of our statistical analysis we predict a possibly deeper minimum with the hydrogen atom slightly offset from the center of the reference ring and interacting with the π cloud above and below the C–C bonds. A second predicted energy minimum is at the parallel configuration with $d(z) = 3.3$ and $d(xy) = 4.4$ Å.

Kinetics and Mechanisms of Complex Formation of Uranyl Ion with 18-Crown-6 and Diaza-18-crown-6 Ligands in Propylene Carbonate

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Abstract: Complex formation between uranyl ion and 18C6 or diaza-18C6 ligand has been studied by stopped-flow spectrophotometric measurements, at 25 °C, in propylene carbonate (TEAClO$_4$ 0.1 M). For the experimental conditions employed the $UO_2-(18C6)^{2+}$ and $UO_2-(diaza-18C6)_2^{2+}$ complexes are entirely formed. In the presence of an excess of ligand, the kinetic process indicates three consecutive steps with the 18C6 and four observed consecutive steps with the diaza-18C6. The proposed mechanisms show the prominent role of the second and first solvation shells of the uranyl ion in the kinetic processes which can be summarized as follows: very fast formation (preequilibrium) of outer-sphere complexes with one or two ligands entering in the second solvation shell of the uranyl ion; one to four interchange steps with the loss of solvent in the inner solvation shell of UO_2^{2+} and with the formation of a metal–ligand bond.

Kinetic studies of the complexation of common crown ethers and cryptands with alkali, alkaline earth, transition, and heavy metal ions are of great interest and give models for biochemical processes. However, few investigations on the kinetic formation of these complexes have been undertaken, and the main results concern principally the alkali and alkaline earth ions complexation. The literature indicates two main mechanistic schemes for the complexation kinetics of a metal ion by a macrocyclic ligand. Nearly all of the authors propose the so-called Chock mechanism[1] for an alkali metal ion complexed by a crown ether and the more general Eigen[2] mechanism for a main group ion or a transition-metal ion complexed with a multidentate ligand. Chock's mechanism suggests that a rapid conformational preequilibrium of the ligand is followed by a reaction of the "open" form of the crown ether with the cation; the rate-determining step is the complexation step. The Eigen mechanism assumes that the formation of an outer-sphere complex between the metal and the entering ligand followed by a metal desolvation and ligand rearrangement step is the rate-determining step. As the rates of these reactions of complex formations are very fast, the kinetic measurements have been generally carried out using T jump, ultrasonic absorption, or NMR techniques. Some results are obtained in water medium,[3–9] but most in nonaqueous media.[10–24]

Only very few kinetic studies on the complexation of polyatomic units by crown ethers or cryptands have been carried out. Liesegang et al.[3] have determined the complexation rate constant of the NH$_4^+$ cation by the 18C6 ligand in aqueous medium. To our knowledge, there is no information available on the complexation kinetics of the uranyl ion UO_2^{2+} with any crown ether or cryptand. However, the complexation properties of that cationic unit should be of great interest because of the increasing interest in nuclear chemistry. In a preliminary study, the stability of various crown ethers and cryptands (especially of 18C6 and diaza-18C6) with uranyl ion has been investigated in propylene carbonate medium.[25,26] The 18C6 reacts with uranyl ion to give

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only 1:1 complex (log β_{11} = 5.30). The 1:2, 2:2, and 2:1 complexes (metal:ligand) are observed with the diaza-18C6 ligand (log β_{12} = 12.40; log β_{11} = 7.45; log β_{21} = 14.49). In the present paper, the formation kinetics of the mononuclear complexes of uranyl ion with the 18C6 and diaza-18C6 ligands are reported. The formation rate constants of these reactions are several orders of magnitude lower than those normally encountered for cations complexed by analogous ligands which are near diffusion controlled so that the measurements could be carried out by stopped-flow spectrophotometry.

