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Solution Chemistry of Uranyl Ion with Iminodiacetate and Oxydiacetate: A Combined NMR/EXAFS and Potentiometry/Calorimetry Study

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The solution chemistry of uranyl ion with iminodiacetate (IDA) and oxydiacetate (ODA) was investigated using NMR and EXAFS spectroscopies, potentiometry, and calorimetry. From the NMR and EXAFS data and depending on stoichiometry and pH, three types of metal:ligand complex were identified in solution in the pH range 3–7: 1:1 and 1:2 monomers; a 2:2 dimer. From NMR and EXAFS data for the IDA system and previous studies, we propose the three complex types are $[UO_2(IDA)(H_2O)_2]$, $[UO_2(IDA)_2]^{2-}$, and $[(UO_2)_2(IDA)_2(\mu\text{-}OH)_2]^{2-}$. From EXAFS spectroscopy, similar 1:1, 2:2, and 1:2 complexes are found for the ODA system, although ^{13}C NMR spectroscopy was not a useful probe in this system. For the 1:1 and 1:2 complexes in solution, EXAFS spectroscopy is ambiguous because the data can be fitted with either a long $U–N/O_{ether}$ value (ca. 2.9 Å) suggesting 1,7-coordination of the ligand or a U–C interaction at a similar distance, consistent with terminal bidentate coordination. However, the NMR data of the IDA system suggest that 1,7-coordination is the more likely. The stability constants of the three complexes were determined by potentiometric titrations; the log β values are $9.90 \pm {}^{0.08}_{0.09}$, $16.42 \pm {}^{0.14}_{0.21}$, and $10.80 \pm {}^{0.15}_{0.22}$ for the 1:1, 1:2, and 2:2 uranyl–IDA complexes, respectively, and $5.77 \pm {}^{0.20}_{0.36}$, $7.84 \pm {}^{0.28}_{0.63}$, and $4.29 \pm {}^{0.27}_{0.90}$ for the 1:1, 1:2, and 2:2 uranyl–ODA complexes, respectively. The thermodynamic constants for the complexes were calculated from calorimetric titrations; the enthalpy changes (kJ mol^{-1}) and entropy changes (J K^{-1} mol^{-1}) of complexation for the 1:1, 1:2, and 2:2 complexes respectively are the following. IDA: 12 ± 2, 230 ± 8; 8 ± 2, 151 ± 9; -33 ± 3, -283 ± 11. ODA: 26 ± 2, 198 ± 12; 20 ± 2, 106 ± 8; -24 ± 2; -219 ± 8.

Introduction

The solution chemistry of uranyl ion with carboxylate ligands has been studied using a number of different methods including potentiometry, calorimetry, and NMR spectroscopy.[1−8] EXAFS has also been used to study the solution chemistry of uranyl ion with a variety of ligands including water, carbonate, chloride, fluoride, and sulfate[9−16] although

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systems involving carboxylate ligands have been less extensively studied.[17−19] On the basis of NMR, EXAFS, and other spectroscopic results, a variety of structures have been proposed for uranyl−carboxylate complexes in aqueous solution, including dimers and trimers, with the carboxylate ligands acting both as terminal and bridging ligands and coordinating through one or both O atoms in the carboxylate group.[20−24] For example, Kakihana et al.[25] studied the interaction of uranyl ion with several carboxylic acids in aqueous solution using NMR and IR spectroscopies. They proposed that, in their system, acetate and tricarballylate coordinate to uranyl through both O atoms in the carboxylate groups, while glycolate, lactate, tartrate, and citrate coordinate through one O atom from each carboxylate group and the O atom from the alcohol groups. Allen et al.[18] suggested the formation of a dimeric complex in uranyl−tartrate systems, with the ligands coordinating to each uranyl ion through one carboxylate oxygen and the α-hydroxyl groups bridging between the metal centers.

The interactions of uranyl with iminodiacetic acid (H_2IDA) and oxydiacetic acid (H_2ODA) have previously been studied to some extent;[2,26−29] 1:1 chelates have been proposed, and the relatively high values of the formation constants suggest tridentate coordination of the ligands through the two carboxylate groups and the central nitrogen or oxygen atom.[26] However, there have been no detailed NMR or EXAFS studies of the aqueous chemistry of these ligands with uranyl. Here we report the spectroscopic characterization of uranyl−IDA/ODA complexes in solution and determination of solution thermodynamic parameters.

Experimental Section

Chemicals. Aqueous uranyl nitrate (BDH AR grade) solutions were prepared and standardized using ICPOES. Aqueous solutions of H_2IDA (Aldrich, AR grade) and H_2ODA (Lancaster, AR grade) were standardized potentiometrically with standard carbonate-free NaOH. Buffered ligand solutions were obtained by exact neutralization of calculated amounts of acid with standard carbonate-free NaOH (Fisher, AR grade) standardized against potassium hydrogen phthalate (Aldrich, ACS acidimetric standard). All solutions used in potentiometry and calorimetry were adjusted to an ionic strength of 0.1 M using sodium perchlorate (BDH, AR grade) as the background electrolyte.

