Conclusion

The variation of the ^{7}Li chemical shift of $[Li.C21C_5]^+$ with the nature of the solvent is consistent with significant proportions of this cryptate being in the exclusive form in solution despite its existence in the inclusive form in the solid state. The stability constants characterizing $[Li.C21C_5]^+$ are smaller than those of $[Na.C21C_5]^+$, which is also consistent with the former cryptate existing substantially in the exclusive form. The exchange of Li^+ on $[Li.C21C_5]^+$ proceeds through a monomolecular mechanism, and the decomplexation rate constant, k_d, increases with solvent D_N, consistent with increasingly strong solvation of the transition state producing decreases in ΔG_d^* for decomplexation.

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Complexation of the Uranyl Ion (UO_2^{2+}) with Phenylene-1,2-dioxydiacetic Acid

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Complexation of uranyl cations by phenylene-1,2-dioxydiacetic acid has been studied by potentiometry, calorimetry, solvent extraction, and ^{1}H NMR spectroscopy. Complexation parameters at 298 K and 0.1 M ($NaClO_4$) ionic strength are as follows: $\log \beta_{101} = 3.01 \pm 0.05$; $\log \beta_{111} = 5.22 \pm 0.04$; $\Delta H_{101} = 16.8 \pm 0.2$ kJ mol^{-1}; $\Delta S_{101} = 114 \pm 5$ J K^{-1} mol^{-1}; $\Delta H_{111} = 10.4 \pm 0.5$ kJ mol^{-1}; $\Delta S_{111} = 68 \pm 5$ J K^{-1} mol^{-1}. The thermodynamic and NMR data are consistent with bonding of UO_2^{2+} to the carboxylate groups of the ligand, with weak or no interaction with the ether oxygens. No 1:2 complexation was observed.

Introduction

Earlier studies[1,2] from this laboratory of the complexation of trivalent lanthanides by phenylene-1,2-dioxydiacetic acid showed that the ether oxygens are involved in the tetradentate chelation. The nuclear magnetic resonance study[2] of the complexes in solution provided evidence for strong bonding of the ether oxygens to the lanthanide ions in the 1:1 complex but weaker bonding and longer metal–ether oxygen distances in the 1:2 complex. In the present work potentiometry, solvent extraction, nuclear magnetic resonance spectroscopy, and calorimetry have been employed to study the complexation between the uranyl cation (UO_2^{2+}) and phenylene-1,2-dioxydiacetic acid. The data on uranyl complexation are compared to those on lanthanide complexation to clarify the effects of cationic charge and of the steric interactions imposed by the linear structure of the uranyl cation.

Experimental Section

Reagents. Phenylene-1,2-dioxydiacetic acid (PDOA), from Aldrich Chemical Co., was recrystallized twice from water. For the potentiometric titrations and the solvent extraction experiments, a stock solution of 0.02 M was prepared by dissolving the purified compound in 0.01 M NaOH. The pH of the stock solution ranged from 2.5 to 3.5. Working solutions were made by dilution of the stock solution with appropriate amounts of $NaClO_4$ solution to obtain an ionic strength of 0.10 M. For the nuclear magnetic resonance experiments, all solutions were prepared in D_2O and the stock solution of PDOA was prepared by dissolving it in NaOD.

The stock solution of uranyl perchlorate was prepared from reagent grade $UO_2(ClO_4)_2(H_2O)_6$ (Aldrich Chemical Co.) and was standardized by spectrophotometry.[3] In the solvent extraction experiments, the stock solution of ^{233}U tracer was prepared from high-purity $^{233}UO_2$ (Oak Ridge National Laboratory) by dissolution in fuming HNO_3, evaporation to dryness, and redissolution in $HClO_4$.

The extracting agent was dinonylnaphthalenesulfonic acid, HDNNS, from R. T. Vanderbilt Co., and was used without further purification. The stock solution of HDNNS was standardized by following the procedures described in an early work.[4] The heptane solutions used for extraction study were prepared at the desired concentrations by dilution of the stock solution.