Experimental Section

Reagents. All chemicals were analytical reagent grade. The crown ether 18C6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and the coronand diaza-18C6 (1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) were obtained from Merck. The tetraethylammonium perchlorate TEAClO₄ was purchased from Fluka and the uranium perchlorate $UO_2(ClO_4)_2 \cdot xH_2O$ from Ventron GMBH. The perchlorates of tetraethylammonium and uranium were carefully dried in vacuo to less than 0.02% H_2O and dissolved in propylene carbonate (PC). PC (Fluka) was purified according to Gosse.[27] In kinetic measurements, all the solutions in PC contained after purification between 75 and 100 ppm of H_2O. The residual water content was determined by Karl Fischer titration. The uncertainty limits of the water determination in PC by this method were ±10%. But, we have checked that quantities of water between 50 and 200 ppm did not significantly change the spectra of our studied species, the values of their stability constants,[25] and the measured rate constants. The concentration of the uranyl ion in PC solutions was determined by pulse polarography (a sample of the stock solution was diluted in aqueous 0.5 M hydrochloric acid[28]). Ionic strength was maintained at 0.1 M by addition of TEAClO₄.

Kinetic Measurements. The stopped-flow spectrophotometer, type Durrum Gibson equipped with a transient recorder Datalab DL 905, was interfaced to an Apple II microcomputer. The on-line data acquisition and treatment system was described in a previous paper.[29] In all kinetic studies, solutions of $UO_2(ClO_4)_2$ (10^{-4} or 4×10^{-4} M) were mixed with solutions of ligand (L) in concentrations of 10^{-3} to 3×10^{-2} M (L = 18C6 or diaza-18C6). In these concentration conditions the $UO_2(18C6)^{2+}$ or $UO_2(diaza-18C6)_2^{2+}$ complex was only entirely formed at the end of the reaction. The kinetic measurements showed that the reactions of complex formation occurred in several steps with rate constants of two consecutive steps in a ratio greater than 8. Each step was treated separately: the absorbance of the solutions was measured in a time range so that the faster and(or) slower steps could be neglected. Furthermore, the ligand concentration was in sufficient excess (at least a tenfold excess in each run) to ensure that each observed step of the formation reaction was always pseudo first order with respect to the uranium reacting species. For each step, the plot ln $|A_t - A_\infty|$ vs. time was linear for the selected time range: A_t is the absorbance of the system at reaction time t and A_∞ that at t_∞ (for the slowest step) or t = 0 of the following slower step (for the other steps). The slope of these plots gives the observed pseudo-first-order rate of the studied reaction step (k_{obsd}) by linear least-squares analysis. Each value of k_{obsd} is the average of at least three determinations. In the conditions mentioned above, this calculation is in good agreement with a more sophisticated calculation where all the steps are simultaneously treated. For both methods, the rate constant determination is less accurate in the case of a set of consecutive steps than in the case of only one step. For this reason, we observe a small scatter in the k_{obsd} determinations, but the genuineness of the number of the observed steps is obvious. The existence of each treated reaction step was checked at different wavelengths between 270 and 310 nm, and for different concentrations in UO_2^{2+} and ligand.

Results

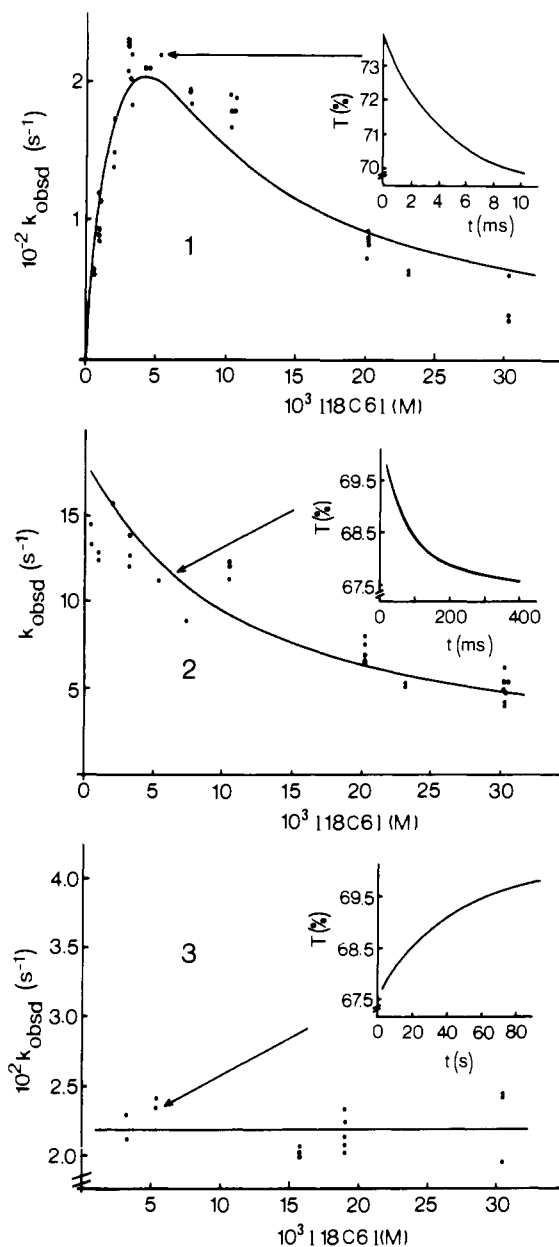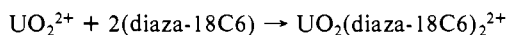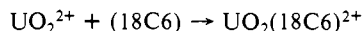The following two reactions of complex formation were studied

