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Hydroxide-Assisted Dissociation of Lead(II) Cryptates

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The dissociation rate constants of two lead cryptates, $Pb(2.2.2)^{2+}$ and $Pb(2.2.1)^{2+}$, in strongly basic solution (pH ≥11) have been measured at 25.0 °C and ionic strength 0.5. The formation constant of the monohydroxide adduct, $Pb(2.2.2)OH^+$, has also been determined. In the presence of excess hydroxide ion, both cryptates are rapidly converted to the monohydroxide adduct ($t_{1/2} \leq$ 4 ms), which subsequently undergoes second-order hydroxide-assisted dissociation with $k_{obsd} = k_{OH}[OH]^2$. The nature of the electrolyte ($LiClO_4$, $NaClO_4$, KCF_3SO_3) has little effect on the values of k_{OH} obtained. In $NaOH/NaClO_4$ medium, the values of k_{OH} are 16.3 ± 0.2 and 2320 ± 50 $M^{-2}\ s^{-1}$ for $Pb(2.2.2)^{2+}$ and $Pb(2.2.1)^{2+}$, respectively, and $K_{PbCOH} = (1.8 \pm 0.2) \times 10^4\ M^{-1}$ for $Pb(2.2.2)^{2+} + OH^- \rightleftarrows Pb(2.2.2)OH^+$.

Introduction

The dissociation kinetics of metal ion complexes of the bicyclic polyether polyamine cryptands, shown in Figure 1, have been studied extensively. The reaction is initiated by mixing the cryptate, $M(Cryp)^{m+}$, with an excess of some scavenger species as shown in eq 1a-e, where the proton, H^+ (or a weak acid, HA),

$$M(Cryp)^{m+} \rightleftarrows M^{m+} + Cryp; \quad k_d,\ k_f \tag{1a}$$

$$H^+ + Cryp \rightarrow HCryp^+; \quad k_p \tag{1b}$$

$$M^{*n+} + Cryp \rightarrow M^*(Cryp)^{n+}; \quad k_M \tag{1c}$$

$$M^{m+} + L^{z-} \rightarrow ML^{m-z}; \quad k_L \tag{1d}$$

$$M^{m+} + aX^{y-} \rightarrow M(X)_a{}^{m-ay}; \quad k_X \tag{1e}$$

or an auxiliary metal ion, M^{*n+}, is used as a scavenger for the free cryptand, Cryp (eq 1b,c). Alternatively, an auxiliary multidentate ligand, L^{z-}, or unidentate anion, X^{y-}, is used as a scavenger for the free metal ion, M^{m+} (eq 1d,e). The most frequently employed methods to study cryptate dissociation kinetics are based on the reactions represented in eq 1a-c.[1-7] In most cases, the observed rate constant shows a first-order dependence on $[H^+]$ (or [HA])

$$k_{obsd} = k_d + k_H[H^+]\ (+\ k_{HA}[HA]) \tag{2}$$

indicating a pathway involving attack by H^+ (or HA) prior to or at the rate-determining step.[1,4,8] Generally, the rate of dissociation is independent of the auxiliary metal ion (eq 1c).[3,5-7] Ligand-ligand-exchange kinetics (eq 1a,d) have not been studied extensively. With alkali-metal and alkaline-earth-metal cryptates in polar solvents, no bimolecular pathway was found involving the scavenger ligand.[6,9,10] However, with heavy-metal-ion cryptates (Ag^+, Pb^{2+}), bimolecular pathways have been observed in some cases.[9,10] Very little work has been reported on the effects of hydroxide ion or other unidentate anions on the dissociation kinetics of cryptates. Gansow, Weaver, and co-workers noted that OH^- and F^- formed stable 1:1 and 2:1 complexes with Eu^{3+} and Yb^{3+} cryptates and that the rates of dissociation increased markedly in the presence of these anions.[3,11] Cox et al. have found that the dissociation reactions of several Ca^{2+} cryptates in methanol are catalyzed by chloride ion.[12] Gresser et al. have found that the activation parameters for the dissociation of $K(2.2.2)^+$ depend on both the concentration and nature (Cl^-, Br^-, I^-/Et_4N^+) of the supporting electrolyte.[8] In a recent study of the reactions of cryptands with Cu(II) in strongly basic media, we found that the dissociation rate of $Cu(2_N.2.2)^{2+}$ had a third-order $[OH^-]$ dependence.[13] Furthermore, we have also found that the rates of ligand-ligand exchange (eq 1a,d) of several Pb^{2+} cryptates appear to have a first-order hydroxide dependence.[14] The current work was carried out in order to obtain a quantitative picture of the role of small anions, such as hydroxide ion, in the dissociation and exchange kinetics of heavy-metal cryptates. The system chosen for study was the dissociation kinetics of lead(II) cryptates in the presence of an excess of alkali-metal hydroxide