The ^{15}N-labeled H_2IDA used in ^{15}N NMR was prepared from ^{15}N-labeled glycine (Sigma & Aldrich, 98 atom %) and chloroacetic acid (Lancaster) and separated from other species by cation exchange (Amberlite IR-120, hydrogen form, 1.5 × 70 cm).[30] The product was purified by recrystallization from water and characterized. Anal. Found: C, 36.00; H, 5.29; N, 10.53. Calcd for $C_4H_7{}^{15}NO_4$: C, 35.82; H, 5.22; ^{15}N, 11.19%). Mass spectrometry (*m*/*z*): 133, 100%; 134, 4%; 267, 5%. Mass spectrometry for commercial H_2IDA from Aldrich (*m*/*z*): 132, 100%; 133, 5%; 265, 3%. ^{13}C NMR: 50.167 and 172.125 ppm. ^{15}N NMR: see later, Figure 1a. D_2O (Fluorochem Limited, 99.9 atom % D) was used as solvent in all ^{13}C and ^{15}N NMR experiments, and pH was adjusted with NaOD (Sigma, 99+ atom % D) or DCl (Aldrich, 99.5 atom % D) solutions.

Procedures. NMR Spectroscopy. All samples were prepared by adding the required amount of NaOD or DCl to the IDA (or ^{15}N-labeled IDA) ligand, mixing thoroughly, and then adding the required amount of uranyl solution in this order, to prevent precipitation. The concentration of uranyl was 0.107 M where it was used. The concentration of ligand was 0.107 or 0.214 M as required. The pH values were measured using a UNICAM 9460 ion-selective meter and a Mettler-Toledo InLab40 combination pH electrode. The values reported are direct meter readings without correction for deuterium isotope effects. The ^{1}H NMR spectra were measured using a Bruker Avance 400 MHz spectrometer and referenced to internal dimethyl sulfoxide (δ = 2.71 ppm relative to TMS δ = 0.00 ppm). For low-temperature spectra 4% pure methanol in methanol-d_4 was used to calibrate the temperature to within ±0.1 K.[31] The ^{13}C NMR (referenced externally to TMS, δ = 0.00 ppm) and ^{15}N NMR (referenced externally to liquid ammonia, δ = 0.00 ppm) spectra were measured at room temperature using a Varian Inova 300 spectrometer at 75.469 MHz and a Varian Inova 400 spectrometer at 40.546 MHz, respectively. For the ^{15}N NMR the spectrum of the ligand was measured on three widely different occasions to check the precision of the chemical shifts. The deviation is ±0.1 ppm, showing that the absolute chemical shifts can be used in the characterization of species, together with the number of signals.

Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy. Solution samples were prepared at different metal:ligand ratios and pH values and were purged with carbonate-free N_2. Station 16.5 of the CCLRC Daresbury SRS facility, operating at ca. 2.0 GeV with ca. 180 mA current, was used for data collection. The monochromator was a channel cut Si(311) crystal, detuned to 50% of the maximum intensity to minimize harmonic contamination. The data were collected in fluorescence mode using a 32-element semiconductor detector. Four scans were measured for each sample. The EXAFS data for all samples were calibrated and background was subtracted using the EXCALIB[32] and EXBACK[33]

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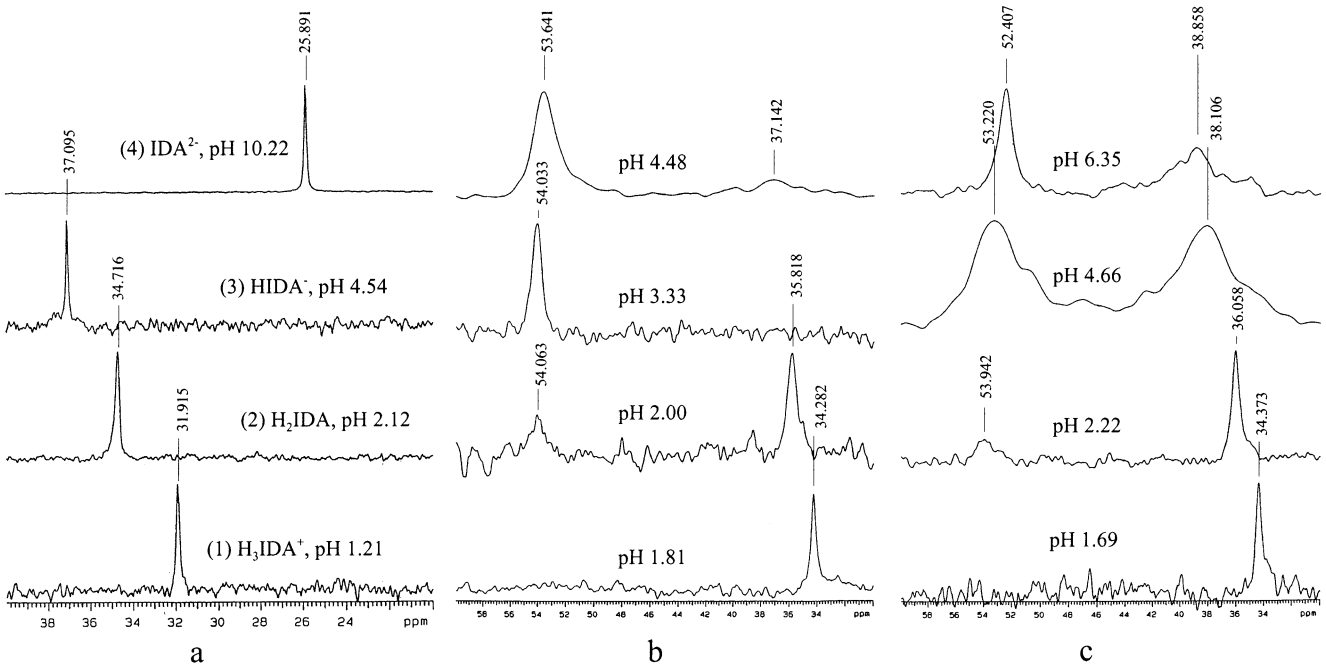

