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# Energetics and Structure of Uranium(VI)–Acetate Complexes in Dimethyl Sulfoxide

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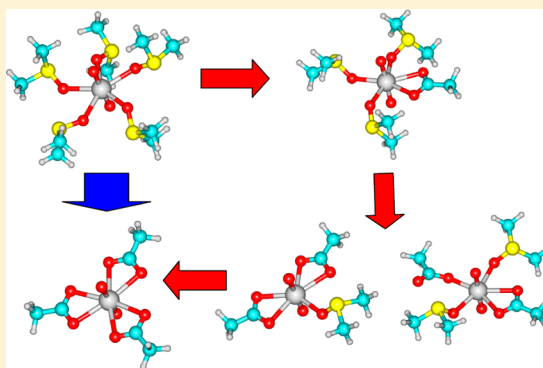
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## Supporting Information

**ABSTRACT:** The thermodynamics of the complexation between uranium(VI) and acetate in dimethyl sulfoxide (DMSO) was studied at 298 K in an ionic medium of 0.1 mol dm<sup>-3</sup> tetrabutyl ammonium perchlorate. The results show that the uranyl ion forms three strong successive mononuclear complexes with acetate. The complexes, both enthalpically and entropically stabilized, are significantly more stable in DMSO than in water. This feature can be ascribed to the weak solvation of acetate in DMSO. The thermodynamic parameters for the formation of the uranium(VI) complexes with acetate in DMSO are compared with those with ethylenediamine in the same solvent. The difference between the two ligand systems reveals that, for the complexation reactions involving charge neutralization, the reorganization of the solvent gives a very important contribution to the overall complexation energetics. The coordination mode of acetate in the uranyl complexes and the changes of the solvation sphere of UO<sub>2</sub><sup>2+</sup> upon complexation were investigated by FT-IR spectroscopy in DMSO and in acetonitrile/DMSO mixtures. In addition, DFT calculations were performed to provide an accurate description of the complexation at the molecular level. The experimental and calculated results suggest that acetate is solely bidentate to UO<sub>2</sub><sup>2+</sup> in the 1:1 and 1:3 complexes but mono- and bidentate in the 1:2 complexes. The DFT calculations also indicate that the medium effects must always be taken into account in order to gain accurate information on the complex formation in solution. In fact, the relative stability of the reaction products changes markedly when the DFT calculations are carried out in vacuum or in DMSO solution.



## INTRODUCTION

The thermodynamics and structure of uranium(VI) carboxylate complexes are a subject of many experimental<sup>1–9</sup> and theoretical<sup>10–16</sup> studies due to their high relevance in the treatment of nuclear wastes and in the migration of uranium in the environment. Uranium(VI) shows a marked tendency to form strong complexes with oxygen donor ligands, inorganic (e.g., carbonate, sulfate, phosphate) and organic (e.g., acetate, oxalate and phenols), commonly present in soil or in nuclear waste streams. Such tendency is expected for the interactions between the “hard” acids (e.g., the actinide ions in all their oxidation states) and “hard” bases.<sup>17</sup> In the past, thermodynamic studies on the complexation of actinide ions have been predominantly carried out in water,<sup>14,18–20</sup> due to the relevance of this medium to the environmental behavior of actinides. Much less frequently, the complex formation in nonaqueous solvents has been specifically studied,<sup>21,22</sup> probably because of the lack of direct relevance to the environmental behavior and the difficulty involved in studying nonaqueous systems. In fact,

many nonaqueous solvents are not suitable for thermodynamic studies due to their low affinity to salts and the formation of ion pairs in the media with low dielectric constant.<sup>23</sup>

However, in recent years, interest has grown on the speciation and structure of uranium in nonaqueous solvents<sup>24–26</sup> and ionic liquids.<sup>25,27</sup> At the applied level, such studies provide information that is necessary for the development of novel separation processes and disposal strategies. At the fundamental level, an appropriate choice of the solvent can allow to gain fundamental insight into the thermodynamics of the interactions that are difficult to study in water. For example, previous studies from the authors demonstrated that the use of dimethyl sulfoxide (DMSO) as solvent allows to monitor several complex formation reactions [between hard ions (lanthanides(III) and uranium(VI)) and neutral nitrogen