$$Pb(Cryp)^{2+} + OH^-_{ex} \xrightarrow[M^+]{k_{obsd}} Pb(OH)_n{}^{2-n} + M(Cryp)^+ \tag{3}$$

where Cryp = 2.2.1 or 2.2.2 and $M^+ = Li^+$, Na^+, or K^+. The system shown in eq 3 was chosen for several reasons. The reactant, $Pb(Cryp)^{2+}$, is readily and quantitatively (≥99.9%) formed at neutral pH. The formation constants for $Pb(OH)_n{}^{2-n}$ are sufficiently large to force the dissociation reaction, eq 3, to completion (≥95%). Unlike those of several other heavy-metal cations (Cd^{2+}, Hg^{2+}), the hydrolysis reactions of aquolead(II) to form $Pb(OH)_n{}^{2-n}$ are very fast relative to the reaction of interest and the product, $Pb(OH)_n{}^{2-n}$ (n = 2, 3), is stable. Finally, the spectral properties of $Pb(Cryp)^{2+}$ and $Pb(OH)_n{}^{2-n}$ are sufficiently different to provide a convenient means to monitor the reaction progress.

Experimental Section

Reagents. Cryptands 2.2.1 and 2.2.2 were obtained from E. Merck and used without further purification. The ligands were dried in a desiccator over P_2O_5 and stock solutions prepared by weight. The cryptand solutions were standardized by spectrophotometric titration with Pb(II).[15] The titration results indicated that the ligand purity was ≥98-99% based on the weight taken. The lead stock solutions were standardized by titration with primary standard EDTA (Aldrich, Gold Label).[16] NaOH and KOH solutions were prepared from low-carbonate samples (Baker). Carbonate-free LiOH solutions were prepared by dilution of a saturated solution of LiOH (Aldrich). A solution of KCF_3SO_3 was prepared by neutralization of standardized HCF_3SO_3 (Aldrich) with sufficient KOH to raise the pH to ~6.0. The HCF_3SO_3 was purified by distillation from

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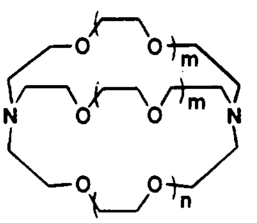

[2.2.1] m = 1, n = 0

[2.2.2] m = 1, n = 1

Figure 1. Structure of cryptands 2.2.1 and 2.2.2.

a mixture of HCF_3SO_3/H_2SO_4. All other compounds used were reagent grade, and all solutions were prepared with freshly boiled doubly distilled water.

Spectral and Kinetic Measurements. All spectra were recorded by using either a Hitachi 100-80 or a Cary 118 spectrophotometer equipped with a thermostated cell holder. Kinetic studies were done by using either a Hitachi 100-80 spectrophotometer or a Durrum D-130 stopped-flow instrument interfaced to a Cromemco Z2-D computer system. The temperature of the observation cell was maintained at 25.0 ± 0.1 °C. All reactions were first order, and the data were treated by standard least-squares techniques.

