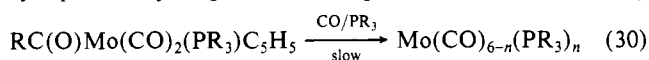


phosphine we found (under 1 atm of CO) slow cleavage of the cyclopentadienyl ring as shown in eq 30. The increased stability



of  $\text{RC(O)Mo(CO)}_2(\text{L})\text{C}_5\text{H}_5$  complexes ( $\text{L} = \text{PR}_3 > \text{L} = \text{CO}$ ) is twofold: They are thermodynamically more stable to decarbonylation in the absence of CO. In addition, they are protected by kinetic barriers from further reaction with  $\text{CO/PR}_3$ . Nevertheless,  $\text{Mo(CO)}_{6-n}(\text{PR}_3)_n$  is a thermodynamic sink for these systems and it is a dominant factor in determining the catalytic chemistry in molybdenum.

### Conclusion

The enthalpy of carbonyl insertion depends on both the alkyl and phosphine substituents on molybdenum. Reaction of the Mo-Et complex is on average 2.8 kcal/mol more exothermic than that of the Mo-Me complex due to the weaker Mo-Et bond. The enthalpy of the Mo-Me reaction is close to that predicted on the assumption that the Mo-Me and Mo-C(O)CH<sub>3</sub> bonds are similar in strength. For both the ethyl and methyl complexes more basic phosphines favor carbonyl insertion. This is interpreted in terms of preferential stabilization of the Mo-acyl bond through resonance delocalization. The range of influence of the phosphine is only 2 kcal/mol, but this is important since the entropy of carbonyl insertion is unfavorable and nearly cancels the favorable enthalpy of reaction. Any small variation in the enthalpy of reaction could have a pronounced effect on the position of the alkyl/acyl equilibrium.

The phosphine-promoted carbonyl insertion shows a wider range of behavior as a function of phosphine ligand, since this reaction

incorporates both CO displacement (by  $\text{PR}_3$ ) and CO insertion. A range of about 6 kcal/mol exists, reflecting primarily the greater difference in Mo- $\text{PR}_3$  bond strengths. These reactions are generally more favorable than CO insertion. Only in the case of the  $\text{PPh}_3$  complex, which has a Mo- $\text{PPh}_3$  bond weaker than a Mo-CO bond, is the reaction less favored than the catalytic insertion. The choice of incoming ligand and alkyl group can span about 10 kcal/mol for  $\text{CO/MeMo(CO)}_2(\text{P(OMe)}_3)_2\text{C}_5\text{H}_5$  (-12.8 kcal/mol) to  $\text{PMe}_3/\text{EtMo(CO)}_3\text{C}_5\text{H}_5$  (-22.6 kcal/mol). Coupled with entropy estimates, these measurements can be used as a guide in predicting equilibrium constants for ligand-promoted carbonyl insertion.

Due to its weaker donor ability relative to that for phosphine ligands, the simple acyl complexes  $\text{RC(O)Mo(CO)}_3\text{C}_5\text{H}_5$  are predicted to have marginal thermodynamic stability with regard to decarbonylation. Attempts to prepare  $\text{EtC(O)Mo(CO)}_3\text{C}_5\text{H}_5$  under mild conditions led to facile cleavage of the  $\text{EtC(O)C}_5\text{H}_5$  group and production of  $\text{Mo(CO)}_6$ , which is a "thermodynamic sink" under these conditions. Similar migrations from the metal to the coordinated cyclopentadienyl ring occur under more forcing conditions for related compounds. Extension of the thermochemical methods discussed here to other systems as well as additional kinetic studies are in progress.

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**Registry No.**  $\text{HMo(CO)}_3\text{C}_5\text{H}_5$ , 12176-06-6;  $\text{MeMo(CO)}_3\text{C}_5\text{H}_5$ , 12082-25-6;  $\text{EtMo(CO)}_3\text{C}_5\text{H}_5$ , 12083-68-0;  $\text{PMe}_3$ , 594-09-2;  $\text{PBU}_3$ , 998-40-3;  $\text{P(OMe)}_3$ , 121-45-9;  $\text{PMe}_2\text{Ph}$ , 672-66-2;  $\text{PMePh}_2$ , 1486-28-8;  $\text{PPh}_3$ , 603-35-0.