Figure 1. ^{15}N NMR spectra at different pH values of (from left to right) (a) iminodiacetic acid, (b) the 1:1 uranyl−IDA system, and (c) the 1:2 uranyl−IDA system.

programs, and data were analyzed with EXCURV98[34] using Rehr−Albers theory.[35] Phase shifts were calculated using Hedin−Lundqvist potentials and von Barth ground states. Single scattering was used in the analysis. Fits to the small peaks at 3−5 Å of the Fourier transform were assigned to be significant if the *R* value (goodness of fit) dropped by 5% or more with their inclusion. Full cluster multiple scattering calculations were also carried out, but although there was a superficially better fit for the peak at ca. 3.6 Å, the overall goodness of fit and the best fit parameters were essentially unaffected. The crystal structures of uranyl complexes with IDA and ODA, which had been determined previously by X-ray crystallography,[36] were used as models in the analysis.

Potentiometric Titrations. All titrations were carried out at 25 °C under an N_2 atmosphere, using a UNICAM 9460 ion-selective meter and a UNICAM CE1 combination pH electrode. The required amounts of the acid form of the ligand and $NaClO_4$ solutions were added slowly with stirring to a known amount of $UO_2(NO_3)_2$ solution ($V_{UO_2(NO_3)_2} = 0$ cm^3 when determining the protonation constants of ligands). The solution was made up to 50.00 cm^3 with deionized water and maintained at the ionic strength of 0.1 M $NaClO_4$. The cell was sealed and slowly titrated with standard NaOH solution in 0.100 cm^3 increments until a slight excess of NaOH over H_2IDA or H_2ODA had been added. The data obtained from the titration were analyzed with the BEST program.[37] Refinement was continued until no combination of adjustments gave rise to a lower σ value. σ is a goodness of fit parameter, calculated from the weighted sum of the squares of the difference between observed and calculated pH values.

Calorimetric Titrations. For the measurement of the enthalpy changes associated with protonation of ligand, the reaction ampule was charged with ligand solution and fitted into a twin ampule calorimetric unit (model 2277, Thermometric UK). The syringe was charged with NaOH solution. After equilibration at 25 °C and dynamic calibration, 15 × 0.010 cm^3 aliquots of NaOH were injected into the reaction ampule via a cannula. In parallel, microscale potentiometric titration equipment was employed to measure the pH value of the solution at each titration point. For the measurement of the enthalpy changes of uranyl−ligand complexation, the reaction ampule was charged with $UO_2(NO_3)_2$ solution (in 0.10 M $NaClO_4$), and titrated with buffered ligand solution using increments of 0.010 cm^3. The pH value of the solution at each point was measured separately using microscale potentiometric titration under identical experimental conditions. The heat of dilution was measured by incremental addition of the titrant into the reaction ampule, which was charged with 0.10 M background electrolyte only but no titrand.

Results and Discussion

Spectroscopic Investigations. NMR and EXAFS spectroscopies were used to identify the dominant complexes in aqueous solution at specific stoichiometries and pH values and to provide information on their structures.

NMR Spectroscopy of Uranyl Complexation with IDA. The ^{15}N NMR spectra for IDA and the 1:1 uranyl−IDA and 1:2 uranyl−IDA systems are shown in Figure 1. The ^{15}N NMR spectra of IDA at different pH values show the effect of proton removal (Figure 1a). The ^{15}N signal shifts from $[H_3IDA]^+$ (31.9 ppm, pH 1.21) to $[H_2IDA]$ (34.7 ppm, pH 2.12) to $[HIDA]^-$ (37.1 ppm, pH 4.54) with a sudden drop in chemical shift for $[IDA]^{2-}$ (25.9 ppm, pH 10.22) indicating a change from quaternary to tertiary nitrogen in accord with protonation constant data.[38] Similar changes in ^{15}N chemical

