_2O_5 in vacuo and used without further purification. Cryptand solutions in $(CH_3)_2SO$ were stored in the dark in amber bottles and used no more than 3 days after preparation. Murexide solutions were used immediately after

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(18) Supporting electrolytes are often used in order to maintain constant activity coefficients of reactant ions in solution. In the dilute solutions employed in this work, the Debye-Hückel limiting law can be applied to calculate $\gamma_\pm$. With appropriate solvent parameters for $(CH_3)_2SO$, $\gamma_\pm = 0.87 \pm 0.06$ for the triunivalent systems considered over the range of ionic concentrations employed. This variation is considerably less than the experimental errors generally encountered in the determination of stability constants by the technique (see also ref 17).

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Table I. Stability Constants[a] for Murexide and Cryptate Complexes of Some Group 2A and Lanthanide Ions in $(CH_3)_2SO$ at 25 °C

cation	log *K* murexide	222	221	211
Ca^{2+}	4.57 ± 0.05	1.91 ± 0.05	3.29 ± 0.03	⩽2
Sr^{2+}	4.31 ± 0.04	4.77 ± 0.17	5.41 ± 0.32	⩽2
Sr^{2+} [b]	3.93 ± 0.04		5.11 ± 0.37	
Ba^{2+}	3.89 ± 0.06	5.13 ± 0.46	2.99 ± 0.18	⩽2
Pr^{3+}	5.45 ± 0.08	3.22 ± 0.07	3.47 ± 0.07	3.86 ± 0.05
Nd^{3+}	5.50 ± 0.13	3.26 ± 0.14	3.01 ± 0.31	3.97 ± 0.14
Gd^{3+}	5.53 ± 0.09	3.45 ± 0.11	3.26 ± 0.09	3.87 ± 0.14
Ho^{3+}	5.73 ± 0.12	3.47 ± 0.15	3.11 ± 0.23	3.80 ± 0.05
Yb^{3+}	6.20 ± 0.10	4.11 ± 0.11	4.00 ± 0.23	4.43 ± 0.11
Yb^{3+} [b]	5.41 ± 0.06	3.00 ± 0.17		

[a] Error reported as ± standard deviation. [b] Measured with 0.02 M $(CH_3)_4NCl$ added.

preparation. All spectra were taken at 25 °C on a Cary 17 UV-visible spectrophotometer.

Stability constants for the metal ion-murexide complexes were determined by recording the spectra of a series of solutions in which varying amounts of the metal ion were added to fixed amounts of murexide. The absorption maximum for murexide occurs at 535 nm, and the various lanthanide-murexide complex ions have absorption maxima at ca. 485 nm with isosbestic points at ca. 515 cm. The stability constants for the various cryptate complexes were determined by recording the spectra of a series of solutions in which varying amounts of cryptand were added to fixed amounts of metal-murexide complex as described previously.[17] The fact that equilibrium had been attained is supported by the observaton that addition of cryptand produces an immediate spectral change with no further change noted after several hours. While excellent isosbestic points were observed in the experiments with group 2A ions, the spectra involving lanthanide ions were somewhat problematic with deviations from isosbestic behavior at 515 nm of at most ±3%. Concentrations of metal ion and murexide in all experiments were in the range 10^{-5}–10^{-4} M. In the case of the lanthanide ions, a 5–15-fold excess of cryptand was required to effect significant spectral changes. Errors associated with the various reported stability constants are contained in the tables.

The fact that excess water had a negligible effect was determined by addition of 1% water by volume, which produced no appreciable change in the spectra.

Results and Discussion

All of the measured stability constants are presented in Table I. The alkaline earth cryptates show a pattern of metal ion specificity similar to that displayed in water.[3] In contrast, lanthanide cryptate formation shows no appreciable metal ion specificity with, at most, Yb^{3+} (the smallest lanthanide ion studied) forming slightly more stable complexes than the other lanthanide ions. This increase in stability is fairly small when compared with the specificity displayed by the group 2A ions. [211] lanthanide cryptates are somewhat more stable than lanthanide cryptates with the larger ligands, but again, the difference is not dramatic. These results are displayed in Figure 1.