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donors (polyamines)] that cannot be studied in water due to the prevailing metal ion hydrolysis.<sup>21–23,28,29</sup>

Since the pioneering study by Åhrland,<sup>9</sup> the interaction of uranium(VI) with acetate in water has been intensively investigated from both an experimental<sup>6,30</sup> and theoretical<sup>10,15,16</sup> point of view. It is generally accepted that in water U(VI) forms with acetate three successive mononuclear complexes which are mostly entropically stabilized. The formation of the 1:4 complex was reported in an early study,<sup>31</sup> but its formation might be the result of an experimental artifact due to large changes in the ionic medium. On the contrary, experiments directed to the study of the thermodynamics of complex formation in organic solvents are very scarce and, in DMSO, limited to a single polarographic study.<sup>32</sup> In that work, no thermodynamic data were obtained, but it was demonstrated that U(VI) formed with acetate at least three successive mononuclear complexes that were much more stable than in water.

In this work, thermodynamics and coordination modes of the interaction between uranyl(VI) and acetate have been studied in DMSO with the objective of elucidating the effect of the solvent affinity toward the metal ion and ligand on the stability of the complexes formed. Thermodynamic parameters for the protonation of acetate and for its complexation with uranium(VI) have been determined by potentiometry and calorimetry. Thermodynamic and structural factors controlling the complex formation between a "hard" acid and either a charged or neutral ligand are also discussed. Vibrational spectroscopy and density functional theory (DFT) calculations have been used to obtain information on the structure and coordination modes of acetate in solution.

## ■ EXPERIMENTAL SECTION

**Chemicals.** Given the particularly strong affinity of water for DMSO and the higher basicity of acetate in the latter solvent,<sup>33,34</sup> great care has been taken throughout the work to maintain anhydrous conditions. All chemicals and solutions were handled and stored under a dry N<sub>2</sub> atmosphere (less than 1 ppm of water) in a stainless steel glovebox (Braun Model MB 150B-G-I). Dimethyl sulfoxide (Aldrich, 0.01% water) was purified according to the usual procedures.<sup>35</sup> Anhydrous acetonitrile (Aldrich, absolute, water content <0.001%) was kept over freshly activated 4 Å molecular sieves and used without further purification.

The adduct [UO<sub>2</sub>(DMSO)<sub>5</sub>](ClO<sub>4</sub>)<sub>2</sub> was prepared as previously described<sup>22</sup> and characterized by elemental analysis. The uranyl(VI) content in the adduct was determined by ion exchange analysis using a cation resin in the H<sup>+</sup> form.<sup>22</sup> Stock solutions of the adduct in DMSO were prepared by weight and standardized as previously described.<sup>22</sup> Dry uranyl acetate was obtained by heating UO<sub>2</sub>Ac<sub>2</sub>•2H<sub>2</sub>O at ~373 K under vacuum (*p* < 1 Pa) for several days. Tetrabutyl ammonium acetate (Fluka) was dried for several days at 100 °C under vacuum. Tetrabutyl ammonium perchlorate (Fluka) was recrystallized as described.<sup>35</sup> A stock solution of trifluoromethanesulfonic acid in DMSO (~100 mmol dm<sup>-3</sup>) was prepared by slowly adding trifluoromethanesulfonic acid (Acros Organics, 99%) to anhydrous DMSO. The amount of water in the stock solutions was checked by Karl Fisher coulometric titration. The ionic strength in all the solutions used for the potentiometric and calorimetric studies was adjusted to 0.1 mol dm<sup>-3</sup> by addition of appropriate amounts of tetrabutyl ammonium perchlorate.