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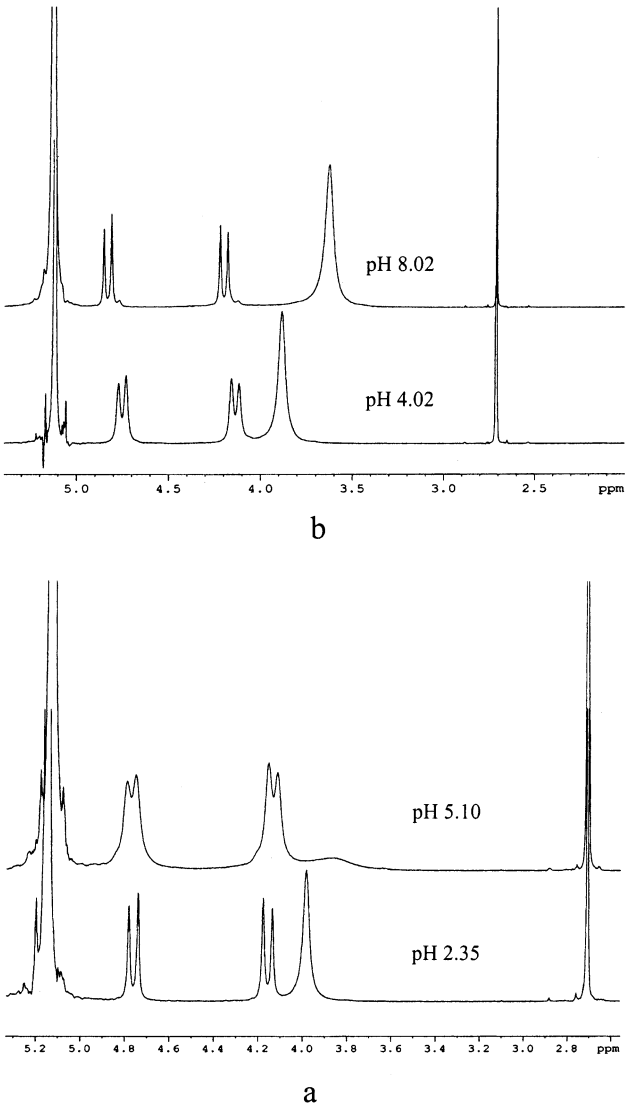

Figure 2. (a) ^{1}H spectra of the 1:1 uranyl−IDA system and (b) the 1:2 uranyl−IDA system at 268 K. Spectra are referenced to internal dimethyl sulfoxide $\delta = 2.71$ ppm, and the peak at $\delta = 5.15-5.20$ ppm is residual water.

shift values with changing acidity are observed for glycine.[39−41] The ^{1}H and ^{13}C NMR spectra show the expected shifts of signals upfield as the pH is increased, consistent with fast proton exchange and giving a weighted average chemical shift for all the IDA species.

The ^{15}N NMR spectra for the 1:1 uranyl−IDA system at varying pH values are shown in Figure 1b. Coordinated IDA ($\delta = 53-54$ ppm) has a distinctive chemical shift compared to noncoordinated ligand ($\delta = 34-37$ ppm); such a large shift downfield is evidence for coordination of the central nitrogen atom to the uranyl ion. The ^{1}H NMR spectra for this system (Figures 2a and Supporting Information S1−S4) provide further evidence for this. The spectra taken at −5 °C reveal two resolved doublets (4.77 and 4.16 ppm,

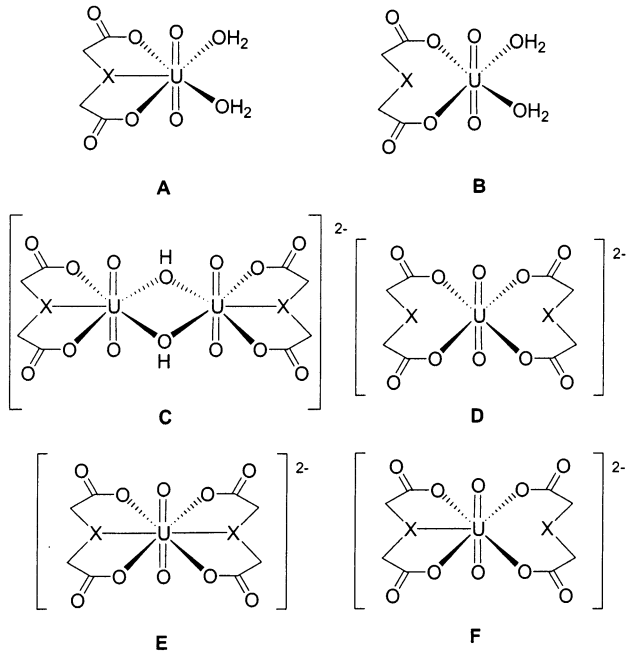

Figure 3. Structures for the species proposed in solution. X = N for IDA and O for ODA.

$^{2}J_{HH} = 16.4$ Hz) which are coupled and reside on magnetically equivalent carbons, consistent with the presence of a chelate ring system with the CH_2 protons in magnetically distinct axial and equatorial conformations. From previous studies,[36] we suggest that this species is a 1:1 complex (Figure 3, **A**) with tridentate IDA, coordinating through one O atom from each carboxylate group and the central N atom.

There is an additional peak at ∼3.99 ppm in the ^{1}H NMR spectra, indicating the presence of at least one other species. This broad signal moves upfield and broadens as the pH increases from 2.35 to 5.10. The line width is too great for this signal to be just free ligand exchanging protons, so it is probably due to exchange between complexed and free ligand. Also, ^{15}N NMR, as discussed earlier, shows that this complexation process is unlikely to involve the nitrogen atom. As the pH is increased past ∼4.00, all of the signals start to broaden, suggesting the establishment of another equilibrium involving free ligand. No diagnostic signal for the 2:2 dimeric species, proposed from EXAFS spectroscopy (see later, Figure 3, **C**) can be identified in the ^{1}H NMR spectra.