The reactions were initiated by mixing a solution of the cryptate with an equal volume of hydroxide ion solution. The cryptate solution contained the complex, $[\mathrm{Cryp}] = [\mathrm{Pb}^{2+}] = (4.4\text{–}6.0) \times 10^{-5}$ M, and sufficient electrolyte ($LiClO_4$, $NaClO_4$, or KCF_3SO_3) to adjust the ionic strength to 0.50 M. The hydroxide ion solutions contained the appropriate alkali-metal hydroxide (LiOH, 0.0766–0.486 M; NaOH, 0.0102–0.504 M; KOH, 0.0152–0.506 M) and a sufficient amount of the corresponding electrolyte ($LiClO_4$, $NaClO_4$, KCF_3SO_3) to bring the ionic strength to 0.50 M. The concentrations given for Pb^{2+}, Cryp, and MOH refer to the values before mixing. The pH of the cryptate solutions was adjusted to 6.5 ± 0.1 with the appropriate alkali-metal hydroxide or strong acid. Reactions were monitored at 250 nm. All observed reactions obeyed pseudo-first-order kinetics, and the individual values of k_{obsd} were obtained from a least-squares fit of the data to the expression

$$\ln |A_t - A_\infty| = \ln |A_0 - A_\infty| - k_{\mathrm{obsd}}t$$

where A_t, A_0, and A_∞ are the instantaneous, initial, and final values of the absorbance, respectively, and t is the time in seconds. The value used for A_∞ was the average of 50 points taken after 8 half-lives. $\bar{R}^2$ values for the individual fits were in the range 0.991–0.999. Five to seven replicates were run at each set of conditions and the results averaged to obtain the reported value, k_{obsd}.

Blank experiments were carried out by mixing equal volumes of a solution containing lead ($[\mathrm{Pb}^{2+}] = (4.0\text{–}7.9) \times 10^{-5}$ M, $\mu = 0.50$ M, $NaClO_4$) with a solution of NaOH ($[\mathrm{OH}^-] = (5.0\text{–}50.0) \times 10^{-3}$ M, $\mu = 0.50$ M, $NaClO_4$). The reaction was complete in the mixing time of the stopped-flow instrument (≤4 ms), and the spectrum of the product solution corresponded to that of $\mathrm{Pb(OH)}_n^{2-n}$ (see Figure 2A, spectrum 3).

Results

Formation of the Monohydroxide Adduct. Preliminary kinetic studies with both cryptates indicated the presence of a rapid reaction during the mixing time of the reagents. However, at low $[\mathrm{OH}^-]$ the dissociation reaction of $\mathrm{Pb(2.2.2)}^{2+}$ is slow enough to allow complete spectra to be recorded. Figure 2A shows that an intermediate species is formed when $\mathrm{Pb(2.2.2)}^{2+}$ is mixed with an excess of hydroxide ion. Stopped-flow experiments indicated that the intermediate was formed during the mixing time of the instrument (~4 ms). Figure 2B shows the results of a spectrophotometric titration of a solution of $\mathrm{Pb(2.2.2)}^{2+}$ with $(C_2H_5)_4$NOH. The data are consistent with the formation of a stable monohydroxide adduct

$$\mathrm{Pb(Crypt)}^{2+} + \mathrm{OH}^- \rightleftarrows \mathrm{Pb(Cryp)OH}^+; \quad K_{\mathrm{PbCOH}} \qquad (4)$$

The data were fit to the expression

$$A_i = \left[\frac{\epsilon_{\mathrm{PbC}} + \epsilon_{\mathrm{PbCOH}}K_{\mathrm{PbCOH}}[\mathrm{OH}^-]'}{1 + K_{\mathrm{PbCOH}}[\mathrm{OH}^-]'}\right][\mathrm{Pb(Cryp)}]_{\mathrm{tot}} \qquad (5)$$