$$UO_2^{2+} + (18C6) \rightarrow UO_2(18C6)^{2+}$$

$$UO_2^{2+} + 2(diaza-18C6) \rightarrow UO_2(diaza-18C6)_2^{2+}$$

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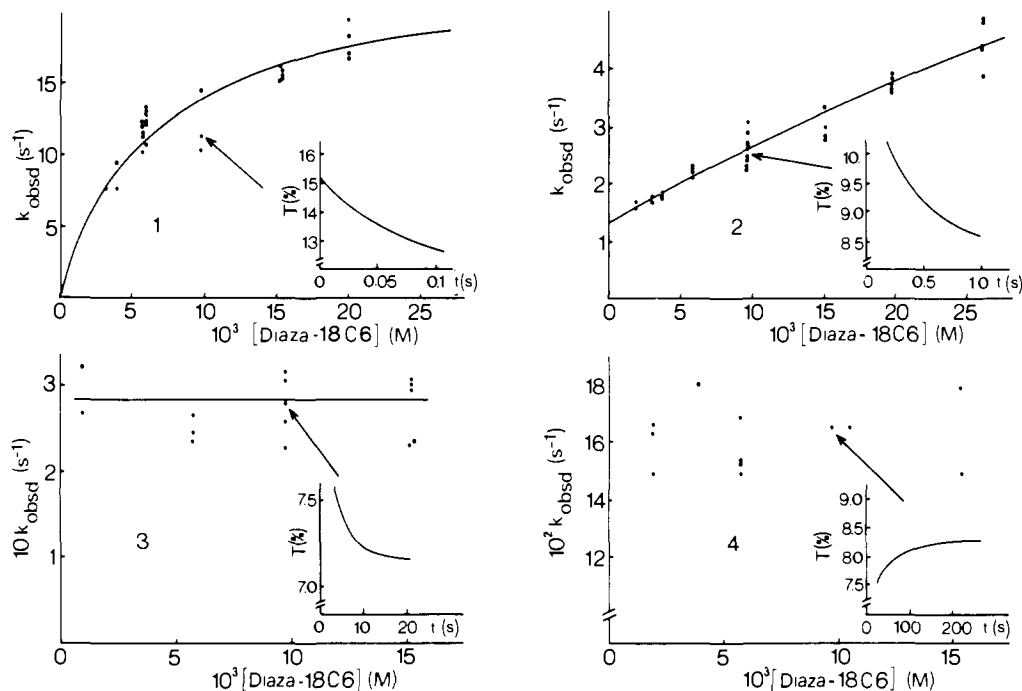(29) Lagrange, J.; Lagrange, P. *J. Chim. Phys. Phys.-Chim. Biol.* **1984**, *81*, 425.

Figure 1. Pseudo-first-order observed rate constants for the $UO_2(18C6)^{2+}$ complex formation as a function of ligand concentration in propylene carbonate (TEAClO₄ 0.1 M): (1) first step; (2) second step; (3) third step. The points are experimental data and the curves correspond to recalculated k_{obsd} values. The curves T % (transmittance) = $f(t)$ give examples of experimental data obtained with a solution where concentrations after mixing are the following: [18C6] = 5.39 × 10^{-3} M, [UO_2^{2+}] = 2.205 × 10^{-4} M (λ = 290 nm). Linear regression analysis of these curves gives the k_{obsd} indicated by the arrow.

