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Discussion on the Complexing Ability of the Uranyl Ion with Several Crown Ethers and Cryptands in Water and in Propylene Carbonate

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Interactions of the uranyl ion (UO_2^{2+}) with some common crown ethers (12C4, 15C5, 18C6, DB-18C6) and cryptands (22, 222) are investigated in aqueous and propylene carbonate (PC) solutions, $I = 0.1$ M ((TEA)ClO_4). Stability constants of the complexes formed are determined by potentiometric and spectrophotometric measurements. Discussions on the stability constants of the complexes allow us to postulate whether or not direct uranyl–macrocycle bonds are obtained. In PC solution, uranyl inner-sphere complexes with 18C6, DB-18C6, 22, and 222 are formed with the uranyl ion probably inside or partially enclosed in the ligand cavity. In aqueous media, complexation occurs only with crown ethers by formation of hydrogen bonds between hydrogen of water molecules of the hydrate shell of the uranyl ion and oxygen atoms of the crown ether (UO_2^{2+} outer-sphere complexes).

Recently, some investigations on the complexation of the uranyl ion with macrocyclic ligands have been undertaken, especially with crown ethers and cryptands.[1-14] These studies are of great interest as far as possible uses in solvent extraction and isotope separation are concerned for example. Complexes between the uranyl ion and crown ethers or cryptands have been prepared in the solid state and have been well characterized by infrared and electronic spectra or radiocrystallographic and NMR studies.[1-11] But there is a lack of information in solution, where only a few studies have been done.[6,7,13,14] Results obtained by Spiess[12] show no complexation between the uranyl ion and 222 or 21 in aqueous solution. Izatt[13,14] has found no uranyl complex with 18C6 in methanol and with dicyclohexyl-18C6 in aqueous solution by calorimetric titrations. A similar result was obtained by Tomaja[11] by NMR measurements. NMR results of Costes[6] prove that a UO_2-222^{2+} complex exists in $CDCl_3$ solution. A UO_2-$18C6^{2+}$ complex in acetonitrile has been reported by Folcher;[7] this author shows the dissociation of this species in Me_2SO and water media.

In this paper, the complex formation ability of the uranyl ion UO_2^{2+} with several common crown ethers, 1,4,7,10-tetraoxacyclododecane (12C4), 1,4,7,10,13-pentaoxacyclopentadecane (15C5), 1,4,7,10,13,16-hexacyclooctadecane (18C6), and 2,3:11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (DB-18C6), and cryptands, 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (22) and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (222), is reported in aqueous and propylene carbonate (PC) solutions. The stoichiometry and the stability constants of the complexes formed between the uranyl ion and 18C6, 15C5, or 12C4 in an acidic aqueous medium were studied by two different competitive potentiometric methods. Na^+ or Pb^{2+} was used as an auxiliary ion. Na^+-free concentrations were measured with a cationic glass electrode; Pb^{2+}-free concentrations, with a specific electrode. In PC solutions, the uranyl ion complexed to 18C6 (DB-18C6, 15C5, 22, or 222) was studied spectrophotometrically.

Experimental Section

Reagents. All chemicals were analytical reagent grade. The crown ethers, cryptands ("Kryptofix"), and sodium perchlorate ($NaClO_4$) were obtained from Merck. The tetraethylammonium perchlorate ((TEA)ClO_4) was purchased from Fluka, and the uranium perchlorate ($UO_2(ClO_4)_2 \cdot xH_2O$) from Ventron GmbH. The lead perchlorate ($Pb(ClO_4)_2$) was prepared by action of perchloric acid (Merck) on lead oxide (PbO) (Prolabo) and titrated by polarography.[15] The perchlorates of tetraethylammonium and uranium were carefully dried in vacuo to less than 0.02% H_2O. Propylene carbonate (Fluka) was purified according to Gosse;[16] all solutions with PC contained less than 100 ppm of H_2O after purification. The residual water content was determined by Karl Fischer titration. The concentration of the uranyl ion in both the aqueous solution and in the PC solution was determined by pulse polarography (a sample of the stock solution was diluted in aqueous 0.5 M hydrochloric acid[17]). Ionic strength was maintained at 0.1 M by addition of (TEA)ClO_4.