Contribution from the Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland, and Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, West Germany

## Kinetics and Equilibria of $\text{Ag}^+$ and $\text{Pb}^{2+}$ Cryptates in Dimethyl Sulfoxide

B. G. Cox,\*† J. Garcia-Rosas,† H. Schneider,\*† and Ng. van Truong†

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Rates and equilibria of complex formation between  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  and several cryptands have been investigated in dimethyl sulfoxide. Both  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  complexes show considerably enhanced stabilities compared with those formed by alkali-metal and alkaline-earth-metal cations of similar size, attributable to additional covalent interactions in the complexes. For  $\text{Ag}^+$  complexes, the higher stabilities are reflected primarily in lower dissociation rate constants, whereas for  $\text{Pb}^{2+}$  cryptates, the formation rate constants are considerably higher than those of corresponding alkaline-earth cryptates and the dissociation rate constants are very similar. Implications of these results for transition-state structures and interactions are discussed.

### Introduction

The ability of diaza polyoxa macrobicyclic or cryptand (Cry)<sup>1</sup> ligands to form very stable and selective complexes (cryptates) with alkali-metal and alkaline-earth-metal cations is well documented. Extensive studies of both the rates and equilibria of complexation reactions have appeared in recent years.<sup>2-5</sup>

Much less is known about cryptate complexes of transition-metal and heavy-metal cations, especially their kinetic properties, which have received almost no attention. Stability constants of  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Pb}^{2+}$  complexes in several solvents are available from the work of Anderegg<sup>6</sup> and in particular Arnaud-Neu, Schwing-Weill, and co-workers.<sup>7,8</sup> An extensive set of  $\text{Ag}^+$  cryptate stabilities in different solvents has also been reported, in conjunction with its use as an indicator ion in stability constant determinations for complexes of other cations.<sup>4,5</sup> Kinetic measurements on the other hand are limited to silver(I) complexes of cryptands and diaza polyethers in acetonitrile-water mixtures,<sup>9</sup> copper(II) complexes of cryptand (2,2,1) in dimethyl sulfoxide,<sup>10</sup>

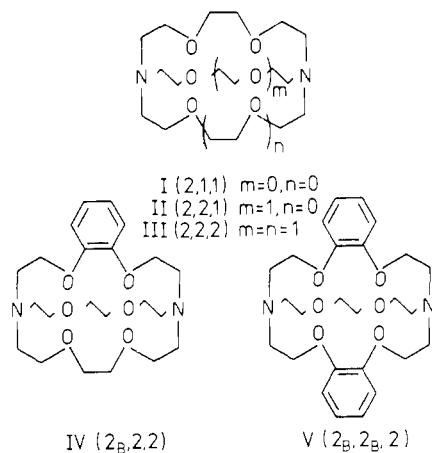
and lead(II) complexation by cryptand (2,1,1) in methanol.<sup>11</sup>

In this paper we report on the kinetics and stabilities of complex formation between silver(I) and lead(II) with a series of five cryptand ligands (I-V) in dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ). Both cations form an extensive range of very stable complexes<sup>12,13</sup> with

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\* University of Stirling.

† Max-Planck-Institut für Biophysikalische Chemie.

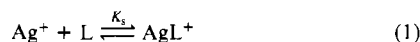


a variety of different ligands that often exhibit a considerable degree of covalency in the bonding. In keeping with this, cryptate complexes of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  are significantly more stable than those of alkali-metal and alkaline-earth-metal cations of similar ionic radii ( $\text{Na}^+/\text{K}^+$  and  $\text{Sr}^{2+}$ , respectively).<sup>14</sup> It is therefore of some interest to investigate the kinetics and equilibria of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  cryptates and to compare the results with those obtained for the more commonly studied alkali-metal and alkaline-earth-metal complexes. Dimethyl sulfoxide was chosen as a convenient solvent in which the complexes are sufficiently labile to enable measurements over a range of ligands.