In the presence of an excess of ligand, the two observed kinetic processes show three consecutive steps for the $UO_2(18C6)^{2+}$ complex formation and four consecutive steps for the $UO_2(diaza-18C6)_2^{2+}$ complex. All these steps appear to be pseudo first order with respect to the uranium reacting species. For each concentration of the ligand (18C6 or diaza-18C6), the observed rate constants were calculated for two different concentrations of UO_2^{2+} and different wavelengths: between 275 and 300 nm with the 18C6 and between 270 and 310 nm with the diaza-18C6. The k_{obsd} values are reported in Figures 1 and 2 and do not show significant influence of these last two parameters.

As the concentration of 18C6 increases, the k_{obsd} = f[(18C6)] function passes through a maximum for the first step, decreases for the second step, and is constant for the third step (Figure 1).

As the concentration of diaza-18C6 increases, the k_{obsd} = f-[(diaza-18C6)] function increases and is of the hyperbolic type

Figure 2. Pseudo-first-order observed rate constants of the $UO_2(diaza-18C6)_2^{2+}$ complex formation as a function of ligand concentration in propylene carbonate ($TEAClO_4$ 0.1 M): (1) first step; (2) second step; (3) third step; (4) fourth step. The points are experimental data and the curves correspond to recalculated k_{obsd} values. The curves $T\%$ (transmittance) $= f(t)$ give examples of experimental data obtained with a solution where concentrations after mixing are the following: [diaza-18C6] $= 9.740 \times 10^{-3}$ M, $[UO_2^{2+}] = 1.780 \times 10^{-4}$ M ($\lambda = 290$ mm). Linear regression analysis of these curves gives the k_{obsd} indicated by the arrow.

for the first and second steps. It seems to be constant for the third and fourth steps (Figure 2).

Proposed Mechanism. The preceding experimental information allows us to propose a preliminary hypothesis concerning elementary reactions involved in each observed step of the overall reactions. (a) For the first and second steps of the $UO_2(diaza-18C6)_2^{2+}$ complex formation, the k_{obsd} values increase, when the concentration of the ligand increases, and seem to be almost independent of this concentration above a certain limit. We explain this observation by proposing that, at the beginning of each of these steps, there is a fast preequilibrium between the uranium reacting species and the entering ligand. Thus, rearrangements which are rate determining give the products of the observed step. (b) For the first and second steps of the UO_2-$(18C6)^{2+}$ complex formation, the k_{obsd} values decrease when the concentration of the entering ligand increases above a certain limit. For these steps the elementary reactions are of the same type as for the first and second steps of the $UO_2(diaza-18C6)_2^{2+}$ formation. In addition, we explain the inhibition effect by the formation in fast preequilibria of at least one intermediate with a stoichiometry in ligand greater than that of the product of the observed step. These particular intermediates would not give rearrangements which are rate determining, their formation would have an inhibiting effect. (c) For the third step of the two studied reactions the k_{obsd} values do not depend on ligand concentration. Thus only structural rearrangement paths may be considered.

$UO_2(18C6)^{2+}$ **Formation.** Previous thermodynamic results[26] allow one to show that 18C6 reacts with uranyl ion to give only 1:1 complex. Therefore, we have postulated that the thermodynamically stable 1:1 complex is a mixture of two isomers in equilibrium where the coordination center UO_2^{2+} is either completely desolvated and inside the ligand cavity ("inclusive" isomer) or partially solvated and enclosed in the ligand cavity ("exclusive" isomer). Thus we may propose a mechanism of formation of the $UO_2(18C6)^{2+}$ complex given by Figure 3 and discussed as follows.