Potentiometric Measurements in Aqueous Solutions. The determination of the stability constants of complexes formed by the uranyl ion with 18C6, 15C5, and 12C4 in aqueous medium was undertaken by potentiometric measurements using an Aries 20000 Tacussel millivoltmeter and a Tacussel Isis 20000 pH meter. Two competitive potentiometric methods have been performed with Na^+ (or Pb^{2+}) used as an auxiliary ion. Measurements of sodium ion concentrations were carried out with a sodium glass electrode (PMeV; Tacussel), and measurement of lead ion concentrations with a compacted polycrystalline electrode (PB1; Tacussel). All measurements were made in acidic medium (pH ≤ 3) to avoid the hydrolysis of the uranyl ion. H^+ concentrations were measured with a "high-alkalinity" glass electrode (TB/HA; Tacussel). The reference electrode was a Ag/AgCl electrode.[18] Titrations were carried out in a thermostated cell at 25.0 ± 0.1 °C. C_X is the analytical concentration of the species X, and [X] is the free concentration.

(a) Na^+ Measurements with the PMeV Electrode. The first series of experiments was conducted with the PMeV electrode. The half-cell potential of a monovalent-ion-selective glass electrode in the presence of one monovalent interfering ion can be written in the general form of the Nicolsky equation[19]

$$E = E^\circ + 2.303(RT/F) \log (a_i + K_{i/j}{}^* a_j) \quad (1)$$

where a_i is the activity of the primary ion to which the electrode is selective, a_j the activity of the interfering ion, and $K_{i/j}{}^*$ the potential

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Table I. Potentiometric Determination of Sodium, Lead, and Uranyl Complexes in Water (0.1 M (TEA)ClO$_4$, 25 °C)[a]

ligand	stoichiometry of complex (metal:ligand)	competition with Na$^+$: log β_{xy}(Na$^+$)	competition with Na$^+$: log β_{xy}(UO$_2$$^{2+}$)	competition with Pb^{2+}: log β_{xy}(Pb^{2+})	competition with Pb^{2+}: log β_{xy}(UO$_2$$^{2+}$)
15C5	1:1	1.08 ± 0.03	0.7 ± 0.2	0.95 ± 0.10	0.5 ± 0.2
	1:2		3.3 ± 0.1		3.8 ± 0.2
18C6	1:1	1.09 ± 0.03	2.1 ± 0.1	3.58 ± 0.04	2.0 ± 0.1
	1:2		3.9 ± 0.1		3.7 ± 0.1

[a] The uncertainty limits are twice the computed standard deviation.

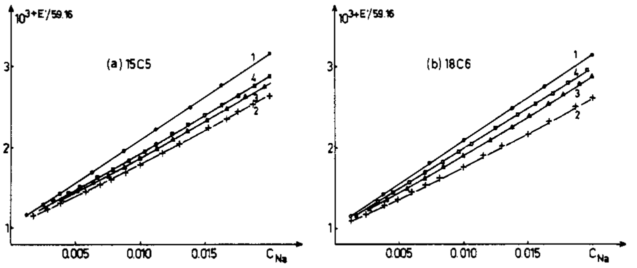

Figure 1. Titration by 10^{-1} M NaClO$_4$ of solutions (20 mL) containing (a) L = 15C5 or (b) L = 18C6: (1) $C_U = 0$, $C_L = 0$; (2) $C_U = 0$, $C_L = 4 \times 10^{-2}$ M; (3) $C_U = 2 \times 10^{-2}$ M, $C_L = 4 \times 10^{-2}$ M; (4) $C_U = 4 \times 10^{-2}$ M, $C_L = 4 \times 10^{-2}$ M. C_{Na} is the analytical concentration (M) of the sodium ion; $I = 0.1$ M (maintained constant with (TEA)ClO$_4$).