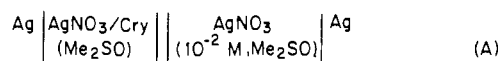
#### Experimental Section and Results

**Materials.** Cryptands (I–V) were used as purchased (Merck). Dimethyl sulfoxide was dried and purified by distillation under reduced pressure from calcium hydride.  $\text{AgClO}_4$ ,  $\text{AgNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$ , methanesulfonic acid, dichloroacetic acid, and tetraethylammonium perchlorate were the same as used previously.<sup>4,5,9–11</sup>

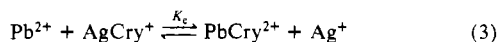
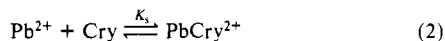
**Stability Constants.** The stability constants  $K_s$  for complexation of  $\text{Ag}^+$  with the various ligands (eq 1) were determined by pAg potentiometric titrations for which two silver electrodes were used, one in the reaction vessel and the other in the reference compartment (cell A). The



metric titrations for which two silver electrodes were used, one in the reaction vessel and the other in the reference compartment (cell A). The



two half-cells were separated by a salt bridge containing 0.1 M tetraethylammonium perchlorate in dimethyl sulfoxide. The detailed procedure has been described previously.<sup>15</sup> The stability constants of the lead cryptates (eq 2) were determined by the disproportionation reaction of  $\text{Pb}^{2+}$  with the corresponding  $\text{Ag}^+$  complex (eq 3), using cell A to monitor



the equilibrium concentration of  $\text{Ag}^+$ .<sup>15</sup> Total metal ion concentrations were  $(1-9) \times 10^{-3}$  M ( $[\text{Ag}^+] = \text{ca. } 2 \times 10^{-4}$  M), and ligand concentrations were in the range  $4 \times 10^{-4}$ – $2 \times 10^{-3}$  M. It was assumed that equilibrium 3 is independent of ionic strength at the relatively low concentrations used, as reactants and products have the same charge. The activity coefficients used in calculating silver ion concentrations from measured cell potentials were determined from the Davies equation, as described previously.<sup>4b</sup> The stability constants obtained from these measurements and previous studies<sup>4,5,8</sup> are listed in Table I.

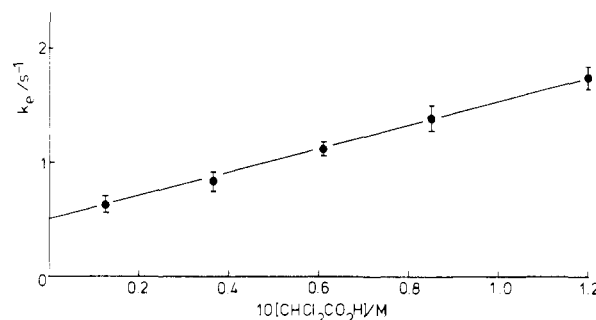
**Rate Constants.** The rate constants for the complexation reactions were determined by several techniques, involving conductometric, potentiometric, and optical monitoring of the reactions.

(i) **Acid Scavenging.** The dissociation rate constants may be determined by mixing cryptate solutions with an excess of acid, resulting in protonation of the cryptand and liberation of the cation.<sup>4a</sup> The pseudo-

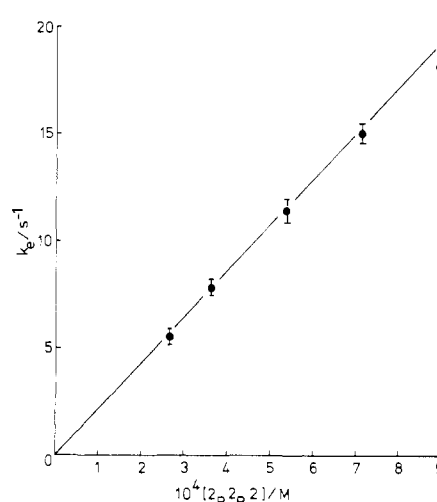
**Table I.** Stability Constants of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  Cryptates in Dimethyl Sulfoxide<sup>a</sup> at 25 °C

cation	$\log K_s$				
	(2,1,1)	(2,2,1)	(2,2,2)	(2 <sub>B</sub> ,2,2)	(2 <sub>B</sub> ,2 <sub>B</sub> ,2)
$\text{Ag}^+$	6.17	9.55	7.27	6.95 <sup>c</sup>	6.75 <sup>c</sup>
$\text{Pb}^{2+}$	3.68 <sup>d</sup>	(9.61) <sup>b</sup>	(7.30) <sup>b</sup>	6.30	5.40 ( $\pm 0.15$ )

<sup>a</sup>  $\log K_s \pm 0.1$ . <sup>b</sup> Reference 4. <sup>c</sup> Reference 5. <sup>d</sup> Reference 8.