Ecolume (ICN Radiochemicals) was used as the scintillation solution for counting the α-radioactivity of ^{233}U on a Packard Tri-Carb 4000 Series liquid scintillation counter.

Procedures. Potentiometric titrations were performed in a glass vessel jacketed to allow a flow of water from a water bath to maintain the temperature at 25.0 ± 0.1 °C. The hydrogen ion concentration was measured with a Corning 130 pH meter equipped with a Corning combination electrode.

Solvent extraction was carried out by using the methods described in previous publications.[5] Aqueous solutions (5 mL) of PDOA, in concentrations ≤0.02 M, plus $^{233}UO_2^{2+}$, at tracer concentrations, were equilibrated with equal volumes of heptane solutions of HDNNS. After overnight equilibration at 25.0 °C in a water bath, the phases were separated. Aliquots of 1.00 mL were taken from each phase and mixed with 5 mL of Ecolume for counting the radioactivity.

The NMR measurements were performed on the Bruker 270-MHz spectrometer of the FSU NMR Laboratory on samples prepared by mixing weighed amounts of uranyl perchlorate and PDOA/D_2O solutions. The pD of these samples was adjusted with NaOD solution to about 4.2. Sodium 2,2-dimethyl-2-silapentanesulfonate (DSS) was used as an internal standard.

Calorimetric titrations were performed by using a calorimeter and by techniques that have been described previously.[6] The titration was duplicated in a beaker outside the calorimeter to measure the pH values after each addition of titrant. The titrations were done with the $UO_2(ClO_4)_2$ solution (ca. 5 mM) in the calorimeter cup and with the ligand buffer solution (ca. 12 mM) as the titrant. The corrections for the heats of dilution of the metal and the ligand were determined in separate runs. Values of the enthalpies of protonation for the PDOA ligand from ref 2 were used in the calculations.

Data Analysis. The proton dissociation constants of PDOA were calculated from the potentiometric titration data by least-squares methods using the equation

$$\frac{\bar{n}_H}{(1-\bar{n}_H)[H^+]} = \frac{1}{K_{a2}} + \frac{1}{K_{a1}K_{a2}}\,\frac{(2-\bar{n}_H)[H^+]}{1-\bar{n}_H} \qquad (1)$$

where $\bar{n}_H$ is the average number of ionizable hydrogen atoms bound per ligand anion and K_{a1} and K_{a2} are the first and second acid dissociation constants, respectively.

The linear least-squares method was used for calculation of the stability constants of the metal complexes (β_{101} for ML and β_{102} for ML_2) from the potentiometric titration data according to the equation[7]

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_{101} + \frac{(2-\bar{n})}{1-\bar{n}}\beta_{102}[L] \qquad (2)$$

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Table I. pK_a Values of Phenylene-1,2-dioxydiacetic Acid (I = 0.10 M (NaClO$_4$), T = 298 K)

pK_{a1}	pK_{a2}	ref
2.56 ± 0.10	3.47 ± 0.05	pw[a]
2.70	3.40	1
2.40	3.45	7

[a] pw = present work.

Table II. pH Titration Data for the UO_2^{2+}–Phenylene-1,2-dioxydiacetate System[a] (I = 0.10 M (NaClO$_4$), T = 298 K)

vol of titrant, mL	pH	10^4[L], M	$\bar{n}$
0	3.061	0	0
0.5	3.009	0.469	0.045
1.0	2.974	0.958	0.074
1.5	2.950	1.390	0.102
2.0	2.934	1.805	0.127
2.5	2.922	2.201	0.149
3.0	2.914	2.587	0.170
3.5	2.908	2.921	0.193
4.0	2.903	3.314	0.209
4.5	2.899	3.655	0.228
5.0	2.898	4.023	0.244
5.5	2.897	4.374	0.259
6.0	2.896	4.709	0.275
6.5	2.896	5.053	0.289
7.0	2.895	5.348	0.306
7.5	2.895	5.668	0.319
8.0	2.895	5.972	0.334
8.5	2.894	6.241	0.350
9.0	2.894	6.520	0.364
9.5	2.894	6.792	0.379
10.0	2.894	7.055	0.393