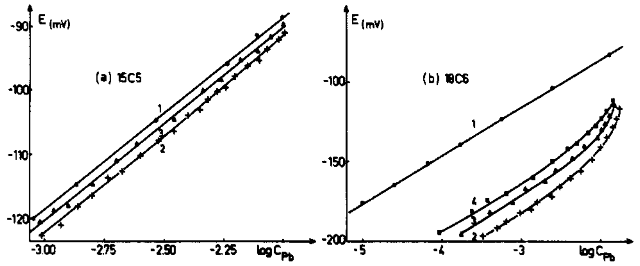

Figure 2. Titration by 3.33×10^{-2} M Pb(ClO$_4$)$_2$ of solutions (20 mL) containing (a) L = 15C5 or (b) L = 18C6: (1) $C_U = 0$, $C_L = 0$; (2) $C_U = 0$, $C_L = 4 \times 10^{-2}$ M; (3) $C_U = 2 \times 10^{-2}$ M, $C_L = 4 \times 10^{-2}$ M; (4) $C_U = 4 \times 10^{-2}$ M, $C_L = 4 \times 10^{-2}$ M. C_{Pb} is the analytical concentration (M) of the lead ion; $I = 0.1$ M (maintained constant with (TEA)ClO$_4$).

selectivity constant. $K_{i/j}^* = (U_i/U_j)K_{i/j}$ where U_i/U_j is the ratio of the individual ionic mobilities in the glass and $K_{i/j}$ the ion-exchange equilibrium constant. Because sodium ion concentration determinations had to be conducted in the presence of H$^+$ as an interfering ion, H$^+$ concentration was simultaneously measured with a H$^+$ glass electrode (HGE) in the potentiometric double cell (I).

PMeV HGE	test soln in H$_2$O (TEA)ClO$_4$, I = 0.1 M	(TEA)ClO$_4$ 0.1 M in H$_2$O	(TEA)Cl 0.1 M in H$_2$O	AgCl	Ag	(I)

Equation 1, where i is Na$^+$ and j is H$^+$, leads to the electromotive force (mV) of the cell (I) with the PMeV electrode:

$$E' = E'^{\circ} + 59.16 \log ([\mathrm{Na}^+] + K_{\mathrm{Na/H}}{}^* a_{\mathrm{H}}/f_{\mathrm{Na}}) \qquad (2)$$

Equation 2 can be written

$$10^{E'/59.16} = 10^{E'^{\circ}/59.16}[\mathrm{Na}^+] + 10^{E'^{\circ}/59.16}(a_{\mathrm{H}}/f_{\mathrm{Na}})K_{\mathrm{Na/H}}{}^* \qquad (3)$$

where E'° is a constant (function of the PMeV standard potential, logarithm of Na$^+$ activity factor, junction potential, and reference electrode potential). All measurements were carried out at a pH value of 3.00 (measured in the cell (I) with the HGE electrode), which was maintained constant by dropwise addition of carbonate-free sodium hydroxide or perchloric acid in a nitrogen atmosphere, leading to a constant value of a_H. f_{Na} is constant (constant ionic strength). In a first study the PMeV response was studied in 10^{-3} to 2×10^{-2} M NaClO$_4$ solutions; the plot of $10^{E'/59.16}$ vs. Na$^+$ concentration is a straight line showing that $K_{Na/H}^*$ is a constant at a constant pH of 3 (curves 1, Figure 1, where the analytical Na$^+$ concentration is equal to the free Na$^+$ concentration). This calibration curve allows us to calculate the free Na$^+$ concentration in the following studies of the complexation of the Na$^+$ and UO$_2$$^{2+}$ ions with 12C4, 15C5, and 18C6. The H$^+$ concentration must be limited in order to obtain an accurate measurement of the free Na$^+$ concentration. A pH value of 3 ensures that the PMeV electrode works properly and that the hydrolysis of UO$_2$$^{2+}$ is avoided. UO$_2$$^{2+}$ does not affect the PMeV potential response.

(b) Pb^{2+} Measurements with the PB1 Electrode. This lead-selective electrode does not give any interference with H$^+$ and UO$_2$$^{2+}$. Curves 1, Figure 2, show that the PB1 electrode potential (E) is a linear function of the logarithm of the free Pb^{2+} concentration (Nernstian slope 29.58 mV) in the range of lead concentration 2×10^{-5} to 2×10^{-2} M. All measurements were carried out at a constant pH of 2.

Spectrophotometric Measurements in PC Solutions. Spectrophotometric measurements were performed with a Cary 17D spectrophotometer with thermostated (25.0 ± 0.1 °C) 20-mm quartz cells. The spectrophotometer was interfaced to a data acquisition system: a Periferic Zip 30 rapid printer and puncher that records the data at each selected wavelength.