First Observed Kinetic Step. Two consecutive fast preequilibria leading to the formation of two outer sphere type complexes of solvated uranyl ion with one and two molecules of ligand (L) are proposed: $(UO_2,L)^{2+}$ and $(L,UO_2,L)^{2+}$. These fast equilibria are followed by partial metal desolvation and ligand metal bond
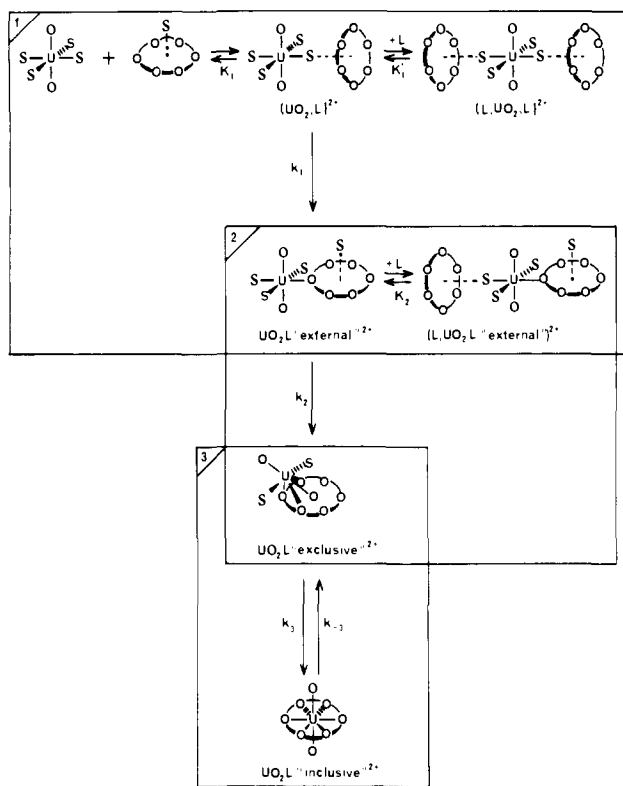

Figure 3. Mechanism of the $UO_2(18C6)^{2+}$ complex formation in three steps. Each step is isolated in a rectangle. The number quoted in the rectangle corresponds to the number of the observed step. The number of solvent molecules in the inner solvation sphere of uranyl ion is not known (four or probably more). Only four molecules are drawn on the figure.

formation in the outer sphere complex $(UO_2,L)^{2+}$ which are rate determining and give the UO_2L"external"$^{2+}$ complex. In the "external" complex, the coordination center is outside the cavity and interacts with only one (or two) O atom of the ligand.

Mathematical treatment of this first step leads to the following equations:

$$-\frac{d[U]_T}{dt} = k_{obsd}[U]_T = k_1[(UO_2,L)^{2+}]$$

with

$$[U]_T = [UO_2^{2+}] + [(UO_2,L)^{2+}] + [(L,UO_2,L)^{2+}]$$

$$K_1 = \frac{[(UO_2,L)^{2+}]}{[UO_2^{2+}][L]} \text{ and } K_1' = \frac{[(L,UO_2,L)^{2+}]}{[(UO_2,L)^{2+}][L]}$$

$$k_{obsd} = \frac{k_1 K_1[L]}{1 + K_1[L] + K_1 K_1'[L]^2}$$

The parameters of the k_{obsd} function are adjusted by a generalized least-squares method by the LETAGROP program in its MODEL FUNCTION version.[30]

$$K_1 = 145 \pm 10 \text{ dm}^3 \text{ mol}^{-1} \qquad K_1' = 420 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$$

$$k_1 = 930 \pm 50 \text{ s}^{-1}$$

The hypothesis of the fast formation of the two $(UO_2,L)^{2+}$ and $(L,UO_2,L)^{2+}$ intermediate outer sphere complexes is supported by three remarks: (1) For each kinetic experiment the absorbance corresponding to time zero by addition of the absorbances for each of the reactants after mixing may be calculated. The difference between this calculated value and the experimental one is not significant and in favor of the formation of outer sphere type complexes. (2) In aqueous solution (where the inner solvation of uranyl ion by water is greater than that by propylene carbonate), these two outer sphere complexes are the thermodynamic stable complexes ($K_1 = 112$ mol^{-1} dm^3; $K_1' = 56$ mol^{-1} dm^3) and their formation appears instantaneous when the stopped-flow technique is used. The values of K_1 or K_1' obtained in water or in propylene carbonate are analogous and they are of an order of magnitude similar to that usually found for outer sphere complex formation. (3) From the former calculation the pseudo-first-order rate constant may be recalculated. The calculated and the experimental values of k_{obsd} (Figure 1) are in good agreement, showing the consistency of our hypotheses. A calculation taking into account, in addition, a rearrangement determining rate of the $(L,UO_2,L)^{2+}$ complex shows that this path is negligible.