The doublets observed in the ^{1}H NMR spectra of the 1:1 system are also seen in the 1:2 uranyl−IDA system at pH 2.76−4.02 (Figures 2b and Supporting Information S5 and S6), suggesting the presence of the same 1:1 tridentate species. At a given pH value and in the low pH region (pH < 4), the broad peak in the ^{1}H NMR spectra of the 1:2 system is larger, relative to the size of the resolved doublets, and shifted upfield relative to the equivalent signal in the 1:1 system. This is indicative of more free ligand in the system (free ligand at pH 2.76, $\delta = 3.67$ ppm). All of the signals observed in the 1:2 system broaden above pH 4.00 and then sharpen again above pH 7.00, resulting in another set of two doublets (4.83 and 4.20 ppm) which are slightly downfield from those observed at lower pH and a broad peak at ∼3.65

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Table 1. Species Proposed in Uranyl−IDA Solution and the Assigned Chemical Shifts

	chem shifts δ (ppm)			
			^{13}C	
species	^{1}H CH_2	^{15}N	C═O	CH_2
H_3IDA^+	4.0	31.9		
H_2IDA	3.8	34.7	171.0	49.1
$HIDA^-$	3.6	37.1		
IDA^{2-}	3.4	25.9	181.8	54.2
1:1 complex: N coordinating	4.2, 4.8	53.6−54.1	184.8	57.7
1:1 complex: N noncoordinating (rapid exchange with proligand)	4.0	35.8−37.1	172.5−173.2	50.2−51.6
1:2 complex: N coordinating	4.2, 4.8	52.4	184.2	56.7
1:2 complex: N noncoordinating	3.7	38.9	171.6	49.2

ppm (Figures 2b and Supporting Information S6). In the ^{15}N spectra (Figure 1c) in this pH range, there are two broad peaks at ∼38 ppm and ∼53 ppm. These data are consistent with the presence of 1:2 uranyl−IDA complexes (Figure 3, **D**−**F**), with one or both IDA ligands coordinating through one O atom from each carboxylate group and the central N atom, in dynamic equilibrium with 1:2 complexes with IDA coordinating through the carboxylate groups only. The doublets at 4.83 and 4.20 ppm each display a small shoulder. These shoulders are at the same chemical shift (4.77 and 4.16 ppm) as the doublets observed in both uranyl−IDA systems at lower pH values, suggesting that the 1:1 tridentate complex present at lower pH values exists as a minor species at higher pH.

These ^{1}H NMR titration experiments illustrate the necessity for careful examination of solutions over the whole pH range. Changes in speciation occur within quite narrow pH ranges, and the full picture is required to interpret the data correctly.

In summary, we suggest the following species (Table 1) in solution, based on these NMR data and our previous studies on the solid-state structures.[36] The ^{13}C NMR data are not as informative as the ^{15}N and ^{1}H NMR data but are totally consistent with the following hypothesis. In the 1:1 uranyl−IDA system, the main species in solution up to pH 5 are free ligand and 1:1 complexes with coordination of IDA either tridentate through the two carboxylate groups and the central nitrogen atom or bidentate through the two carboxylate groups only. Above pH 5 precipitation limits NMR measurements in the 1:1 system. In the 1:2 uranyl−IDA system, the same species as suggested for the 1:1 system are present at lower pH values. At higher pH values (pH > 4) the main species are 1:2 complexes, with each carboxylate group coordinating to uranyl through one O atom and with the central N atoms either coordinating or noncoordinating.

The uranyl−ODA system was studied using ^{13}C NMR spectroscopy, but no observable change of chemical shifts occurred under the experimental conditions investigated. This may be a result of a very dynamic process taking place, which is fast compared to the time scale of the NMR experiment. Two possible processes are protonation−deprotonation or the breaking and re-forming of the U−O_{ether} bond. The second possibility is consistent with the suggestion of Choppin et al.[42] that the U−O_{ether} bond could be relatively more labile than the U−N bond and therefore a stronger interaction of uranyl with the central nitrogen in IDA may occur than with the ether oxygen in ODA.

Table 2. Best Fit Parameters, Occupancy, and Debye−Waller Factor ($2\sigma^2$ (Å^2)) for U L_3-Edge EXAFS of Uranyl−IDA/ODA Systems[a]

	1:1 uranyl−IDA at pH = 2.39 (R = 33.3)			1:1 uranyl−ODA at pH = 1.90 (R = 36.1)		
shell	occ	r (Å)	$2\sigma^2$ (Å^2)	occ	r (Å)	$2\sigma^2$ (Å^2)
1	2 O	1.77 ± 0.02	0.004	2 O	1.77 ± 0.02	0
2	4 O	2.41 ± 0.02	0.015	4 O	2.38 ± 0.02	0.014
3	1 N	2.92 ± 0.02	0.012	1 O	2.91 ± 0.02	0.011
	1:1 uranyl−IDA at pH = 4.39 (R = 34.6)			1:1 uranyl−ODA at pH = 3.42 (R = 31.8)		
shell	occ	r (Å)	$2\sigma^2$ (Å^2)	occ	r (Å)	$2\sigma^2$ (Å^2)
1	2 O	1.79 ± 0.02	0.003	2 O	1.79 ± 0.02	0
2	4 O	2.37 ± 0.02	0.014	4 O	2.36 ± 0.02	0.013
3	1 N	2.54 ± 0.02	0.004	1 O	2.50 ± 0.02	0.01
4	4 C	3.42 ± 0.03	0.017	4 C	3.45 ± 0.03	0.017
5	1 U	4.33 ± 0.05	0.008	1 U	4.31 ± 0.05	0.01
	1:2 uranyl−IDA at pH = 6.09 (R = 28.6)			1:3 uranyl−ODA at pH = 4.36 (R = 28.9)		
shell	occ	r (Å)	$2\sigma^2$ (Å^2)	occ	r (Å)	$2\sigma^2$ (Å^2)
1	2 O	1.78 ± 0.02	0.003	2 O	1.78 ± 0.02	0
2	4 O	2.36 ± 0.02	0.017	4 O	2.36 ± 0.02	0.014
3	2 N	2.91 ± 0.03	0.004	2 O	2.90 ± 0.03	0.01
4	4 C	3.17 ± 0.03	0.01	4 C	3.21 ± 0.03	0.018
5	4 C	3.38 ± 0.03	0.004	4 C	3.41 ± 0.03	0.01