Results

Stability Constants of Uranyl Complexes in Aqueous Medium. The determination of the stability constants of the complexes of the uranyl ion by 18C6, 15C5, and 12C4 has been performed by potentiometry. The low solubility of DB-18C6 in water hinders the study of the complexation of the uranyl ion by it in this medium. After the determinations of the calibration curves of the PMeV and the PB1 electrodes, titrations by Na$^+$ or Pb^{2+} of solutions containing U(VI) (0 to 4×10^{-2} M) and crown ether (4×10^{-2} M) were undertaken. Plots of $10^{E'/59.16}$ vs. C_{Na}, Figure 1 (competition with Na$^+$), and plots of E vs. log C_{Pb}, Figure 2 (competition with Pb^{2+}), show some experimental titration curves and allow one to calculate easily the free sodium or lead concentration for each point of the titration curves.

Titration curves for the complexation of 12C4 by Na$^+$ (or Pb^{2+}) with or without UO$_2$$^{2+}$ are the same. The complexation of the uranyl ion by this crown ether is too weak to be measured. Stability constants of the 1:1 complex formed between Na$^+$ (or Pb^{2+}) and the two crown ethers under study (18C6 and 15C5) are calculated from the titration curves obtained without the uranyl ion by the MINIQUAD[20] computer program. For uranyl complexation by 18C6 or 15C5 (L), the general equilibria can be written

$$\begin{gathered} \mathrm{Na}^+ + \mathrm{L} \rightleftarrows \mathrm{NaL}^+ \\ (\text{or: } \mathrm{Pb}^{2+} + \mathrm{L} \rightleftarrows \mathrm{PbL}^{2+}) \\ x\mathrm{UO_2}^{2+} + y\mathrm{L} \rightleftarrows (\mathrm{UO_2})_x\mathrm{L}_y{}^{2x+} \end{gathered} \qquad (4)$$

The stoichiometry of the uranyl complexes and their stability constants (β_{xy}) were determined with the same computer program. The values of these stability constants are given in Table I.

Stability Constants of Uranyl Complexes in PC. The determination of the stability constants of the complexes of the uranyl ion by 15C5, 18C6, DB-18C6, 22, and 222 has been performed by spectrophotometric measurements.

Titrations were directly carried out in the 20-mm spectrophotometric cell. The UV absorption spectra of a 5-mL uranyl solution (~10^{-4} M) to which known amounts of 18C6, 22, and 222 were added (0 to 10^{-3} M) were recorded between 240 and 400 nm. Several typical spectra obtained during titrations are given in Figure 3a,c,d. These ligands show negligible absorbance

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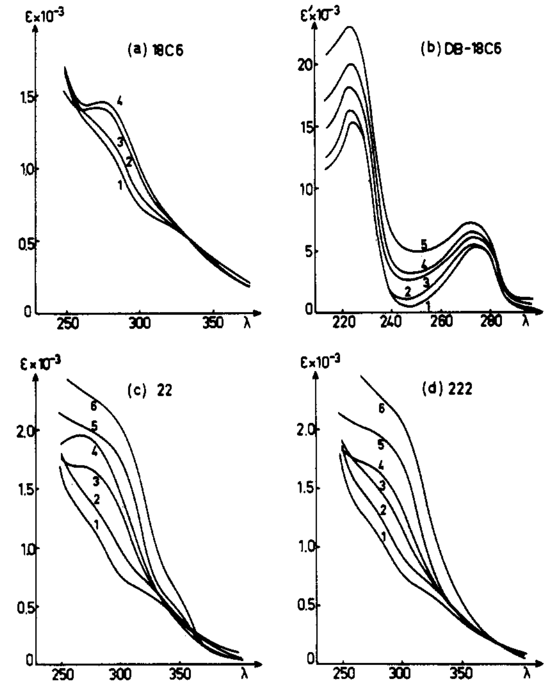