where A_i is the measured absorbance, ϵ_{PbC} and $\epsilon_{\mathrm{PbCOH}}$ are the molar absorptivity values of the cryptate and monohydroxide adduct, respectively, $[\mathrm{OH}^-]' = [\mathrm{OH}^-]\gamma_{\mathrm{PbC}}$, and $[\mathrm{Pb(Cryp)}]_{\mathrm{tot}} = [\mathrm{Pb(Cryp)}^{2+}] + [\mathrm{Pb(Cryp)OH}^+]$. The value of γ_{PbC} was calculated at each point by using the Davies equation.[17] A value of $(1.8 \pm 0.2) \times 10^4$ M^{-1} for K_{PbCOH} was obtained by using a nonlinear-least-squares program to fit the data to eq 5. At $[\mathrm{OH}^-]$ levels sufficient to form appreciable amounts of $\mathrm{Pb(2.2.1)OH}^+$, dissociation of the cryptate to $\mathrm{Pb(OH)}_n^{2-n}$ occurred; therefore, a value of K_{PbCOH} (C = 2.2.1) could not be obtained.

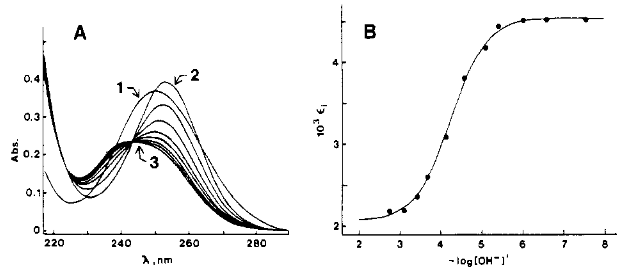

Figure 2. (A) Time scans of the decomposition of $\mathrm{Pb(2.2.2)}^{2+}$ in strongly basic solution ($[\mathrm{Pb(2.2.2)}^{2+}]_{\mathrm{tot}} = 5.5 \times 10^{-5}$ M): (1) $t = 0$ s, pH 7.5, $\mathrm{Pb(2.2.2)}^{2+}$; (2) $t = 20$ s, $[\mathrm{OH}^-] = 5.8 \times 10^{-3}$ M, $\mathrm{Pb(2.2.2)OH}^+$; (3) $t = 3600$ s, $[\mathrm{OH}^-] = 5.8 \times 10^{-3}$ M, $\mathrm{Pb(OH)}_n^{2-n}$. Intermediate spectra were recorded at 80-s intervals. (B) Spectrophotometric titration of $\mathrm{Pb(2.2.2)}^{2+}$ with OH^- (Et_4N^+) to form $\mathrm{Pb(2.2.2)OH}^+$ (λ = 240 nm; $[\mathrm{Pb(2.2.2)}^{2+}]_{\mathrm{tot}} = 5.5 \times 10^{-5}$ M). Solid line was calculated by using eq 5; $[\mathrm{OH}^-]' = [\mathrm{OH}^-]\gamma_{\mathrm{MC}}$.

Dissociation Kinetics. In basic solution, Pb(II) undergoes hydrolysis to form a variety of soluble monomeric and polymeric species[18,19] according to the equation

$$x\mathrm{Pb}^{2+} \rightleftarrows \mathrm{Pb}_x(\mathrm{OH})_n^{2x-y} + y\mathrm{H}^+ \qquad (6)$$

Under the conditions employed in this study ($[\mathrm{Pb}^{2+}] = (2.2\text{–}3.0) \times 10^{-5}$ M; $[\mathrm{OH}^-] = (0.5\text{–}25.0) \times 10^{-2}$ M), species distribution calculations[20] indicate that the predominant lead–hydroxy species are $\mathrm{Pb(OH)_3}^-$ (≥92%) and $\mathrm{Pb(OH)_2}$ (≤8%). Furthermore, in the absence of cryptand, the hydrolysis reaction represented by eq 6 is complete in the mixing time (~4 ms) of the stopped-flow instrument for the experimental conditions noted above.