**Caution.** Uranyl salts are chemotoxic and moderately radioactive ( $\alpha$ -radiation). Therefore, some precautions to avoid contact with the salts (gloves) or inhalation of dust particles (dust mask) are needed when working with uranyl salts. Though the perchlorate salts prepared and/or used in this work did not show any problems of instability, great attention has to be paid in preparing and handling perchlorate salts, especially when

they are in the nonaqueous media. Trifluoromethanesulfonic acid is very corrosive and hygroscopic and should be handled in dry atmosphere.

**Potentiometric Measurements.** Potentiometric titrations were carried out to determine the protonation constants of acetate as well as the complexation constants of uranyl with acetate in DMSO. The method of competitive reactions<sup>36</sup> was chosen to follow the metal complex formation equilibria. A first attempt to use silver(I) as the competing ion for uranium(VI) was unsuccessful, because the silver(I)–acetate complexes are too weak in DMSO. [In 0.1 mol dm<sup>-3</sup> tetrabutyl ammonium perchlorate  $\log \beta_{AgAcj}^{(j-1)-}$  are  $3.44 \pm 0.01$  and  $5.59 \pm 0.02$  for *j* = 1 and 2, respectively.] The competition with the hydrogen ion was found to be satisfactory, despite that the slow response of the glass electrode in DMSO limited the number of experimental points which could be collected in a reasonable time window.

The potentiometric titrations were carried out at 298.15 K with a constant temperature titration set up. The concentration of the free hydrogen ion was measured by a glass electrode (Metrohm, 6.0102.000) that had been etched in aqueous 4% hydrofluoric acid for a few minutes and conditioned in anhydrous DMSO for several days.<sup>37,38</sup> A silver/silver(I) electrode (Metrohm, 6.0718.000) in contact with the working solution by a 0.1 mol dm<sup>-3</sup> tetrabutyl ammonium perchlorate salt bridge was used as the reference electrode. A ground glass sleeve joint guaranteed the contact between the working solution and the salt bridge. The response of the electrode system to the hydrogen ion concentration (slow, but reversible) was found by adding 0.1 mol dm<sup>-3</sup> trifluoromethanesulfonic acid (triflic acid) to 0.1 mol dm<sup>-3</sup> tetrabutylammonium perchlorate in DMSO. The plots of the emf readings vs the values of  $-\log[H^+]$  are linear in the range of  $[H^+]$  from  $10^{-4}$  to  $10^{-2}$  M, with a slope of  $60 \pm 3$  mV.

The electromotive force (e.m.f.) between the electrodes of the potentiometric cell was measured with an Amel Mod. 338 pH meter connected to a computer-controlled data collection system. Due to the slow response of the glass electrode, a strict criterion was adopted to collect equilibrium potentiometric data: the pH meter reading was acquired only when two successive emf values remained unchanged for more than 240 s. Typically, the time interval between two adjacent readings was close to 40 min.

In the two titrations to measure the protonation and homoconjugation constants of acetate, a solution of tetrabutyl ammonium acetate (TBAAC,  $C_{Ac^-} = 100.3$  mmol dm<sup>-3</sup>) was added to known volumes of solutions containing different amounts of triflic acid (3.71 and 12.06 mmol dm<sup>-3</sup>, respectively). In the three titrations, carried out to obtain the stability constants of uranyl(VI)–acetate complexes, the solution of 100.3 mM TBAAC was added to solutions containing different concentrations of uranyl ion and triflic acid ( $C_U^0/C_H^0 = 4.49/1.83$ ;  $3.35/4.56$ ;  $0.96/2.93$  mmol dm<sup>-3</sup>, respectively). The protonation and homoconjugation constants of acetate,  $\beta_{HAc}$  and  $\beta_{HAc2}$ , and the formation constants of uranyl–acetate complexes,  $\beta_j$  (*j* = 1, 2, 3), were preliminarily calculated with the potentiometric data by the program Superquad<sup>39</sup> and finally determined from a cumulative analysis of both potentiometric and calorimetric data.