**Figure 1.** Dissociation of  $\text{Pb}(2,1,1)^{2+}$  in the presence of dichloroacetic acid in dimethyl sulfoxide at 25 °C.



**Figure 2.** Rate of reaction between  $\text{Pb}^{2+}$  and (2<sub>B</sub>,2<sub>B</sub>,2) in dimethyl sulfoxide at 25 °C.

first-order rate constant is linearly dependent upon the average concentration of the acid (HA) during reaction<sup>4a,16–18</sup> as in eq 4, in which  $k_d$  is

$$k_c = k_d + k_{\text{HA}}[\text{HA}] \quad (4)$$

the dissociation rate constant of the cryptate.  $k_d$  values then may be obtained by extrapolation to zero [HA] as illustrated in Figure 1. These may be combined with the measured stability constants to give rate constants for complex formation  $k_f$  ( $k_f = K_s k_d$ ). This method was used for the following cryptates:  $\text{Pb}(2,1,1)^{2+}$ ,  $\text{Pb}(2,2,1)^{2+}$ ,  $\text{Pb}(2,2,2)^{2+}$ ,  $\text{Pb}(2,2,2)^{2+}$ ,  $\text{Pb}(2,2,2)^{2+}$ ,  $\text{Ag}(2,1,1)^+$ ,  $\text{Ag}(2,2,2)^+$ ,  $\text{Ag}(2,2,2)^+$ ,  $\text{Ag}(2,2,2)^+$ . The acid used was either methanesulfonic acid (for  $\text{Pb}(2,2,1)^{2+}$ ) or dichloroacetic acid, with [HA] in the range  $3 \times 10^{-3}$ – $2.5 \times 10^{-1}$  M; cryptand concentrations were ca.  $(2-4) \times 10^{-4}$  M, with metal ion concentrations slightly in excess of the cryptands. Methanesulfonic acid is considerably stronger than dichloroacetic acid in  $\text{Me}_2\text{SO}$ , but as both acids are only partially dissociated, the concentration of ions, and hence the conductance, increases when the cryptands are protonated.<sup>4a,10</sup> Reactions of  $\text{Pb}(2,2,1)^{2+}$  were monitored optically at 262.5 nm, and the remainder conductometrically. The  $k_d$  value for  $\text{Pb}(2,2,1)^{2+}$ , the most stable of the lead cryptates, was determined independently with  $\text{Ag}^+$  as a scavenger, the reaction also being monitored optically. The  $k_d$  values determined by the two methods were in good agreement. Dissociation

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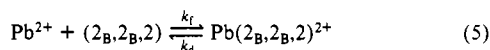
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rates for Pb<sup>2+</sup> cryptates, except those for Pb(2,1,1)<sup>2+</sup> and Pb(2,2,1)<sup>2+</sup>, were independent of acid concentration in the range studied, whereas those for Ag<sup>+</sup> cryptates except for Ag(2<sub>B</sub>,2<sub>B</sub>,2)<sup>+</sup> were all subject to acid catalysis.

(ii) **Direct Complexation.** The rate constant for formation of Pb(2<sub>B</sub>,2<sub>B</sub>,2)<sup>2+</sup> was obtained from a direct determination of the rate of approach to equilibrium as in eq 5. The reactions were monitored con-



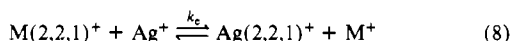
ductometrically by using a stopped-flow apparatus. Solutions of Pb<sup>2+</sup> (2–5) × 10<sup>-5</sup> M were mixed with an excess of (2<sub>B</sub>,2<sub>B</sub>,2) (2.7–9.1) × 10<sup>-4</sup> M, and under these conditions the observed rate law was of the form shown in eq 6 and 7. The *k<sub>f</sub>* value was obtained from a plot of *k<sub>e</sub>* vs.

$$-d([\text{Pb}(2_{\text{B}},2_{\text{B}},2)^{2+}]_{\infty} - [\text{Pb}(2_{\text{B}},2_{\text{B}},2)^{2+}]) / dt = k_{\text{c}}([\text{Pb}(2_{\text{B}},2_{\text{B}},2)^{2+}]_{\infty} - [\text{Pb}(2_{\text{B}},2_{\text{B}},2)^{2+}]) \quad (6)$$