Figure 3. Apparent molar absorption coefficients ε (vs. UO_2^{2+}) and ε′ (vs. DB-18C6) as functions of λ (nm). (a) L = 18C6: titration of 5 mL of 9.132×10^{-5} M $UO_2(ClO_4)_2$ by addition of a solution of L ($C_L = 8.682 \times 10^{-4}$ M). Added volume (mL): (1) 0; (2) 0.15; (3) 0.55; (4) 1.65. (b) L = DB-18C6: solution compositions ($C_L = 2.074 \times 10^{-4}$ M). C_U (M): (1) 0; (2) 2.739×10^{-5}; (3) 7.306×10^{-5}; (4) 1.461×10^{-4}; (5) 2.739×10^{-4}. (c) L = 22: titration of 5 mL of 9.132×10^{-5} M $UO_2(ClO_4)_2$ by addition of a solution of L ($C_L = 5.895 \times 10^{-5}$ M). Added volume (mL): (1) 0; (2) 0.19; (3) 0.46; (4) 0.56; (5) 0.86; (6) 1.66. (d) L = 222: titration of 5 mL of 9.132×10^{-5} M $UO_2(ClO_4)_2$ by addition of a solution of L ($C_L = 9.989 \times 10^{-4}$ M). Added volume (mL): (1) 0; (2) 0.08; (3) 0.18; (4) 0.27; (5) 0.68; (6) 2.28.

in the studied wavelength range. On the other hand, because the crown ether DB-18C6 shows a high absorbance[21] for wavelengths less than 290 nm, a different titration technique had to be employed. The absorbance of a series of solutions containing this ligand at a constant concentration of about 2×10^{-4} M and the uranyl ion in concentrations of 2×10^{-5} to 5×10^{-4} M has been measured in a 1-mm quartz cell between 220 and 300 nm (Figure 3b).

The stoichiometry and the stability constant of the uranyl complexes formed are calculated by applying Sillen's generalized least-squares method in its spectrophotometric version: LETAGROP-SPEFO.[22] Previously the comparison of the treatments of the same spectrophotometric data was done by the LETAGROP-SPEFO program and by an original nonlinear least-squares program, based on the Marquardt method,[23] recently developed in our laboratory by Meullemeestre et al.[24] Results (selected model, stability constants, and molar extinction coefficients of all the species) obtained by these two different methods of calculation are in good agreement. Generally, measurements of absorbance, at 20 different wavelengths, of 25 solutions of various compositions (usually obtained by titration) are simultaneously treated (500 points). Results are given in Table II. The molar extinction coefficients of each complex formed are given in Figure 4.

For the DB-18C6 complex, the stability constant is determined with a larger uncertainty than for the other studied complexes. This result is due to the high and nearly similar values of the molar extinction coefficients of the two compounds DB-18C6 and UO_2–DB-18C6^{2+} (absorption of the benzyl groups). In order to check the selected model (only 1:1 complex) and to obtain a better value of the stability constant, potentiometric measurements were performed.[25] A competitive potentiometric method with Na^+ as an auxiliary ion was undertaken in PC solution in a larger range of DB-18C6 concentrations (as high as 10^{-2} M). The exploitation of the potentiometric results by the MINIQUAD program leads to an only 1:1 complex with a logarithm of stability constant equal to 5.50 ± 0.12 and confirms the results obtained by spectrophotometric measurements.

Table II. Spectrophotometric Determination of Uranyl Complexes in Propylene Carbonate (0.1 M $(TEA)ClO_4$, 25 °C)[a]

ligand	stoichiometry of complex (metal:ligand)	$\log \beta_{xy}(UO_2^{2+})$
18C6	1:1	5.29 ± 0.01
DB-18C6	1:1	5.51 ± 0.31
22	1:1	7.45 ± 0.05
	2:1	14.49 ± 0.05
	1:2	12.40 ± 0.04
222	1:1	7.70 ± 0.10
	2:1	13.10 ± 0.12
	1:2	13.00 ± 0.10

[a] The uncertainty limits are twice the computed standard deviation.