[a] Occupancy is the number of atoms in the shell ± 25 %. R is a measure of the overall goodness of fit.

Determination of Structures of Uranyl Complexes in Solution by EXAFS. To confirm the existence of the uranyl−IDA/ODA complexes predicted by these NMR studies, selected systems were studied using EXAFS to determine the uranium coordination environments of the complexes present. The best fit parameters are presented in Table 2, and possible structures for the uranyl−IDA/ODA complexes suggested by these parameters are illustrated in Figure 3. The EXAFS spectra are in Supporting Information Figure S10.

1:1 Complexes (A, B). In the 1:1 uranyl−IDA/ODA solutions at low pH (2.39 and 1.90, respectively), monomeric 1:1 complexes have been identified. The first coordination shell comprises the two oxygen atoms of the linear uranyl group, at 1.77 Å from the central uranium atom, within the normal range of U−O distance for the uranyl ion. The second shell comprises four oxygen atoms, two from the carboxylate groups in IDA/ODA and two, presumably, from water molecules. The equatorial U−O distances are 2.41 Å for IDA

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and 2.38 Å for ODA, which are normal. The last shell can be fitted with one nitrogen atom at 2.92 Å in the case of the IDA sample and one oxygen atom at 2.91 Å in the case of the ODA sample or with one carbon atom at 2.92 Å in both cases. Normally, EXAFS cannot distinguish among nitrogen, oxygen, and carbon in the molecule, but in this case, the *R* value (goodness of fit parameter) was decreased by ca. 10% by using N to fit the IDA data and O to fit the ODA data, although neither of these can be distinguished from carbon. These distances are longer than the normal equatorial U−N or U−O distances but would be reasonable for a U−C distance in a complex formed by terminal bidentate coordination through a single carboxylate group.[18] However, the NMR data discussed earlier show a significant interaction between U and N and the presence of chelate rings containing methylene carbon atoms with inequivalent protons. Therefore, terminal bidentate coordination is unlikely. The peak at 3.6 Å is ascribed to multiple scattering in the uranyl unit. Therefore, the EXAFS analysis is consistent with the presence of monomeric 1:1 uranyl−IDA/ODA complexes in low pH aqueous solution, in which the uranyl group is coordinated by one IDA/ODA and two water molecules, although the mode of coordination of the ligand cannot be defined unambiguously.

2:2 Complexes (C). The 2:2 uranyl−IDA/ODA dimeric complexes isolated in the solid state were found in the 1:1 solutions at intermediate pH values (4.39 for IDA and 3.42 for ODA), although these species were not predictable from the NMR data and their existence in solution should be viewed with a degree of caution. This could arise either from the presence of an equilibrium between 1:1 and 2:2 species which favors the 2:2 species at higher pH, but the 2:2 complex is never dominant because of the onset of precipitation, or from the signal of the 2:2 uranyl−IDA complex overlapping with that of the 1:1 complex. In these species, two uranyl groups are bonded together by two μ_2-hydroxo bridges, and each IDA/ODA ligand is tridentate to one uranyl center. The total coordination number for each uranium atom is seven. The U−O, U−N/O_{ether}, and U−C distances are in very good agreement with those obtained from X-ray crystallographic study of the 2:2 dimeric complexes.[36] The U−U distances, determined by solution EXAFS analysis, are 4.33 Å for the IDA complex and 4.31 Å for the ODA complex, longer than the results obtained crystallographically for these dimeric complexes in the solid state (3.85(1) and 3.76(1) Å for the IDA and ODA complexes, respectively). This difference is consistent with a relaxation of the structure in the solution phase, which suggests that the physical state, and hence the local surroundings of the complex, affects the μ_2-hydroxo bridging. This U−U distance suggests an O−O distance of ∼2 Å which, although substantially less than the equivalent distance in the solid state, is still greater than the sum of the relevant van der Waals radii.