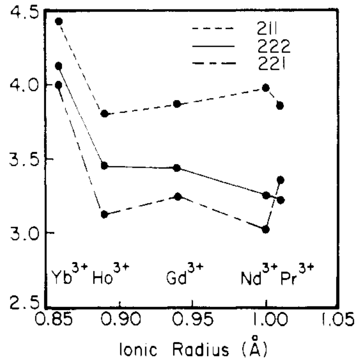

Figure 1. Lanthanide cryptate stability constants in $(CH_3)_2SO$.

Table II. Stability Constants for Cryptate Complexes in Water at 25 °C

cation	log *K* 222	221	211
Na^{+} [a]	3.9	5.4	3.2
Ca^{2+} [a]	4.4	7.0	2.5
Eu^{3+}	3.3[b]	5.9[b]	
	5.9[c]	6.8[c]	

[a] Reference 3. [b] Reference 9. [c] Reference 13.

The lack of observed metal ion specificity in the case of lanthanide cryptate formation supports the previous results of a pH titration study[13] in water and is not in accord with electrochemical work[9] showing specificity in one case. Literature data for some examples of cryptate formation in water are collected in Table II. The ions have similar radii.[20] The increase in charge for ions of comparable radius is generally reflected in higher stability constants for cryptate formation. Hence, one would expect comparable or higher stability constants for Eu^{3+} cryptates compared with Ca^{2+} cryptates. The pH titration data[13] support this contention, and our results in $(CH_3)_2SO$ are in accord with this idea.[21]

There are at least two factors that may account for the lack of specificity in lanthanide cryptate formation. First, the radii decrease by only ca. 0.2Å from Pr^{3+} ($4f^2$) to Yb^{3+} ($4f^{13}$). This is much less than the differences in radii among the ions of groups 1A and 2A. Second, the solvent may specifically interact with the cryptate complex. In some cases (notably $Li^+\subset 211$) the encapsulated ion is effectively shielded from solvent. This is shown by solvent-independent ^7Li chemical shifts while $Li^+\subset 221$ and $Li^+\subset 222$ show solvent-dependent chemical shifts.[22] Thermodynamic studies[23] have also shown that the enthalpy of transfer of a cryptate from one solvent to another is dependent on the nature of the encapsulated ion. Further thermodynamic studies[24] show considerable interaction of divalent cryptates with solvent. Extension of these ideas to lanthanide ions suggests that because of their higher charge and higher coordination number[25,26] lanthanide cryptates may interact significantly with solvent.

Stability constants for cryptate formation in $(CH_3)_2SO$ for both alkaline earth ions and lanthanide ions are less than such constants in water by 2 orders of magnitude or more. While this is in contrast to results for alkali metal cryptates,[24] it is consistent with results on the complexation of transition[24,27,28] and heavy-metal[28] cations. In order to determine whether

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(20) Effective ionic radii for coordination number 6: Na^+, 1.02 Å; Ca^{2+}, 1.00 Å; Eu^{3+} 0.95 Å (Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751).

(21) A recent study (Anderegg, G. *Helv. Chim. Acta* **1981**, *64*, 1790) shows $Ce^{3+}\subset 222$ (log *K* = 8.4) to be less stable than $La^{3+}\subset 222$ (log *K* = 9.4) in 95:5 methanol-water. Attempts to measure stability constants for other lanthanide ions and other cryptands were unsuccessful due to metal ion hydrolysis. The relatively large values of the measured constants are consistent with cryptate formation in methanol and methanol-water solvents.[2,24] Since results are reported only for two ions at the beginning of the lanthanide series, it is not yet clear whether any significant metal ion specificity exists in this solvent.

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added water has any effect on the results, up to 1% water by volume was added without causing any significant spectral changes. This is in accord with results of alkali metal cryptate stability constant determinations,[24] although a marked kinetic effect of added water was noted[7] in the dissociation of Cu^{2+}-$\subset$222 in $(CH_3)_2SO$.