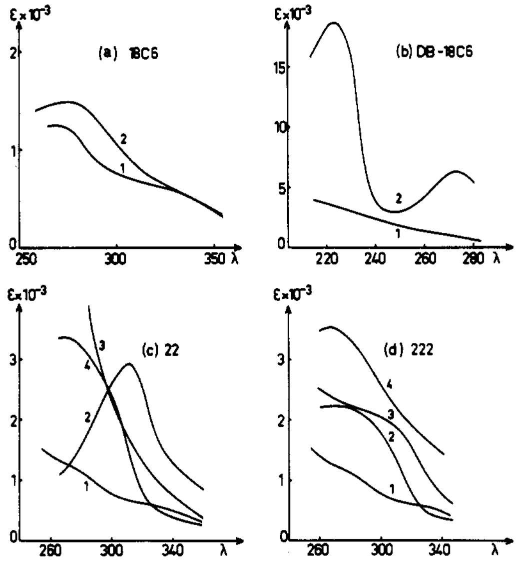

Figure 4. Molar extinction coefficient ε of species where (a) L = 18C6, (b) L = DB-18C6, (c) L = 22, or (d) L = 222: (1) UO_2^{2+}; (2) UO_2L^{2+}; (3) $UO_2L_2^{2+}$; (4) $(UO_2)_2L^{4+}$.

Discussion

22 and 222 Complexes. 22 and 222 do not complex UO_2^{2+} in acidic aqueous solutions (pH ≤3). Under these conditions, the protonation of the amine groups of the ligands and the hydration of the uranyl ion do not allow the complexation of the uranyl ion by both cryptands. At higher pH, the hydrolysis of UO_2^{2+} occurs, leading to the formation of polynuclear species that hinder the complexation with 22 and 222. This result was previously observed by Schwing-Weill and co-workers.[12] In PC, these hindrances do not exist and 1:2, 1:1, and 2:1 complexes (metal:ligand) were observed (Table II). In the absence of experimental evidence, these complexes invite speculation concerning their structure. It is known that cryptands exist as an equilibrium mixture of three conformations,[26] endo–endo, endo–exo, and exo–exo, according

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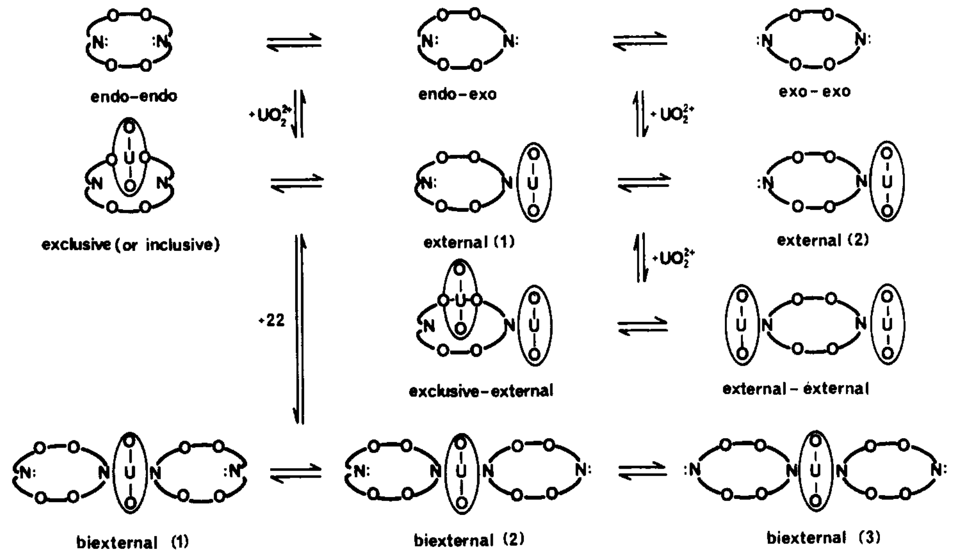

Figure 5. Most probable structures for the complexes of the uranyl ion with the 22 ligand.