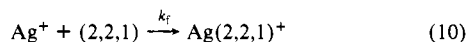
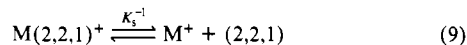
$$k_{\text{e}} = k_{\text{f}}[(2_{\text{B}},2_{\text{B}},2)] + k_{\text{d}} \quad (7)$$

[(2<sub>B</sub>,2<sub>B</sub>,2)] as shown in Figure 2. The low intercept meant that *k<sub>d</sub>* could not be determined from these measurements, but *K<sub>s</sub>* obtained from *k<sub>f</sub>* as determined via eq 7 and *k<sub>d</sub>* (eq 4) (*K<sub>s</sub>* = *k<sub>f</sub>*/*k<sub>d</sub>*) agreed within experimental error with that measured potentiometrically.

(iii) **Potentiometric Measurements.** The rate constant for formation of Ag(2,2,1)<sup>+</sup>, the most stable of the Ag<sup>+</sup> cryptates, was determined by monitoring potentiometrically the rate of approach to equilibrium of reaction 8 in which M = Na<sup>+</sup> or K<sup>+</sup>. An electrochemical cell similar to



that shown in (A) for the determination of stability constants was used. Reactions were carried out with initial [Ag<sup>+</sup>] of ca. (2–4) × 10<sup>-4</sup> M and excess [M<sup>+</sup>] (1 × 10<sup>-3</sup>–4 × 10<sup>-2</sup>) and [MCry<sup>+</sup>] ((1–2) × 10<sup>-3</sup> M). The high stability of Ag(2,2,1)<sup>+</sup> means that the reverse reaction is negligible for the major part of the reaction, which may be represented by eq 9 and 10. This leads to the integrated rate equation shown in eq 11 and 12.



$$\ln [\text{Ag}^+] = -k_{\text{e}}t + \ln [\text{Ag}^+]_0 \quad (11)$$

$$k_{\text{e}} = k_{\text{f}}[\text{M}(2,2,1)^+] / K_{\text{s}}[\text{M}^+] \quad (12)$$

It can then be readily shown that eq 11 gives eq 13, in which *E* is the potential of cell A. Thus the value of *k<sub>e</sub>* may be obtained from the slope of the linear plot of *E* vs. time, and hence *k<sub>f</sub>* from eq 12. The basis of this method was earlier established for monitoring the irreversible halogenation of various organic substrates by Bell and co-workers.<sup>19</sup> In practice for the present system, linear plots according to eq 13 were obtained for the major part of the reaction (99% in terms of [Ag<sup>+</sup>], >100 mV in *E*) but became curved when [Ag<sup>+</sup>] was sufficiently low that the reverse reaction became comparable to the formation reaction. The *k<sub>f</sub>* value obtained was independent of whether Na<sup>+</sup> or K<sup>+</sup> was used as M<sup>+</sup> in eq 8. It was again assumed that, at the ionic strengths used, the rates and equilibria represented in eq 8–10 are independent of ionic strength; no change in charge occurs in either the overall equilibrium (eq 8) or the individual steps (eq 9 and 10).

The rate constants obtained by the various methods are listed in Table II.

## Discussion

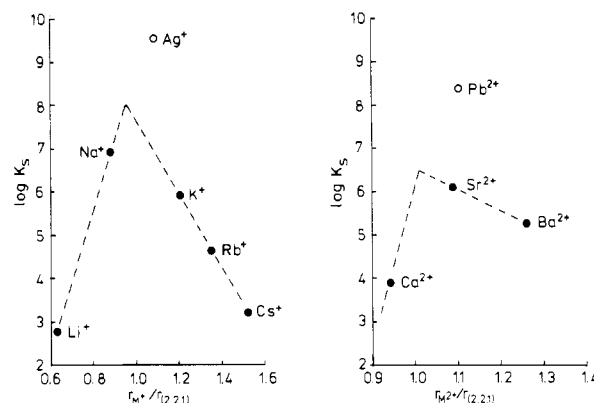
A characteristic of cryptand ligands in their complexation reactions with alkali-metal and alkaline-earth-metal cations is their ability to distinguish sharply between the various cations on the basis of size.<sup>1</sup> For a given ligand within, for example, the series of alkali-metal cations, the most stable complex is formed with the cation whose size most closely matches that of the ligand cavity: Li<sup>+</sup> for (2,1,1), Na<sup>+</sup> for (2,2,1), K<sup>+</sup> for (2,2,2).