Second Observed Kinetic Step. In actual fact, the UO$_2$L"external"$^{2+}$ complex which is the product of the first observed step is instantaneously in equilibrium with the (L,-UO$_2$L"external")$^{2+}$ complex (outer sphere complex between the inner sphere complex UO$_2$L"external"$^{2+}$ and the entering ligand). This fast equilibrium is followed by a rate determining rearrangement reaction in the UO$_2$L"external"$^{2+}$ complex consisting of metal and ligand cavity desolvations with a simultaneous rotation of the uranyl group to give the UO$_2$L"exclusive"$^{2+}$ complex. So we obtain the equations given below which agree with the experimental data (Figure 1).

$$-\frac{d[U]_T}{dt} = k_{obsd}[U]_T = k_2[UO_2L\text{"external"}^{2+}]$$

with

$$[U]_T = [UO_2L\text{"external"}^{2+}] + [(L,UO_2L\text{"external"})^{2+}]$$

and

$$K_2 = \frac{[(L,UO_2L\text{"external"})^{2+}]}{[UO_2L\text{"external"}^{2+}][L]}$$

then

$$k_{obsd} = \frac{k_2}{1 + K_2[L]}$$

k_2 and K_2 parameters are determined by linear regression analysis.

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$$k_2 = 18 \pm 2 \text{ s}^{-1}$$

$$K_2 = 90 \pm 10 \text{ dm}^3 \text{ mol}^{-1}$$

The outer sphere (L,UO$_2$L"external")$^{2+}$ has a formation constant K_2 of the same order of magnitude as the K_1 constant of the (L,UO$_2$,L)$^{2+}$ outer sphere complex formed in the first observed step. These two outer sphere complexes where uranyl ion is bonded to two molecules of ligand show a poor ability to give rearrangements when compared with the $(UO_2,L)^{2+}$ and UO$_2$L"external"$^{2+}$ complexes where uranyl interacts with only one molecule of ligand. The rearrangement in biligand complexes is not rate determining.

Third Observed Kinetic Step. In this last step, the UO$_2$L"exclusive"$^{2+}$ complex leads, in a rearrangement reaction, to the UO$_2$L"inclusive"$^{2+}$ where the uranyl ion is completely desolvated and inside the ligand cavity. This rearrangement step consists either of two opposing reactions or only of the forward reaction. Experimental data do not allow one to choose between these two possibilities. Then, the first-order rate constant ($k_{obsd} = k_3 + k_{-3}$) is independent of the ligand concentration and equal to 0.022 ± 0.002 s^{-1}.

This last kinetic step confirms the existence of the "inclusive" (and "exclusive") isomers found thermodynamically.

UO$_2$(diaza-18C6)$_2$$^{2+}$ Formation. Thermodynamic results[26] have shown that three complexes between the uranyl ion and the di-aza-18C6 ligand (L) may be formed. Their stoichiometries (metal:ligand) are 1:1, 1:2, and 2:1. Discussion on their stability constants leads us to propose, for each type of complex, a series of isomers in equilibrium. In particular, the 1:1 complex is a mixture of three isomers: UO$_2$L"inclusive"$^{2+}$, UO$_2$L"exclusive"$^{2+}$, and UO$_2$L"external"$^{2+}$. Obviously in the 1:2 complex uranyl ion is outside the two ligand cavities (UO$_2$L$_2$"biexternal"$^{2+}$ complex). In the present kinetic study and for our experimental conditions the 1:2 complex is the only complex formed as product of the overall reaction. The experimental results could be interpreted by assuming that an analogous mechanistic scheme, as the one proposed for the UO$_2$(18C6)$^{2+}$ formation, takes place (Figure 4).

First Observed Kinetic Step. An $(UO_2,L)^{2+}$ outer sphere complex is probably quasi-instantaneously formed (preequilibrium), and its transformation (rate determining) would correspond to the formation of the UO$_2$L"external"$^{2+}$ complex where ligand enters in the first solvation sphere of the uranyl ion. This described mechanism (Figure 4, rectangle 1) leads to the following rate law:

$$-\frac{d[U]_T}{dt} = k_{obsd}[U]_T = k_1[(UO_2,L)^{2+}]$$

with

$$[U]_T = [UO_2^{2+}] + [(UO_2,L)^{2+}] \text{ and } K_1 = \frac{[(UO_2,L)^{2+}]}{[UO_2^{2+}][L]}$$

then

$$k_{obsd} = \frac{k_1 K_1[L]}{1 + K_1[L]}$$

The parameters of the k_{obsd} function are adjusted with the LETAGROP program in its MODEL FUNCTION version:

$$K_1 = 158 \pm 22 \text{ dm}^3 \text{ mol}^{-1}$$

$$k_1 = 23 \pm 1 \text{ s}^{-1}$$

With this set of constants, the experimental kinetic data give a good fit to the k_{obsd} values recalculated with the rate equation written above (Figure 2). A calculation taking into account the formation of a second outer sphere complex $(L,UO_2,L)^{2+}$ with or without rearrangement (rate determining) of this complex shows that this additional intermediate could be neglected.