to the orientation of the lone electron pair of the N atoms. Thus, we may propose the schemes of the most probable complexes, formed between uranyl ion and 22, with their structure (Figure 5). The 222 complexes will be entirely analogous. These structures are similar to the proposition of Cox and co-workers[27] for Pb^{2+} cryptands. The UO_2^{2+} ion has an elliptic form with axes of 4.7 and 2.8 Å.[28] The cavity diameters of 22 and 222 are 2.8 Å.[29] Therefore it does not seem likely that the uranyl ion can be located completely inside the ligand 222 (or 22) to give an "inclusive" complex. Thus the coordination center is enclosed, is partially enclosed in the ligand cavity ("exclusive" complex), or is outside the ligand ("external" complex). In the "external" complex, the coordinating center interacts with only one N atom of the ligand. These remarks allow us to propose the following: for 1:1 complexes, one "exclusive" or "inclusive" complex and two "external" complexes; for 2:1 complexes, one "exclusive–external" or "inclusive–external" complex and one "external–external" complex; for 1:2 complexes, three "biexternal" complexes. Discussion on cumulative constants of formation (β) of these complexes allows us to speculate on the existence of "exclusive" (or "inclusive") complexes. The stability constants of the three "biexternal" complexes must be identical because the nitrogen atom not bonded to U(VI) has no influence on the stability, and thus they are equal to the constant β_{12} determined experimentally. Then, we can postulate that

$$\beta_{\text{biexternal}(1)} \sim \beta_{\text{biexternal}(2)} \sim \beta_{\text{biexternal}(3)} \sim \beta_{\text{external–external}} \sim \beta_{\text{external}(1)}^2 \sim \beta_{\text{external}(2)}^2 \qquad (5)$$

We may compare the experimental stability constants of 1:1 (β_{11}) and 2:1 (β_{21}) complexes with those of the "external" or of the "external–external" complex, respectively, calculated from our hypothesis. If the experimental value is greater than the calculated one, an "exclusive" (or "inclusive") isomer of the complex must be proposed. Table III gives this comparison and shows that 1:1 complexes can exist as the "exclusive" (or "inclusive") isomer for 22 and 222. For 2:1 complexes an "exclusive–external" complex can be proposed for 22 but not for 222. To form a binuclear complex ("exclusive–external") from a 1:1 "exclusive" (or "inclusive") complex, it is necessary to dissociate the 1:1 complex and to invert one nitrogen to form this 2:1 complex. This transformation seems more difficult for 222 than for 22. The more stable 222 binuclear complex requires both N atoms in exo conformation.

Table III. Comparison between the Experimental and Calculated (with Eq 5) Stability Constants of Uranyl Complexes in Propylene Carbonate

ligand	exptl	calcd
22	$\log \beta_{11} = 7.45$	$\log \beta_{\text{external}} = 6.2$
	$\log \beta_{21} = 14.49$	$\log \beta_{\text{external-external}} = 12.4$
	$\log \beta_{12} = 12.40$	$\log \beta_{\text{biexternal}} = 12.4$
222	$\log \beta_{11} = 7.70$	$\log \beta_{\text{external}} = 6.5$
	$\log \beta_{21} = 13.10$	$\log \beta_{\text{external-external}} = 13.0$
	$\log \beta_{12} = 13.00$	$\log \beta_{\text{biexternal}} = 13.0$

Crown Ether Complexes. In PC, 18C6 and DB-18C6 react with the uranyl ion to give only 1:1 complexes. No complexation was observed in this solvent with 12C4 and 15C5. This effect may be due to the diameter of the cavity of the crown ethers 12C4 (1.2–1.5 Å), 15C5 (1.7–2.2 Å), and 18C6 (2.6–3.2 Å).[29] Thus 12C4 and 15C5 have cavities that are too small to complex the uranyl ion, and it is possible to consider that 18C6 (or DB-18C6) can form with UO_2^{2+} an "exclusive" (or "inclusive") complex such as those formed by 22 or 222. The differences in the stability constants of 1:1 complexes formed between the uranyl ion and 18C6, DB-18C6, 22, or 222 (which have similar cavities) are not those observed for analogous lanthanide complexes.[30] For these studied macrocycles with nitrogen donor atoms, the logarithm of the stability constant of their complexes is always greater than those for the complexes of similar macrocycles with only oxygen donor atoms. However, the differences in stability constants are about 2 logarithm units for uranyl complexes and about 6 or more for lanthanide complexes. This effect could have two origins. On the one hand, it is well-known that the affinities between actinide acceptors and nitrogen donors are small and the bonding forces operating between actinide ions and the oxygen donor atoms of ligands are stronger than those for other metals. On the other hand, for the 1:1 complexes of UO_2^{2+}, we can postulate the existence of the formation of only one "exclusive" (or "inclusive") complex with 18C6 (or its derivative) and two "exclusive" (or "inclusive") and "external" complexes in equilibrium with 222 (or 22). These two UO_2–222^{2+} (or –22) isomers appear to be less stable overall than a single "exclusive" or ("inclusive") complex. In conclusion, in PC solution, the nonexistence of a 1:1 complex with 15C5 and 12C4 and of a 1:2 or 2:1 complex with 18C6

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confirms the formation of the 18C6 (or DB-18C6) complex with a single "exclusive" (or/and "inclusive") isomer with direct uranyl–macrocycle bonds.