[a] Initial volume = 20.0 mL; $C^\circ_{UO_2}$ = 5.075 × 10^{-3} M; titrant 0.020 M NaPDOA.

where $\bar{n}$ denotes the Bjerrum formation function and [L] is the concentration of the ligand anion.

Methods described in an early publication[8] were used to process the data obtained by solvent extraction to determine stability constants β_{101} and β_{111} for ML and MHL complexes, respectively. A distribution coefficient is defined as

$$D = [M]_o/[M]_a \tag{3}$$

With the assumption of the presence of ML and MHL species in the aqueous phase, this is expanded to

$$D = [M]_o/([M]_a + [ML]_a + [MHL]_a)$$

where L is the complexing anion. This equation can be rewritten as

$$\begin{aligned} D &= [M]_o/([M]_a + \beta_{101}[M]_a[L]_a + \beta_{111}[M]_a[H][L]_a) \\ &= [M]_o/\{[M]_a(1 + \beta_{101} + \beta_{111}[H][L])\} \end{aligned} \tag{4}$$

At constant pH, β_{app} is defined as

$$\beta_{app} = \beta_{101} + \beta_{111}[H] \tag{5}$$

and

$$\begin{aligned} D &= [M]_o/\{[M]_a(1 + \beta_{app}[L])\} \\ &= D_0/(1 + \beta_{app}[L]) \end{aligned} \tag{6}$$

where D_0 is the distribution coefficient in the absence of the complexing ligand. Equation 6 can be rearranged into

$$1/D = 1/D_0 + (\beta_{app}/D_0)[L] \tag{7}$$

From the dependence of $1/D$ on ligand concentration at constant pH, β_{app} can be obtained. These values from experiments with [H$^+$] are used to calculate values of β_{101} and β_{111} from eq 5.

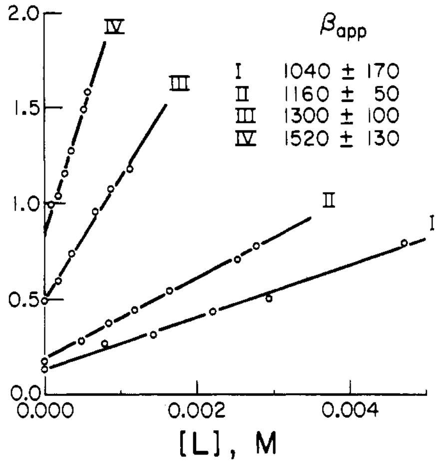

Figure 1. $1/D$ vs [L^{2-}] for UO_2^{2+}–phenyl-1,2-dioxydiacetate complexation at various pH's: (I) 3.20; (II) 2.85; (III) 2.70; (IV) 2.50. The values of β_{app} from each experiment are also listed.

Table III. Stability Constants for the UO_2^{2+}–PDOA System (I = 0.10 M (NaClO$_4$), T = 298 K)

A. Potentiometry

log β_{101}	2.9 ± 0.1

B. Solvent Extraction

	set 1	set 2	av
log β_{101}	2.96 ± 0.01	3.06 ± 0.01	3.01 ± 0.05
log β_{111}	5.19 ± 0.03	5.26 ± 0.03	5.22 ± 0.04
log $\beta_{1(11)}$			1.75 ± 0.09

The method of analysis of the calorimetric titration data has been described previously.[9] The experimental heat, Q_{exp}, was composed of several heat effects: the enthalpy of complexation (ΔH_{101} and ΔH_{111}), the enthalpy of dilution (ΔH_{dil}), and the enthalpies of protonation (ΔH_{011} and ΔH_{021}). Enthalpies of complexation were computed by correcting the observed heat changes for metal and ligand heats of dilution and for ligand protonation.