Second Observed Kinetic Step. The product of the first step, UO$_2$L"external"$^{2+}$, is in fact instantaneously in equilibrium with a "(L,UO$_2$L"external")$^{2+}$ outer sphere complex as in the second step of the UO$_2$(18C6)$^{2+}$ formation. These two complexes lead by rearrangement reactions which are rate determining to the

Complex Formation between Uranyl Ion and Crowns
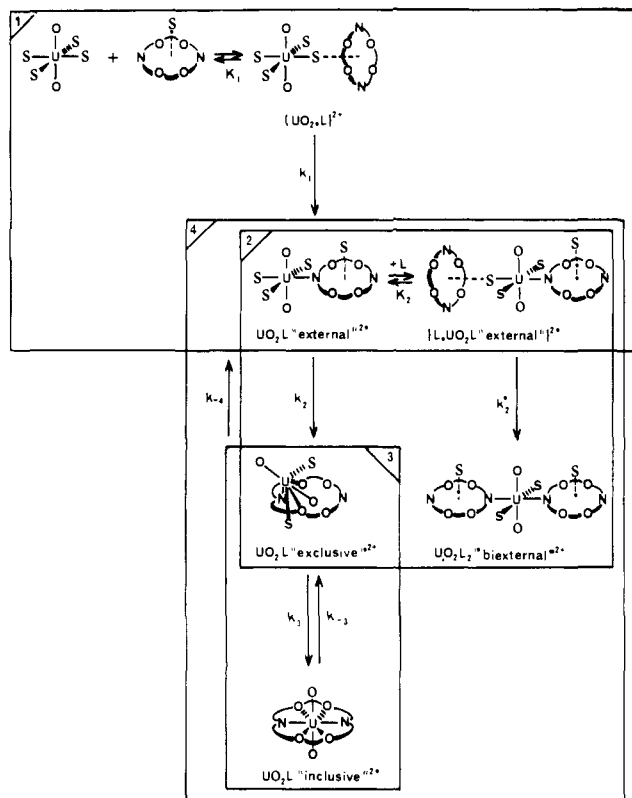
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Figure 4. Mechanism of the $UO_2(diaza\text{-}18C6)_2{}^{2+}$ complex formation in four steps. Each step is isolated in a rectangle. The number quoted in the rectangle corresponds to the number of the observed step. The number of solvent molecules in the inner solvation sphere of uranyl ion is not known (four or probably more). Only four molecules are drawn on the figure.

UO_2L"exclusive"$^{2+}$ and UO_2L_2"biexternal"$^{2+}$ complexes. The experimental results, where k_{obsd} (Figure 2) is a hyperbolic function of the ligand concentration which does not pass through the zero point, agree with the rate law corresponding to this proposed mechanism:

$$-\frac{d[U]_T}{dt} = k_{obsd}[U]_T =$$
$$k_2[UO_2L\text{"external"}^{2+}] + k_2'[(L,UO_2L\text{"external"})^{2+}]$$

with

$$[U]_T = [UO_2L\text{"external"}^{2+}] + [(L,UO_2L\text{"external"})^{2+}]$$

and

$$K_2 = \frac{[(L,UO_2L\text{"external"})^{2+}]}{[UO_2L\text{"external"}^{2+}][L]}$$

then

$$k_{obsd} = \frac{k_2 + k_2'K_2[L]}{1 + K_2[L]}$$

The adjusted parameters are

$$K_2 = 9.3 \pm 0.5 \text{ dm}^3 \text{ mol}^{-1}$$
$$k_2 = 1.3 \pm 0.08 \text{ s}^{-1}$$
$$k_2' = 17 \pm 3 \text{ s}^{-1}$$