In the presence of an excess of hydroxide ion and monovalent scavenger ion, M^+, the overall dissociation reaction, given by eq 3, proceeds appreciably (>95%) to formation of the products. At the appropriate wavelengths (see Figure 2A) a rapid absorbance jump is observed, followed by a single, slower reaction trace. The measured reactions all obeyed pseudo-first-order kinetics, and the average values of k_{obsd}, obtained as a function of excess $[\mathrm{OH}^-]$, are listed in Table I. For both $\mathrm{Pb(2.2.2)}^{2+}$ and $\mathrm{Pb(2.2.1)}^{2+}$, the values of k_{obsd} have a second-order dependence on $[\mathrm{OH}^-]$, as shown in Figure 3, suggesting the relationship

$$k_{\mathrm{obsd}} = k_0 + k_{\mathrm{OH}}[\mathrm{OH}^-]^2 \qquad (7)$$

Least-squares analysis of k_{obsd} vs $[\mathrm{OH}^-]^2$ gave values of the slope, k_{OH}, and intercept, k_0, for the dissociation reactions in the three electrolyte systems. The intercepts, k_0, were all within ±1 standard deviation of the origin, and the values of $\bar{R}^2$ ranged from 0.990 to 0.997. The resolved values of k_{OH} are listed in Table II.

Discussion

Formation of the Monohydrate Adduct. The equilibrium constant for the formation of $\mathrm{Pb(OH)}^+$ from $\mathrm{Pb(OH_2)}^{2+}$ is 1.0×10^6 M^{-1},[21a] and the formation constant for the monohydroxide adduct of the Pb(EDDA) complex is 1.0×10^3 M^{-1}.[21b] Thus, it is not

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Table I. Observed Rate Constants for the Dissociation of Lead(II) Cryptates at 25.0 °C[a]

		k_{obsd}, s^{-1} [b]	
M^+	$10^2[OH^-]$, M[c]	$Pb(2.2.1)^{2+}$	$Pb(2.2.2)^{2+}$
Li^+	3.83	1.71 ± 0.02	0.109 ± 0.002
	8.93	12.9 ± 0.1	0.220 ± 0.005
	14.0	36.6 ± 0.3	0.393 ± 0.007
	19.2	80.0 ± 3.2	0.618 ± 0.009
	24.3	...	0.956 ± 0.018
Na^+	0.51	0.029 ± 0.001	
	2.42	0.879 ± 0.001	
	3.53		0.038 ± 0.001
	5.05	4.42 ± 0.22	
	7.06		0.110 ± 0.001
	10.1	21.7 ± 0.3	
	12.1		0.265 ± 0.009
	15.2	53.2 ± 1.1	
	17.2		0.493 ± 0.002
	25.2		1.06 ± 0.03
K^+	0.76	0.068 ± 0.002	
	7.09		0.118 ± 0.002
	7.86	12.0 ± 0.2	
	15.4	66.1 ± 2.4	0.436 ± 0.039
	20.3	125 ± 4	0.745 ± 0.008
	25.3		1.13 ± 0.06

[a] μ = 0.50 M. [b] Uncertainties are expressed as one standard deviation of the mean of five to seven independent measurements. [c] Values refer to those after mixing.

Table II. Resolved Rate Constants for Hydroxide-Assisted Dissociation of Lead(II) Cryptates at 25.0 °C[a]

	k_{OH}, M^{-2} s^{-1} [b]	
electrolyte	2.2.1	2.2.2[c]
$LiOH/LiClO_4$	2120 ± 50	14.3 ± 0.5
$NaOH/NaClO_4$	2320 ± 50	16.3 ± 0.2
KOH/KCF_3SO_3	2860 ± 230	17.2 ± 0.1

[a] μ = 0.5. [b] Uncertainties are expressed as one standard deviation. [c] $K_{PbCOH} = (1.8 \pm 0.2) \times 10^4$ M^{-1}, average value for two titrations with uncertainty expressed as mean deviation.