Results

Potentiometry. The proton dissociation constants of PDOA determined by potentiometry are listed in Table I and compared with the values from the literature.

Table II is a typical set of pH data for the titration of the UO_2^{2+} solution by a solution of phenylene-1,2-dioxydiacetate. The linear correlation between $\bar{n}/\{(1 - \bar{n})[L]\}$ and $(2 - \bar{n})[L]/(1 - \bar{n})$ is not particularly satisfying, providing only a rough value of log β_{101} of 2.9. Under the present experimental conditions ($\bar{n} \leq 0.39$), no significant formation of the second complex was observed.

Solvent Extraction. Distribution studies were carried out at pH 2.50, 2.70, 2.85, and 3.20. A typical set of results are shown in Figure 1. The linear correlation between $1/D$ and [L] suggests that there were no higher complexes (ML$_2$, M(HL)$_2$, etc.) formed under the experimental conditions (the values of $\bar{n}$ ranged from 0.19 to 0.84). The values of β_{app} obtained from these experiments were analyzed as a function of hydrogen ion concentration to obtain the stability constants. Duplicate sets of distribution experiments were conducted. The calculated stability constants, β_{101} and β_{111}, are listed in Table III where

$$\beta_{101} = [ML]/([M][L]) \tag{8a}$$

$$\beta_{111} = [MHL]/([M][H][L]) \tag{8b}$$

$$\beta_{1(11)} = [MHL]/([M][HL]) \tag{8c}$$

Nuclear Magnetic Resonance Data. Three proton resonances were observed at 4.51, 6.86, and 6.94 ppm (downfield from DSS) for the phenylene-1,2-dioxydiacetate anion in solution. Additions of UO_2^{2+} caused downfield shifts for the resonances of both H-1 and H-2, with the former shifted more significantly. On the contrary, no obvious change in chemical shift for H-3 was observed even when the ratio of C_M/C_L was increased to the value of 1.0. These trends are shown in Figure 2. The limiting shifts for the phenylene-1,2-dioxydiacetate complexes of UO_2^{2+} and La^{3+} are compared in Table IV.

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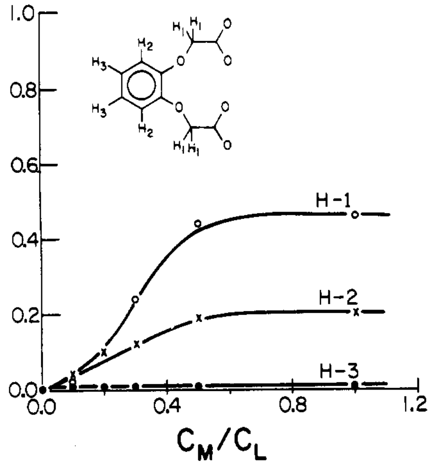

Figure 2. Variation of chemical shift for the protons of phenylene-1,2-dioxydiacetate with the ratio of toal UO_2^{2+} and ligand concentration.

Table IV. Limiting Shifts for Phenylene-1,2-dioxydiacetate Complexes of UO_2^{2+} and La^{3+}

metal	complex	Δδ, ppm H-1	H-2	H-3	ref
UO_2^{2+}	ML	0.46	0.20	0.01	pw[a]
La^{3+}	ML	0.29	0.27	0.21	2
	ML_2	0.28	0.26	0.20	2

[a] pw = present work.