In aqueous solutions the solvation of UO_2^{2+} is much more important and cannot be neglected. The existence of weak 1:1 complexes and 1:2 complexes with 18C6 and 15C5 seems to indicate that coordination occurs by hydrogen bond formation between hydrogens of water molecules of the hydrate shell of the uranyl ion and oxygen atoms of the crown ether. The 1:2 complexes formed could be "sandwich" type[31] with hydrogen bond intervention. These propositions agree with certain previous publications concerning the solid-state structure, which also propose hydrogen bond formation between water molecules coordinated in the equatorial plane of the uranyl ion and oxygen of the crown ether ligands.[8-10]

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Copper(II) Complexes of 2-(Trifluoromethyl)-L-histidine in Aqueous Solution[1]

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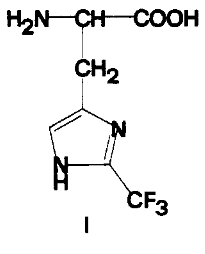
The coordination structures of various binary and ternary complexes of copper(II) and 2-(trifluoromethyl)-L-histidine have been investigated by circular dichroism and compared to the structures of the corresponding complexes of L-histidine. It has been found that 2-(trifluoromethyl)-L-histidine exhibits an exclusive tendency to assume a glycine-like mode of coordination in any binary or ternary system, even those where L-histidine largely prefers to bind histamine-like. This feature has been referred to the strong steric repulsion exerted by the 2-trifluoromethyl substituent of the imidazole ring in the copper equatorial plane, when the amino acid is bound histamine-like, toward any donor group in cis position. In acid medium the 2-(trifluoromethyl)-L-histidine ligand binds as bidentate and contains a protonated imidazole ring, while at neutral pH it binds as tridentate. Apical chelation to copper(II) by the imidazole group is characterized by weak CD activity near 350 and 230 nm (about 1 order of magnitude less intense than that corresponding to equatorial imidazole binding) that is assigned to Im(π_1) → Cu(II) and Im(σ) → Cu(II) LMCT, respectively. The third LMCT transition originating from the imidazole ring occurs in the same range as the LMCT transitions from amino and carboxylate groups and cannot be localized with certainty in the CD spectra.

Introduction

We have recently investigated the coordination structures of the major species existing in various pH ranges of the systems copper(II)–L-histidine (1:2),[2] copper(II)–L-N^{τ}-methylhistidine (1:2),[3] and copper(II)–L-N^{α},N^{α}-dimethylhistidine (1:2)[3] using CD spectroscopy. These studies complement previous investigations on copper(II)–L-histidine and related systems performed with various spectroscopic and potentiometric techniques,[4-9] since CD can easily differentiate the two basic coordination modes of L-histidine residues when apical binding to the metal by the donor atom on the side chain can occur.[10] However, as is usually the case when a potentially tridentate ligand binds a metal ion,[11] the physiologically important,[12] neutral bis(L-histidinato)copper(II) complex exists in solution as an equilibrium mixture of isomeric species and it is difficult to relate the CD features to the individual species. In order to gain an understanding of how each of these species contributes to the CD spectrum, we are extensively investigating the chiroptical properties of ternary systems containing L-histidine as well as those of systems containing appropriate derivatives of this amino acid. By introducing bulky substituents into the L-histidine molecule, we anticipate that a marked preference for a single species at the equilibrium can be imposed, thereby simplifying the appearance and interpretation of the corresponding CD spectrum. In this paper we present an investigation of the CD spectra of the binary systems of copper(II) and 2-(trifluoromethyl)-L-histidine (I) in various pH ranges, together with several related ternary systems at neutral pH. To our knowledge copper(II) complexes of 2-(trifluoromethyl)-L-histidine are reported here for the first time.



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