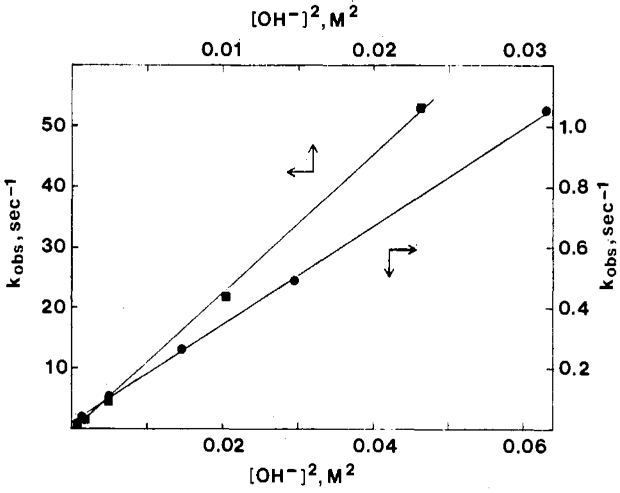

Figure 3. Plots of k_{obsd} vs $[OH^-]^2$ for dissociation of $Pb(2.2.1)^{2+}$ (■) and $Pb(2.2.2)^{2+}$ (●) at 25.0 °C (μ = 0.5 ($NaOH/NaClO_4$); $[Pb(2.2.1)^{2+}] = 2.98 \times 10^{-5}$ M; $[Pb(2.2.2)^{2+}] = 2.2 \times 10^{-5}$ M).

surprising the lead cryptates should also form stable monohydroxide complexes. $Eu(2.2.1)^{3+}$ adds two hydroxide ions with stepwise equilibrium constant values of 3×10^5 M^{-1} and 23 M^{-1}, respectively, and the Eu^{3+} and Yb^{3+} cryptates of 2.2.1 and 2.2.2 form stable 1:1 and 1:2 complexes with F^-.[3] In the present work no detectable amounts of $Pb(Cryp)(OH)_2$ were observed. The tendency to form the higher adducts may increase with the charge on the central ion. Of the known solid-state structures of 2.2.1 cryptates (Na^+, K^+, Co^{2+}, Ni^{2+}), only K(2.2.1)NCS has an anion or solvent molecule coordinated to the central metal ion.[22,23] With 2.2.2, none of the cryptates of monovalent cations (Na^+, K^+, Rb^+, Cs^+, Tl^+, Ag^+) show any anion/solvent interaction.[24] However, 2.2.2 cryptates of divalent (Pb^{2+}, Ca^{2+}, Ba^{2+})[25,26] and lanthanide (La^{3+}, Sm^{3+}, Eu^{3+}, Nd^{3+}) cations have structures with anions and/or water molecules occupying one to four coordination sites in addition to those used by the cryptand.[27-30] Of particular interest to this study is the fact that the $Pb(2.2.2)^{2+}$ cryptate has two thiocyanate ions coordinated to the central lead atom in the solid state.[25] It is clear therefore that one or two hydroxide ions can fit between the polyether strands of the ligand and bind to the lead ion in the cavity.

$$Pb(Cryp)^{2+} + OH^- \underset{}{\overset{K_{PbCOH}}{\rightleftharpoons}} Pb(Cryp)(OH)^+$$

$$Pb(Cryp)(OH)^+ + OH^- \overset{K_{PbC(OH)2}}{\rightleftharpoons} Pb(Cryp)(OH)_2$$

$$Pb(Cryp)(OH)_2 + OH^- \xrightarrow{k_1} Pb(OH)_n^{2-n} + Cryp$$

Figure 4. Reaction scheme for the dissociation of a lead cryptate, Pb(Cryp), in the presence of excess hydroxide ion.

Although a value of K_{PbCOH} could not be obtained for $Pb(2.2.1)OH^+$, an estimate of $(2-4) \times 10^3$ can be obtained from analysis of the kinetic data and the initial portion of the spectrophotometric titration curves. This value is about 4–9 times less than the corresponding value for $Pb(2.2.2)^{2+}$. Steric factors could account for part of the decrease (~3 times) since the openings adjacent to the bridging strand containing a single ether oxygen may not be large enough to accommodate a hydroxide ion. Finally, pH jump (~7→10) experiments with $Pb(Cryp)^{2+}$ indicate that the complexation of the hydroxide ion (or hydrolysis of $Pb(Cryp)(OH_2)^{2+}$) is relatively fast ($t_{1/2} < 2$ ms). Therefore, it is unlikely that the ligand undergoes any substantial rearrangement during adduct formation.