The use of $(CH_3)_2SO$ as a solvent removes complications due to lanthanide ion hydrolysis and the usual acid–base chemistry of the cryptands. The absence of a supporting electrolyte removes to some extent problems associated with the interaction of anions with lanthanide cryptate complexes.[8,9] To examine the effect of added electrolyte in these systems, the most stable alkaline earth cryptate ($Sr^{2+}\subset$221) and one of the most stable lanthanide cryptates ($Yb^{3+}\subset$222) were examined in the presence of added electrolyte (0.02 M $(CH_3)_4NCl$).[29] The Sr^{2+}–murexide and Yb^{3+}–murexide complexes have lower stability constants in the presence of added electrolyte. This result is not unexpected since the reaction is an ion association. However, while the formation of $Sr^{2+}\subset$221 is unaffected by added electrolyte within the limits of experimental error, $Yb^{3+}\subset$222 shows a marked decrease in stability. This is a striking result, and the reason for it is certainly not yet clear. It is possible that chloride ion interacts with lanthanide ions and/or lanthanide cryptates. Electrochemical results[8,9] first suggested the idea of the interaction of small anions in solution with lanthanide cryptates, but such effects were observed for F^- and OH^-, with only small or negligible effects being observed with Cl^-. However, further support for the association of anions with encapsulated lanthanide ions is found in the structures[10,12] of NO_3^- and ClO_4^- salts of lanthanide cryptates, which show direct anion coordination to the metal ion. This is not surprising in itself since the lanthanides display coordination numbers up to 9 with simple unidentate ligands.[25,26] Anion coordination to lanthanide cryptates in solution cannot be general, however, as conductance measurements in CH_3CN show $Eu(ClO_4)_3$ to behave as a 2:1 electrolyte[27] while $(Eu^{3+}\subset 222)(ClO_4)_3$ behaves as a 3:1 electrolyte.[12] X-ray diffraction studies on saturated aqueous lanthanide chloride solutions[26] show no significant inner-sphere chloride, although the authors do point out that experiments were never carried out with an excess of Cl^-. Crystal structures of hydrated lanthanide chloride salts frequently show inner-sphere chloride.[30] The above results from the recent literature show no clear general pattern of behavior concerning the interaction of small anions with lanthanides or lanthanide cryptates. They do support the contention that such interactions are possible, and we suggest that this is responsible for the observed dependence of the $Yb^{3+}\subset$222 stability constant on ionic strength.[31]

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(29) This is almost the limit of solubility of $(CH_3)_4NCl$ in $(CH_3)_2SO$.

(30) A discussion of solid-state structures is in ref 26.

(31) ^{35}Cl NMR studies concerning Cl^- interaction with K^+–18C6 have recently been reported (Sugawara, T.; Ydasaka, M.; Yokoyama, Y.; Fujiyama, T.; Iwamura, H. *J. Phys. Chem.* **1982**, *86*, 2705). An interaction of Cl^- with K^+ incorporated in the crown ether is reported in aqueous solution.

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Stability of Silver(I) Complexes of *N*-Methyl-Substituted 4-Methyldiethylenetriamines in Aqueous Solution

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With use of potentiometric pH and pAg measurements the stability constants and the stoichiometric composition of the Ag(I) complexes with some *N*-methyl-substituted 4-methyldiethylenetriamines in aqueous solution in a medium of ionic strength 1.3 and at a temperature of 25 °C have been determined. It is found that, besides mononuclear complexes, polynuclear and protonated complexes are formed. There is evidence for the formation of hydroxo complexes. The values of the stability constants are discussed in terms of possible structures. The mean amounts of complexed Ag^+, H^+ or OH^-, and L are calculated, by using pH and pAg data and without making any assumption about the stoichiometric composition of the formed complexes.

Introduction

Much work is done[1] on the complexation of Ag(I) with primary and secondary monoamines, in contrast to the quantity of work done on tertiary aliphatic monoamines and polyamines. The latter has something to do with the fact that the complex formation between Ag(I) and polyamines is rather intricate as has been demonstrated by studies performed on the complex formation between Ag(I) and some primary diamines.[2-8] Indeed it has been found that the presence of polynuclear, protonated, and even hydroxo complexes must be taken into account. On the other hand, there exist a great deal of papers where the experimental data of the formation of Ag(I) complexes with polyamines are treated as if the complex formation is purely mononuclear. Nowadays a lot of computer programs are available that can handle complicated systems, and besides, with use of automated or half-automated apparatus, a greater number of experimental data, covering an extended concentration range, can be obtained in an acceptable time. Moreover the calculation and the concentration of free ligand[9] and the complexity sum[10] *S* makes a more accurate analysis of the experimental data possible.

In this investigation the Ag(I) complexes of the following ligands are studied: 1,4-dimethyldiethylenetriamine (STP), 1,4,7-trimethyldiethylenetriamine (STS), 1,1,4-trimethyldiethylenetriamine (TTP), and 1,1,4,7,7-pentamethyldiethylenetriamine (TTT). The shorthand rotations given in

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