1:2 Complexes (D−F). The 1:2 complexes are found in the 1:2 uranyl−IDA solution at pH = 6.09 and in the 1:3 uranyl−ODA solution at pH = 4.36. The U−O distances in the uranyl group are typical. The distance from the four oxygens in the second shell to the central uranium also fall in the normal equatorial U−O range. However, as with the 1:1 complexes, fitting the third shell with two nitrogen atoms at 2.91 Å in IDA and two ether oxygen atoms at 2.90 Å in ODA or two carbon atoms at 2.92 Å in either case gives very similar *R*-factors. There are several possible rationalizations for this result. First, the absence of a formal U−N/O_{ether} bond within the eight-membered chelate ring may reduce steric crowding at the uranium center and accommodate the motion of ligand atoms of the ring in the solution phase. Second, the distance of 2.9 Å may represent a dynamically averaged distance arising from the presence of a nonbonding U−N/O_{ether} interaction arising from one bidentate and one tridentate IDA/ODA ligand, as identified for the ODA ligand in $[(CH_3)_2NH(CH_2)_2NH(CH_3)_2][UO_2(ODA)_2]$.[36] In the EXAFS analysis, the eight carbon atoms belonging to the two IDA/ODA ligands form two groups of four with different distances to uranium. This is consistent with either of these two possible geometries. Third, as noted above, in fluid solution the IDA/ODA ligands may be anchored to uranium by 1,7-bidentate coordination through the carboxylate oxygen atoms, but the nitrogen and ether oxygen atoms may instantaneously present a range of U−N/O_{ether} distances from complex to complex.

From the NMR and EXAFS data, as well as previous studies on the solid-state structures,[36,43] the following complexes are suggested (Figure 3). In the 1:1 uranyl-IDA/ODA system, free ligand and complexes of the types **A** and **B** are dominant at low pH, while type **C** is present in the pH range 4−5. In the 1:2 uranyl-IDA/ODA system, below pH 4 complex types **A** and **B** occur. As the pH is raised, there is a transformation via a complex of type **C**, to give predominantly 1:2 uranyl-IDA/ODA complexes of the types **D**−**F**. A trace of 1:1 complex **A** is still observable above pH 7.

Stability Constants of Uranyl Complexation with IDA and ODA. Experimental and fitted potentiometric titration curves of the ligands and of solutions containing 1:2 molar ratios of uranyl ion to the respective ligand are illustrated in Supporting Information Figure S11. Plots of the difference between the experimental and fitted curves for the 1:2 uranyl−ligand solutions are shown in Supporting Information Figure S12.

The model used to fit the data for the 1:2 uranyl−ligand titrations incorporated the three types of complex (1:1, 1:2, and 2:2) found by NMR and EXAFS spectroscopies. Other models including protonated and (in the case of IDA) zwitterionic ligands were tried, but in most cases the fitting process did not converge to a stable solution. Even in the cases where it did, the improvement in overall goodness of fit was not significant and certainly insufficient to justify the inclusion of the extra (protonated) species without spectroscopic evidence for their presence in solution. Additional support for the proton displacement model used here is obtained from the extensive liberation of protons on complexation to uranium, which could not occur if the complexes were protonated. The protonation and stability

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Table 3. Protonation/Stability Constants and Thermodynamic Constants of Neutralization for H_2IDA/H_2ODA and Uranyl−IDA/ODA Complexes[a]

complex	log β	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	ref
$[HIDA]^-$	9.34	-34 ± 1	63	44, 45[b]
	$9.52 \pm {}^{0.01}_{0.01}$	-37 ± 2	58 ± 7	
H_2IDA	11.95	-5 ± 2	33	44
	$12.06 \pm {}^{0.02}_{0.02}$	-5 ± 2	32 ± 7	
$[H_3IDA]^+$	13.77			44, 45[b]
	$13.73 \pm {}^{0.04}_{0.05}$			
UO_2IDA	8.96			27, 44[b]
	$9.90 \pm {}^{0.08}_{0.09}$	12 ± 2	230 ± 8	
$[UO_2(IDA)_2]^{2-}$	$16.42 \pm {}^{0.14}_{0.21}$	8 ± 2	151 ± 9	
$[(UO_2)_2(IDA)_2(OH)_2]^{2-}$	$10.80 \pm {}^{0.15}_{0.22}$	-33 ± 3	-283 ± 11	
$[HODA]^-$	3.93	3.2	82.8	46, 47[b]
	$3.94 \pm {}^{0.02}_{0.02}$	2.6 ± 0.5	84 ± 2	
H_2ODA	6.72	−1.6	47.3	46, 47[b]
	$6.67 \pm {}^{0.04}_{0.04}$	-2.3 ± 0.5	44 ± 3	
UO_2ODA	5.11			2[c]
	$5.77 \pm {}^{0.20}_{0.36}$	26 ± 2	198 ± 12	
$[UO_2(ODA)_2]^{2-}$	7.54			2[c]
	$7.84 \pm {}^{0.28}_{0.63}$	20 ± 2	106 ± 8	
$[(UO_2)_2(ODA)_2(OH)_2]^{2-}$	$4.29 \pm {}^{0.27}_{0.90}$	-24 ± 2	-219 ± 8	

[a] Results are for this study unless otherwise stated. [b] 25 °C, $I = 0.1$ M KNO_3. [c] 25 °C, $I = 0.1$ M $NaClO_4$.

constants computed for all species are given in Table 3 and compared with values in the literature.[44−47]

The log β values for the 1:1 IDA complex (9.90) are relatively high compared to the log β values for other 1:1 uranyl−carboxylate complexes (6.36 (oxalate),[1,48] 5.43 (malonate),[49,50] and 8.65 (glycine)[51]), suggesting that IDA behaves as a tridentate ligand in this 1:1 complex, coordinating through the two carboxylate groups and the central nitrogen atom. The value found here for the 1:1 complex is a little higher than the published ones, probably because different models were used in the computation. Few stability constants have been published for the 1:2 complex since most workers have interpreted the data in terms of a monomeric 1:1 uranyl−IDA chelate only.