Dissociation Kinetics. On the basis of the results of equilibrium and kinetic studies, the dissociation of lead cryptates in the presence of excess hydroxide ion may be characterized by the following observations: (i) the cryptate is rapidly converted to a stable monohydroxide adduct; (ii) following addition of a second hydroxide ion, attack by a third hydroxide ion occurs at or prior to the rate-determining step; (iii) the nature of the scavenger cation (Li^+, Na^+, or K^+) has little effect on the dissociation rate constants. A mechanistic scheme consistent with these results is shown in Figure 4. The rate expression for the scheme is given by

$$-\frac{d[PbC]_T}{dt} = \frac{d[Cryp]}{dt} = k_{obsd}[PbC]_T = \left[\frac{k_1 K_{PbCOH} K_{PbC(OH)_2}[OH^-]^3}{1 + K_{PbCOH}[OH^-] + K_{PbCOH}K_{PbC(OH)_2}[OH^-]^2}\right][PbC]_T \quad (8)$$

where $[PbC]_T = [Pb(Cryp)^{2+}] + [Pb(Cryp)OH^+] + [Pb(Cryp)(OH)_2]$. Under the conditions employed $K_{PbCOH}[OH^-] \gg$

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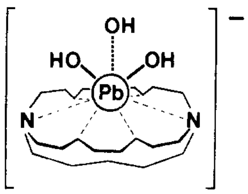

Figure 5. Possible structure of the trihydroxy-lead cryptate species formed at or prior to the rate-determining step of the hydroxide-assisted dissociation of lead(II) cryptates.

1. Since no appreciable concentration of $Pb(Cryp)(OH)_2$ was detected, and since the second stepwise constant for the reaction of $Eu(2.2.1)^{3+}$ with OH^- is ~13 000-fold smaller than the first stepwise constant,[3] it is reasonable to assume that $K_{PbC(OH)_2}[OH^-] < 1$. If this is the case, eq 8 may be reduced to give

$$k_{obsd} = k_1 K_{PbC(OH)_2}[OH^-]^2 \qquad (9)$$

which is consistent with the observed results for $[OH^-] \geq 0.005$ M. Although the $Pb(Cryp)OH^+$ species is stable with respect to dissociation in the pH range 8.5–10.5, the complex readily dissociates in the presence of excess hydroxide ion, pH $\geq$11.5. The addition of a second and third hydroxide ion to $Pb(Cryp)OH^+$ lowers the overall charge of the complex, facilitating removal of the metal ion from the cryptate cavity. Yee et al. proposed a similar argument to explain the enhanced rate of dissociation of lanthanide cryptates in the presence of OH^- and F^-.[3] Since the major species of the final product mixture, $Pb(OH)_3^-$, and the transition-state complex, $(Pb(Cryp)(OH)_3^-)^{\ddagger}$, both contain three hydroxide ions, it seems reasonable that the lead ion is partially removed from the cryptate in the transition-state complex. If the Pb–O(ether) bond(s) are broken in one bridge of the cryptate, the resulting intermediate would be similar to a metal–crown ether complex with the lead ion sitting on or in one face of the cryptand. Figure 5 shows one possible structure of such an intermediate. The bound hydroxides would compensate for the energy required to break the Pb–O(ether) bonds. Unlike the case of proton-assisted dissociation, no conformational change at a bridgehead nitrogen atom is required.[1,2,4] The preceding considerations are consistent with the fact that the value of k_{OH} for $Pb(2.2.1)^{2+}$ is ~150 times greater than the corresponding value for $Pb(2.2.2)^{2+}$ even though $Pb(2.2.1)^{2+}$ is slightly more stable than $Pb(2.2.2)^{2+}$.[29] In the case of $Pb(2.2.1)^{2+}$ only one Pb–O(ether) bond must break to form a pseudo-crown type intermediate whereas two must break for $Pb(2.2.2)^{2+}$.

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Registry No. $Pb(2.2.2)^{2+}$, 61624-56-4; $Pb(2.2.1)^{2+}$, 98970-55-9; $Pb(2.2.2)OH^+$, 111437-94-6; OH^-, 14280-30-9.