Such a simple relationship is not expected to extend directly to cations such as Ag<sup>+</sup> and Pb<sup>2+</sup>, which are known to form stable complexes involving at least partially covalent interactions with many ligands.<sup>12–14</sup> Ag<sup>+</sup> complexes strongly with ligands containing O, N, and S donor atoms,<sup>13</sup> especially nitrogen donors, and Pb<sup>2+</sup>, although it forms fewer complexes exhibiting specifically Pb<sup>2+</sup>...N

**Table II.** Rates of Formation and Dissociation of Ag<sup>+</sup> and Pb<sup>2+</sup> Cryptates in Dimethyl Sulfoxide at 25 °C

cation	cry	<i>k<sub>f</sub></i> <sup>a</sup> /M <sup>-1</sup> s <sup>-1</sup>	<i>k<sub>d</sub></i> <sup>b</sup> /s <sup>-1</sup>
Ag <sup>+</sup>	(2,1,1)	5.2 × 10 <sup>5</sup>	0.36
	(2,2,1)	2.0 (±0.5) × 10 <sup>6</sup> <sup>c</sup>	5.6 × 10 <sup>-4</sup>
	(2,2,2)	2.9 × 10 <sup>6</sup>	0.10
	(2 <sub>B</sub> ,2,2)	1.4 × 10 <sup>6</sup>	0.15
	(2 <sub>B</sub> ,2 <sub>B</sub> ,2)	1.7 × 10 <sup>6</sup>	0.30
Pb <sup>2+</sup>	(2,1,1)	2.4 × 10 <sup>3</sup>	0.50
	(2,2,1)	1.5 × 10 <sup>5</sup>	6.5 × 10 <sup>-4</sup> <sup>d</sup>
	(2,2,2)	2.1 × 10 <sup>5</sup>	1.25 × 10 <sup>-2</sup>
	(2 <sub>B</sub> ,2,2)	8.0 × 10 <sup>4</sup>	4.0 × 10 <sup>-2</sup>
	(2 <sub>B</sub> ,2 <sub>B</sub> ,2)	2.2 × 10 <sup>4</sup> <sup>e,f</sup>	0.13 <sup>f</sup>

<sup>a</sup> Values from *k<sub>f</sub>* = *K<sub>s</sub>**k<sub>d</sub>* unless otherwise stated; ±20%. <sup>b</sup> ±10%. <sup>c</sup> *k<sub>f</sub>* obtained by using Ag<sup>+</sup> potentiometry; see text. <sup>d</sup> Cf. 6.0 (±0.5) × 10<sup>-4</sup> obtained by using Ag<sup>+</sup> as scavenger. <sup>e</sup> Direct measurement of reaction between Pb<sup>2+</sup> and Cry. <sup>f</sup> log (*k<sub>f</sub>*/*k<sub>d</sub>*) = 5.23 (±0.11); cf. log *K<sub>s</sub>* = 5.4 (±0.15) (Table I).



**Figure 3.** Stability constants of (2,2,1) cryptates of alkali-metal ions, alkaline-earth-metal ions, Ag<sup>+</sup>, and Pb<sup>2+</sup> in dimethyl sulfoxide at 25 °C.

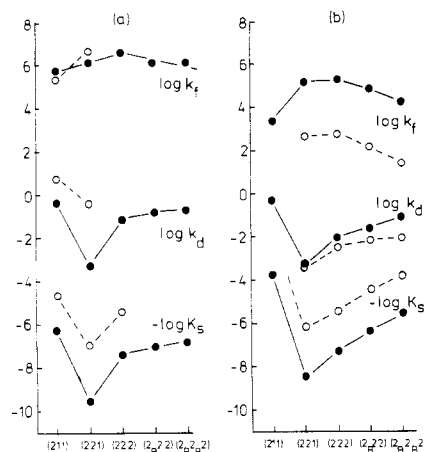
bonds, interacts very strongly with O and S donor atoms.<sup>12</sup>