Table V. Calorimetric Titration Data for UO_2^{2+}–Phenylene-1,2-dioxydiacetate[a] (I = 0.10 M ($NaClO_4$), T = 298 K)

$V_{titrant}$, mL	$-\sum Q_{obs}$,[b] mJ	$-\sum Q_c$,[c] mJ	10[ML], mM	10[MHL], mM	$\bar{n}$
0.5	34.2	48.9	0.5182	0.0925	0.012
1.0	66.4	94.4	0.9858	0.1848	0.024
1.5	97.0	137.2	1.4132	0.2755	0.035
2.0	126.3	177.6	1.8048	0.3642	0.046
2.5	154.2	216.1	2.1696	0.4501	0.056
3.0	180.6	252.1	2.5069	0.5334	0.065
3.5	207.1	287.8	2.8245	0.6135	0.074
4.0	232.8	322.2	3.1218	0.6907	0.083
4.5	256.0	354.8	3.4019	0.7649	0.092
5.0	280.0	387.0	3.6734	0.8356	0.100
5.5	304.0	418.4	3.9271	0.9036	0.109
6.0	326.6	448.3	4.1637	0.9691	0.116
6.5	349.2	477.4	4.3917	1.0317	0.124
7.0	371.3	506.3	4.6129	1.0911	0.132
7.5	393.0	534.4	4.8210	1.1483	0.139
8.0	414.1	562.0	5.0253	1.2025	0.146
8.5	434.5	588.1	5.2094	1.2552	0.153
9.0	455.4	614.7	5.3915	1.3050	0.160
9.5	475.5	640.3	5.5634	1.3528	0.167
10.0	495.1	665.0	5.7255	1.3987	0.173

[a] Experimental conditions: cup solution $[UO_2^{2+}] = 4.936 \times 10^{-3}$ M, V = 50.0 mL, $C_H = 1.047 \times 10^{-3}$ M; titrant C_L = 0.01205 M, $C_H = 1.037 \times 10^{-3}$ M. [b] Heat corrected for dilution. [c] Heat corrected for ligand deprotonation.

Calorimetry. Table V is a typical set of calorimetric titration data. On the basis of the potentiometric titration and solvent extraction data, which showed no higher complexes, the corrected heat, Q_c, is assumed to be associated with the formation of the amount of ML (column 4) and of MHL (column 5) according to the following equation:

$$-Q_c = \Delta n_{ML}\Delta H_{101} + \Delta n_{MHL}\Delta H_{111} \qquad (9)$$

A plot of $-Q_c/\Delta n_{ML}$ vs $\Delta n_{MHL}/\Delta n_{ML}$ gives ΔH_{101} and ΔH_{111} as the intercept and the slope, respectively. Since the increase in the amount of MHL after each addition of titrant was relatively small, the value of ΔH_{111} calculated has a slightly larger error than that of ΔH_{101}. From the plot shown in Figure 3, the values of ΔH_{101} and ΔH_{111} were calculated to be 16.8 ± 0.2 kJ mol^{-1} and 10.4 ± 0.5 kJ mol^{-1}, respectively.

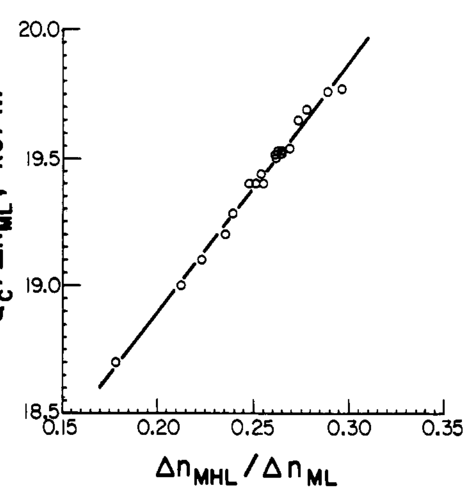

Figure 3. $-Q_c/\Delta n_{ML}$ vs $\Delta n_{MHL}/\Delta n_{ML}$ for the UO_2^{2+}–phenylene-1,2-dioxydiacetate system.