The stability constant for the 1:1 uranyl−ODA complex is lower than that for the 1:1 uranyl−IDA complex, although the EXAFS data suggests that ODA is also tridentate in the 1:1 complex. The lower stabilities of the uranyl−ODA complexes compared to the uranyl−IDA complexes may reflect the difference in ligand basicities as is seen, for example, in the uranyl−glycine and glycolic acid examples. The protonation constant of glycolic acid, log $K_1 = 3.62$, is lower than that of glycine, for which log $K_1 = 9.83$. On coordination to uranyl, the weaker glycolic acid gives lower stability constants (log $\beta_1 = 2.40$) than the glycine complex (log $\beta_1 = 8.65$).[46,51−54] Fewer studies have been carried out on the uranyl−ODA system compared with the uranyl−IDA system, and small differences between constants obtained from this work and those in the literature probably arise from differences in experimental conditions. Di Bernardo et al.[2] have given 10.03 as the log β value for a complex formulated as $[UO_2(HODA)(ODA)]^-$.

Di Bernardo and co-workers have used their stability constants for the uranyl−IDA/ODA systems[2,26] to suggest that the coordinating ability of the nitrogen atom in IDA is greater than that of the central (ether) oxygen atom in ODA. However, the supporting evidence is not very strong. First, H_2ODA is a stronger Brønsted acid than H_2IDA, so ODA^{2-} is a weaker conjugate base. The identity of the heteroatom clearly affects the carboxylate donors in this pair of ligands, so it may not be valid to separate out the effects of the central N and O_{ether} because the carboxylates are not a constant. Second, although the Gibbs free energy change on complexation, as measured by the stability constant, is more favorable for IDA than for ODA, this does not necessarily provide information concerning the relative energies of the U−N and U−O_{ether} bonds since ΔG contains both enthalpic and entropic components. This issue has been further explored in the following calorimetric study, in which the stability constants obtained here were employed.

Thermodynamic Properties of Uranyl Complexes with IDA and ODA. The titration of uranyl using partially neutralized H_2IDA (1 IDA^{2-}, 0.5 H^+, 1.5 Na^+; Supporting Information Figure S13) shows that there are two steps in the reaction. The first part is the endothermic complexation of uranyl with IDA. The second part is exothermic because the neutralization of protons gives out more heat than the complexation of residual uranyl absorbs. In the case of ODA (Supporting Information Figure S13), because complexation is strongly endothermic, the overall reaction is always endothermic, even though the neutralization of protons gives

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out some heat. With allowance for the neutralization of protons, uranyl complexation with ODA is therefore more endothermic than with IDA. The calculated thermodynamic constants for uranyl complexation with IDA and ODA are reported in Table 3 and show that, for the 1:1 and 1:2 complexes, the complexation reactions are stabilized by entropy changes, while the enthalpy components oppose coordination, a common trend in the coordination chemistry of uranyl in aqueous solution.[1,28,55−57] Compared with other carboxylate ligands, the high stability constants and comparable ΔH values reflect the generally larger positive ΔS values. Thus, Di Bernardo et al.[2] have given a ΔS value for 1:1 uranyl−IDA complexation of 161 J K^{-1} mol^{-1} at 25 °C, $I = 0.1$ M ($NaClO_4$), but their ΔH value is −2.2 kJ mol^{-1}. This is unusual, since most reactions of uranyl with proligands are endothermic and accompanied by positive enthalpy changes (but see below).[28] The less positive ΔH and more positive ΔS in uranyl−IDA complexation compared to uranyl−ODA complexation could be explained in terms of a greater covalency in U−N compared with $U-O_{ether}$ bonds.[2] In contrast to the monomeric complexes, the enthalpy changes associated with dimer formation are exothermic, probably due to the incorporation of hydroxide ions in the complex.

Conclusions

On the basis of NMR and EXAFS studies of the uranyl−IDA system and EXAFS study of the uranyl−ODA system, three types of metal:ligand complexes have been identified in solution: 1:1 and 1:2 monomeric; 2:2 dimeric. Because the EXAFS spectra for the three kinds of complexes are distinct, it can be concluded that EXAFS is diagnostic of these three different compositions, although it cannot distinguish unambiguously between terminal bidentate and 1,7-coordination in the monomeric complexes. However, the NMR data provide strong evidence for the 1,7-coordination mode.

The stability constants of the uranyl−IDA/ODA complexes were measured by potentiometric titration, and their thermodynamic constants by calorimetric titration. A three species model incorporating all the complex types identified spectroscopically (1:1 and 1:2 monomers; 2:2 dimer) was used to determine the stability constants and thermodynamic parameters. As is common with uranyl chemistry in aqueous solution, the complexation reactions for the 1:1 and 1:2 uranyl−IDA/ODA complexes are endothermic and stabilized by entropy changes. However, the formations of the 2:2 dimers are unusual as the reactions are exothermic.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra, EXAFS spectra and associated Fourier transforms, and calorimetric titration plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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