The influence of these specific interactions may be seen in the results illustrated in Figure 3. Here the stability constants of Ag<sup>+</sup> and Pb<sup>2+</sup> (2,2,1) cryptates are compared with those of the alkali-metal and alkaline-earth-metal (2,2,1) cryptates, respectively, plotted against the relative size of the cation and ligand cavity. The *r<sub>M+</sub>* values used are an average of the cationic Pauling and Goldschmidt radii,<sup>14</sup> and *r<sub>(2,2,1)</sub>* = 1.1 Å.<sup>1</sup> The stability constants for the GpI and GpII cations show clear maxima in the vicinity of *r<sub>M+</sub>*/*r<sub>(2,2,1)</sub>* = 1, but *K<sub>s</sub>* values for Ag<sup>+</sup> and Pb<sup>2+</sup> cations are some 2.5 orders of magnitude higher than expected on the basis of these correlations. Similar conclusions may be drawn from results obtained in other solvents, although in poorer cation-solvating media such as methanol and propylene carbonate the differences are even larger. For example, in methanol<sup>15,20,21</sup> log *K<sub>s</sub>*(Ag(2,2,1)<sup>+</sup>) – log *K<sub>s</sub>*(Na(2,2,1)<sup>+</sup>) = 5.0 and log *K<sub>s</sub>*(Pb(2,2,1)<sup>2+</sup>) – log *K<sub>s</sub>*(Sr(2,2,1)<sup>2+</sup>) = 4.1.

However, if we consider the variation of stability constant with ligand structure, it is clear that size-dependent interactions are also important for Ag<sup>+</sup> and Pb<sup>2+</sup> cryptates. This may be seen from the results shown in the lower part of Figure 4, in which results for Na<sup>+</sup> and Ag<sup>+</sup> and for Sr<sup>2+</sup> and Pb<sup>2+</sup> are compared. There is a close parallelism between the behaviors of the corresponding pairs of cations. In particular, the occurrence of stability constant maxima for the (2,2,1) complexes of both Ag<sup>+</sup> and Pb<sup>2+</sup> is a strong indicator of the influence of ligand size, as all of the (2,2,2) ligands form less stable complexes despite having an extra donor atom. The lower stability of the benzo-substituted (2,2,2) ligands relative to that of (2,2,2) may also be attributed to a decrease in ligand flexibility and a reduction in the electronegativity of the oxygen

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**Figure 4.** Stability constants and rate constants for formation and dissociation of (a)  $\text{Ag}^+$  (●) and  $\text{Na}^+$  (○) and (b)  $\text{Pb}^{2+}$  (●) and  $\text{Sr}^{2+}$  (○) cryptates in dimethyl sulfoxide at 25 °C.

atoms joined to the benzene ring.

The kinetic behavior of the  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  cryptates is illustrated in Figure 4, which also includes some results for  $\text{Na}^+$  and  $\text{Sr}^{2+}$  cryptates. There is a strong correlation between the variations in stability constants and dissociation rate constants. This has also been observed previously for alkali- and alkaline-earth-metal cryptates in a variety of solvents.<sup>4a,5</sup> The formation rate constants vary over a small range, less than 1 order of magnitude except for the difference between  $\text{Pb}(2,1,1)^{2+}$  and  $\text{Pb}(2,2,1)^{2+}$  ( $\Delta \log k_f = 1.8$ ) and show a maximum for (2,2,2). This can be readily understood in terms of an increase in flexibility and availability of donor atoms from (2,1,1) to (2,2,1) to (2,2,2) and a decrease in ligand flexibility with increasing benzo substitution. The small magnitude of the variation of  $k_f$  and lack of overall correlation with stability constants are in agreement with earlier suggestions<sup>3,4a,5,15</sup> that in the transition state the incoming cation remains outside the ligand cavity. The stability of the transition state is therefore insensitive to the detailed ligand structure, which is crucial in determining the overall stabilities of the complexes.