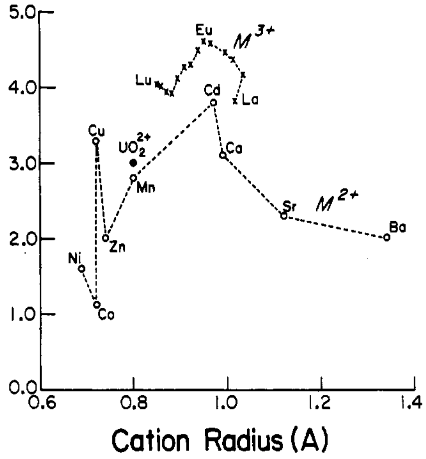

Figure 4. Relationship between cationic radius and log β_{101} for divalent cations (○), trivalent lanthanides (×), and uranyl (●) with phenylene-1,2-dioxydiacetate.

Discussion

Earlier studies have shown that the values of log β_{101} of the complexes of phenylene-1,2-dioxydiacetate with divalent[7] and trivalent[1] cations exhibit a maximum for cation radii between 0.9 and 1.0 Å. This trend is shown in Figure 4 and was interpreted as due to the steric rigidity of the ligand, which favors cations of this size. The value for UO_2^{2+}–phenylene-1,2-dioxydiacetate is greater than the divalent cation curve but less than the trivalent cation curve. Normally, UO_2^{2+} forms stronger complexes than trivalent lanthanides, which has been attributed to its higher effective charge.[10] The weakened complexation could be explained by the steric hindrance in UO_2^{2+}–phenylene-1,2-dioxydiacetate complexation. As previously mentioned, the spherical lanthanide cations were found by NMR study to be bonded in the 1:1 complex to both of the carboxylate groups and to the ether oxygens. However, in the case of UO_2^{2+}–phenylene-1,2-dioxydiacetate complexation, close approach of the uranium atom to the ether oxygens might be hindered by the rigidity of the phenylene-1,2-dioxyacetate molecule and the linear configuration of the UO_2^{2+} cation. As a result, the UO_2^{2+} cation would be bonded only to the two carboxylate groups and the complexation between UO_2^{2+} and phenylene-1,2-dioxydiacetate is accordingly weaker.

Comparison of the limiting chemical shifts for phenylene-1,2-dioxydiacetate complexes of UO_2^{2+} and La^{3+} can provide further insight into the structure of the complex. In the 1:1 and 1:2

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Table VI. Thermodynamic Parameters of Complexation of Dicarboxylate Ligands and UO_2^{2+} (T = 298 K)

ligand		I, M	$-\Delta G$, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, J K^{-1} mol^{-1}	ref
phenylene-1,2-dioxydiacetate	ML	0.1	17.1 ± 0.3	16.8 ± 0.2	114 ± 5	pw[a]
	ML	1.0	14.9 ± 0.3	15.8 ± 0.2	103 ± 5	est[a]
	MHL	0.1	10.0 ± 0.2	10.4 ± 0.5	68 ± 5	pw
thiodiacetate	ML	1.0	16.9	14.6	105	11
malonate	ML	1.0	30.9	8.8	134	14
succinate	ML	1.0	22.0	21.8	146	15
	MHL	1.0	13.0	10.0	77	15
diglycolate	ML	1.0	29.2	16.7	155	12
ethylenedioxydiacetate	ML	1.0	17.6	26.8	151	13

[a] pw = present work. est = estimated.

complexes of La^{3+}–phenylene-1,2-dioxydiacetate, the limiting shifts for all the three types of proton are similar while a pattern of $\Delta\delta$(H-1) > $\Delta\delta$(H-2) > $\Delta\delta$(H-3) is observed for the uranyl complex. The simplest interpretation is that the pattern reflects the pattern of the U--H distances with significant differences between the latter. This interpretation supports the argument that UO_2^{2+} does not bond to the ether oxygens.

In lanthanide complexation, the stability constants of the 1:2 complex (ML_2) were obtained and its structure in solution, as deduced from NMR data, has the two phenylene-1,2-dioxydiacetate ligands in perpendicular planes with decreased Ln--O(ether) interaction. The linear configuration of the UO_2^{2+} cation would interfere with such a ligand structure and could explain our failure to measure the formation of a 1:2 complex.