Third Observed Kinetic Step. This step where k_{obsd} is independent of the ligand concentration is attributed to a reversible reaction between the UO_2L"exclusive"$^{2+}$ and UO_2L"inclusive"$^{2+}$ complexes.

$$k_{obsd} = k_3 + k_{-3} = 0.283 \pm 0.026 \text{ s}^{-1}$$

Fourth Observed Kinetic Step. The single final product of the reaction being the biligand complex, this last step should probably

be due to a reverse reaction: UO_2L"exclusive"$^{2+}$ complex giving slowly the UO_2L"external"$^{2+}$ complex which leads to the UO_2L_2"biexternal"$^{2+}$ complex. Assuming that the stationary state approximation is applicable to the UO_2L"external"$^{2+}$ and $(L,UO_2L$"external"$)^{2+}$ intermediates and that the reactions of formation and dissociation of an outer sphere complex are very fast vs. all the other reactions, the rate law may be written as follows:

$$-\frac{d[U]_T}{dt} = k_{obsd}[U]_T =$$
$$k_{-4}[UO_2L\text{"exclusive"}^{2+}] - k_2[UO_2L\text{"external"}^{2+}]$$
$$[U]_T = [UO_2L\text{"inclusive"}^{2+}] + [UO_2L\text{"exclusive"}^{2+}]$$

Then

$$k_{obsd} \simeq \frac{k_{-4}}{1 + (k_3/k_{-3})} \frac{k_2'K_2[L]}{k_2 + k_2'K_2[L]}$$

as $k_2'K_2[L]/(k_2 + k_2'K_2[L]) \simeq 1$, k_{obsd} is practically independent of the ligand concentration. Furthermore, if we assume $k_3 \simeq k_{-3}$, then $k_{-4} \simeq k_{obsd} = 0.016 \pm 0.001 \text{ s}^{-1}$.

Conclusion

The rate constants of the various steps observed in the reaction of formation of complexes between uranyl ion and 18C6 or diaza-18C6 ligand are several orders of magnitude lower than those obtained with alkali or alkaline-earth cations. We may compare the proposed mechanism described above to the general Chock and Eigen mechanisms.

In the literature, conformational change of the ligand suggested in the Chock mechanism is very fast. This step must appear as a conformational preequilibrium of the ligand and is followed by a complexation reaction which is rate determining. If such a mechanism occurs and is observed in our kinetic studies, it must be attributed to our first two steps. But the Chock mechanism does not explain the variation of k_{obsd}, with the ligand concentration, obtained in this work for the first steps of the reactions of complex formation.

On the other hand, our kinetic hypothesis agrees very closely with the Eigen mechanism. The Eigen mechanism concerning complex formation indicates the fast formation (preequilibrium) of outer sphere complex between solvated metal and entering ligand. In this intermediate, the loosening of the metal–solvent bond and the formation of a new bond between the metal and the entering ligand is rate determining. In case of multiple substitutions, the first metal–ligand bond is formed as described. Then, if the ligand is more strongly bonded to the metal than the rest of the solvent molecules in the inner sphere, the solvent molecules will be labilized and the other steps of the substitution are very fast. Whereas if the ligand is weakly bonded, the solvent molecules are stabilized. It seems that if the rate process is not strongly influenced by the nature of the entering ligand then the main factor in the energetic barrier in the reaction is essentially the loosening of the metal–solvent bond rather than the formation of a new bond between the metal and the entering ligand.

It appears that the two similar mechanistic schemes which we have proposed for $UO_2(18C6)^{2+}$ and $UO_2(diaza\text{-}18C6)_2{}^{2+}$ formation agree with the Eigen mechanism. The variations of k_{obsd} with ligand concentration are explained. The hypothesis of a weak bond between the uranyl ion and the entering ligand in "external" complexes giving a stabilization of the inner solvent molecule leads to an overall reaction which appears in several steps. The more important factor in our different observed kinetic steps is always a solvation–desolvation process which is rate determining. The proposition of an Eigen mechanism to explain the observed phenomenon in PC also agrees with the conclusions of Petrucci et al.[21] in a recent paper on the sodium ion and potassium complexation by the 18C6 in dimethylformamide.

Our kinetic results prove the existence of complexes where uranyl ion is totally encapsulated in the macrocycle cavity— "inclusive" complexes which were only postulated in a previous thermodynamic study.