An interesting difference between the behaviors of  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  cryptates may be seen from the comparisons with corresponding alkali- ( $\text{Na}^+$ ) and alkaline-earth-metal ( $\text{Sr}^{2+}$ ) cryptates in Figure 4. Although the results for  $\text{Na}^+$  cryptates in  $\text{Me}_2\text{SO}$  are somewhat limited, they indicate that the additional stability of  $\text{Ag}^+$  cryptates arises predominantly from a much lower dissociation rate constant compared with that of  $\text{Na}^+$ . The simplest interpretation of this is that the strong specific  $\text{Ag}^+$ -cryptand interactions (especially  $\text{Ag}^+\cdots\text{N}$ ) are largely absent in the transition state, thus leading to low dissociation rate constants, and formation rate constants comparable to those of  $\text{Na}^+$ . However, this is probably an oversimplification, as detailed kinetic studies of  $\text{Ag}^+$

cryptates in acetonitrile-water mixtures<sup>9</sup> suggest that although for the smaller (2,1,1) ligand  $\text{Ag}^+\cdots\text{N}$ (cryptand) interactions are probably absent in the transition state, they play an important role in complexation kinetics for the larger cryptands. The effects would be masked in the present case by the very strong  $\text{Ag}^+\cdots\text{O}=\text{S}(\text{CH}_3)_2$  interactions that must be disrupted in order to form  $\text{Ag}^+\cdots\text{N}$  bonds with the ligand.

The higher stability of lead complexes (Figure 4) with respect to those of  $\text{Sr}^{2+}$  complexes on the other hand shows up mainly as an increased formation rate constant, and indeed the  $k_d$  values for  $\text{Pb}^{2+}$  cryptates are slightly higher than those for  $\text{Sr}^{2+}$ . The  $k_f$  value for  $\text{Pb}(2,2,2)^{2+}$ , for example, is larger than  $k_f(\text{Sr}(2,2,2)^{2+})$  by a factor more than 300 and is within a factor of 10–100 of the  $k_f$  values of alkali-metal cations and  $\text{Ag}^+$ , which has an atomic radius very similar to that of  $\text{Pb}^{2+}$ . Differences on the other hand between alkaline-earth- and alkali-metal cations of similar size are typically 3–4 orders of magnitude. The low  $k_f$  values of alkaline-earth-metal cation cryptates,<sup>5</sup> which in solvents such as  $\text{Me}_2\text{SO}$  are up to 6 orders of magnitude lower than those expected on the basis of a simple Eigen–Wilkins dissociative-interchange ( $I_d$ ) mechanism,<sup>22</sup> may be attributed to a lack of sufficient ligand binding energy in the transition state to compensate fully for the loss of solvation of these highly solvated cations. It is possible that the strong affinity of  $\text{Pb}^{2+}$  for O- (and N-) donor systems is responsible for the lowering of the transition-state energy for  $\text{Pb}^{2+}$  cryptate formation relative to those of the alkaline-earth-metal cations.

Evidence for unusual kinetic behavior in  $\text{Pb}^{2+}$  cryptates was presented earlier in a study of  $\text{Pb}(2,1,1)^{2+}$  in methanol.<sup>11</sup> There it was observed that, on mixing of  $\text{Pb}^{2+}$  and (2,1,1), a moderately stable complex ( $\log K_s = 3.1$ ) was formed rapidly on the stopped-flow time scale and this then was converted to the more stable final complex ( $\log K_s = 8.2$ ).<sup>20</sup> It was not possible to tell from kinetic measurements whether the initial complex was a reaction intermediate, but its lower stability and rapid formation rate are strongly indicative of an external complex; i.e.,  $\text{Pb}^{2+}$  is outside the ligand cavity. This confirms the ability of  $\text{Pb}^{2+}$  to form quite stable complexes without the stabilization conferred by complexation within a cavity containing appropriately oriented donor atoms. No evidence for a stable intermediate or alternative complex was obtained in this study. In principle, this might have been expected to be observed in the complexation of  $\text{Pb}^{2+}$  with (2<sub>B</sub>,2<sub>B</sub>,2), for which the  $k_f$  value was measured directly. However, in  $\text{Me}_2\text{SO}$  the stabilities of any intermediate should be considerably lower than in methanol so that at the concentrations used ( $[(2_{\text{B}},2_{\text{B}},2)] \leq 9 \times 10^{-4} \text{ M}$ ,  $[\text{Pb}^{2+}] = (2-5) \times 10^{-5} \text{ M}$ ) saturation effects would not occur and only the overall formation rate constant, which may be the product of a rate and equilibrium constant,<sup>11</sup> would be measured.

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