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Formation and Reactions of an Organochromium(III)-Acetamido-Pentaamminecobalt(III) Complex

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The reaction of $(NH_3)_5CoNHC(OH)CH_2I^{3+}$ with chromium(II) proceeds in a biphasic manner. The first stage yields $(H_3N)_5CoNHC(OH)CH_2Cr(OH_2)_5^{5+}$ (II) as the major product, and the next stage produces $(H_2O)_5Cr{-}OC(NH_2)CH_2Cr(OH_2)_5^{5+}$ (I) as cobalt(III) is reduced to Co(II). For the first and second stages, respectively, $k_{obsd} = (1.16 \pm 0.05\ M^{-1}\ s^{-1})[Cr^{2+}]$ and $((8.8 \pm 0.25) \times 10^{-5}\ s^{-1})[Cr^{2+}][H^+]^{-1}$, both in 1.0 M $LiClO_4/HClO_4$ at 25 °C. The reaction of II with Hg^{2+} has been studied, and the reactivity of the dimer is compared to that of monomer analogues and the $Co{-}NCCH_2{-}Cr$ dimer. The acidolysis of II is unusual in that it yields two products, which are linkage isomers of II at Co and Cr, respectively. In each case the metal atoms move to the carboxamide oxygen in the products.

Introduction

Chromium(II) reacts with organic halides (RX) to form organochromium(III) species $(RCr(OH_2)_5^{2+})$ by what is believed to be a halide atom abstraction mechanism.[2] It also has been shown that $(NH_3)_5CoNCCH_2I^{3+}$ reacts with chromium(II) to produce $(NH_3)_5Co{-}NCCH_2{-}Cr(OH_2)_5^{5+}$.[3] It was found that the supposed radical intermediate $\{(NH_3)_5CoNCCH_2^{3+}\}$ did not undergo intramolecular electron transfer to give cobalt(II) but rather gave the Co(II)–Cr(III) dimer exclusively.

Recently the reaction of chromium(II) and $ICH_2CO(NH_2)$ has been shown[4] to yield a mixture of $(H_2O)_5CrOC(NH_2)CH_3^{3+}$ and $(H_2O)_5CrCH_2CO(NH_2)^{2+}$. The latter species is a weak base for which the conjugate acid has a pK_a of 1.15. The present study concerns the reaction of $(NH_3)_5CoNHC(OH)CH_2I^{3+}$[5,6] and chromium(II). The products have been separated and quantified and the reactivity of the main product $(NH_3)_5CoNH(OH)CCH_2Cr(OH_2)_5^{5+}$ has been investigated. The results provide comparisons to the analogous nitrile and free organic halide reactions.

The kinetics of the chromium(II) reduction of the acetamido complex of pentaamminecobalt(III) has also been studied. These

Table I. Kinetic Data for the Chromium(III) Reduction of $(NH_3)_5CoNHC(O)CH_3^{2+}$ in Aqueous Acid[a]

		10^5k_{exptl}, s^{-1}		10^5k_{exptl}, s^{-1}
$10^2[Cr(II)]$, M	$[H^+]$, M	346 nm	476 nm	$(10^5k_{calcd}$,[b] $s^{-1})$
3.20	0.0904	2.84	2.74	2.85 (2.93)
1.60	0.122	1.18	1.12	1.10 (1.09)
3.20	0.122	2.35	2.21	2.19 (2.17)
3.20	0.188	1.53	1.43	1.54 (1.41)

[a] $[Co(III)] = 1.0 \times 10^{-3}$ M, ionic strength = 0.973 M ($HClO_4$–$LiClO_4$), 24.7 °C. [b] Values in parentheses assume $k_1 = 0$ and $k_2 = 8.28 \times 10^{-5}\ s^{-1}$ in eq 2.

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(5) The acetamido complex is a weak acid and recent work[6] indicates that the site of protonation is on the carbonyl oxygen. This formulation has been adopted here for the iodoacetamido and other carboxamido complexes.

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