Table VI compares the thermodynamic parameters of complexation of some mono- and dicarboxylate ligands with UO_2^{2+}. Our phenylene-1,2-dioxydiacetate data were obtained in ionic media of 0.1 M. In order to allow comparison with the data on other complexes in Table VI, which were for 1.0 M ionic medium, our data were adjusted to 1.0 M ionic strength as follows. On the basis of available literature data[16] of ΔG and ΔH at different ionic strengths (0.1 and 1.0 M) for the complexes between UO_2^{2+} and several dicarboxylate ligands as well as diacetate ligands, we estimate ΔG_{101} at I = 1.0 M to be 2.2 kJ mol^{-1} more positive than ΔG_{101} at I = 0.1 M (this corresponds to a difference in log β_{101} of 0.40 unit) and ΔH_{101} at I = 1.0 M is estimated to be 1 kJ mol^{-1} less than ΔH_{101} at I = 0.1 M. These estimated values of ΔG_{101} and ΔH_{101} are used to obtain ΔS_{101} at I = 1.0 M. Extensive comparison of the ΔH_{111} and ΔS_{111} values among those dicarboxylic acids is not feasible, since there are not sufficient data on MHL formation between UO_2^{2+} and those ligands. However, the available literature data on MHL formation between UO_2^{2+} and succinic acid are in agreement with those between UO_2^{2+} and PDOA in the present work, as indicated in Table VI.

The ΔS_{101} and ΔH_{101} values for 1:1 complexes of phenylene-1,2-dioxydiacetate (estimated) and thiodiacetate are quite similar and suggest that the net structural and dehydrational effects may be rather similar in these complexes. It was pointed out by Hasegawa and Choppin[1] that, in the complexation of lanthanides by thiodiacetate, the interaction with the sulfur atom must be negligible. Accordingly, it is very likely that UO_2^{2+} does not interact with the S atom in the UO_2^{2+} thiodiacetate complex. The similarity in the entropy and enthalpy changes for 1:1 complexation with phenylene-1,2-dioxydiacetate and thiodiacetate further supports the argument that UO_2^{2+} does not bond to the ether oxygens or to the sulfur in these ligands.

The enthalpy changes for other dicarboxylate complexations are difficult to compare with that of the phenylene-1,2-dioxydiacetate complexation because of variations in the basicities of the carboxylate groups. However, the entropy changes are much less dependent on such effects and, primarily, reflect dehydration and chelate ring lengths.[17] Thus, malonate (6-membered ring) and succinate (7-membered ring) complexation have higher values of ΔS_{101} than does the phenylene-1,2-dioxydiacetate (11-membered ring) complexation. The diglycolate value of 155 J K^{-1} is the highest, which probably reflects the involvement of the α-oxygen to form two 5-membered chelate rings.

The entropy change for UO_2^{2+}–ethylenedioxydiacetate complexation is 151 J K^{-1} mol^{-1}. This suggests that, besides the two carboxylate groups, the two ether oxygens in this ligand might also interact with UO_2^{2+}, resulting in a higher degree of chelation, which causes a larger net structural effect. This is not unreasonable because the ethylene group in ethylenedioxydiacetate is not as rigid as the phenylene group in phenylene-1,2-dioxydiacetate. The energy barrier for the rotation of the ethylene C–C bond is not high, and the two carboxylate groups may not be in the same plane in the complex. This would reduce the steric hindrance for UO_2^{2+} complexation with the ether oxygens in ethylenedioxydiacetate. If this is true, the tendency of forming the 1:2 UO_2^{2+}–ethylenedioxydiacetate complex should be higher than that of the 1:2 UO_2^{2+}–phenylene-1,2-dioxydiacetate complex. Unfortunately, data for the former complex are not available in the literature.

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