**Calorimetric Measurements.** All calorimetric experiments were carried out at  $298.15 \pm 0.02$  K with a Tronac precision titration calorimeter (Model 87-558) equipped with a 25 cm<sup>3</sup> vessel. The original design of the calorimeter head, syringe, and vessel holder has been modified in order to allow the loading of the reactants in a glovebox under anhydrous N<sub>2</sub> atmosphere.<sup>40–42</sup> This setup, sealed with gas-proof gaskets, prevents the contamination of the system by moisture during calorimetric experiments. The calorimeter response was checked by the titration of tris(hydroxymethyl)aminomethane, THAM, with a standard solution of HCl in water. The experimental value of the heat of neutralization of THAM was found to be  $\Delta H^\circ = -47.49$  kJ mol<sup>-1</sup>, in excellent agreement with the accepted value ( $\Delta H^\circ = -47.53 \pm 0.13$  kJ mol<sup>-1</sup>).<sup>18</sup> The calorimetric titrations were performed by adding a ~100 mmol dm<sup>-3</sup> TBAAC solution to a 20.0 cm<sup>3</sup> solution containing either H<sup>+</sup> (10–25 mmol dm<sup>-3</sup>) or U(VI) (5–17 mmol dm<sup>-3</sup>) in the titration vessel.

Usually, for each titration run, *n* experimental values of the stepwise reaction heat produced in the calorimeter vessel ( $Q_{ex,j}$ , *j* = 1 to *n*) were

Table 1. Thermodynamic Parameters for the Protonation of Acetate in DMSO and Water ( $T = 298\text{ K}$ )<sup>c</sup>

reaction	solvent	log $\beta$	$-\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$-\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$T\Delta S^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
$\text{H}^+ + \text{Ac}^- \rightleftharpoons \text{HAc}$	DMSO <sup>a</sup>	$11.86 \pm 0.08$	$67.7 \pm 0.5$	$46.7 \pm 0.2$	$21.0 \pm 0.5$	$70 \pm 2$
$\text{H}^+ + 2\text{Ac}^- \rightleftharpoons \text{HAc}_2^-$	DMSO <sup>a</sup>	$14.41 \pm 0.12$	$82.3 \pm 0.7$	$61.6 \pm 1.2$	$20.7 \pm 1.4$	$69 \pm 5$
$\text{HAc} + \text{Ac}^- \rightleftharpoons \text{HAc}_2^-$	DMSO <sup>a</sup>	$2.54 \pm 0.14$	$14.5 \pm 0.8$	$14.9 \pm 1.2$	$-0.4 \pm 1.5$	$-1 \pm 5$
$\text{H}^+ + \text{Ac}^- \rightleftharpoons \text{HAc}$	water <sup>b</sup>	4.54	25.91	0.4	25.5	85.4

<sup>a</sup>Present work;  $\mu = 0.1\text{ mol dm}^{-3}$ , TBAClO<sub>4</sub>. <sup>b</sup>Reference 66  $\mu = 0.15\text{ mol dm}^{-3}$ , NaClO<sub>4</sub>. <sup>c</sup>Errors are three times the standard deviation obtained with the minimization programs.

calculated as a function of the titrant volume. The values of  $Q_{\text{ex},j}$  were corrected for the dilution heat of the titrant ( $Q_{\text{dil},j} = 1$  to  $n$ ), that was obtained in separate runs. The heat of dilution of the vessel contents was negligible. The total heat per mole of the concerned species ( $\Delta h_{\text{v},n}$ ) was obtained by dividing the total reaction heat  $\sum_{j=1}^n (Q_{\text{ex},j} - Q_{\text{dil},j})$  by the number of moles of U(VI) or acetate in the calorimeter vessel. The calorimetric data were elaborated with a modified version of the computer program Letagrop KALLE<sup>43</sup> using  $\Delta h_{\text{v},j}$  as the error carrying variable to obtain the reaction enthalpies or simultaneously the reaction enthalpies and formation constants.

**FT-IR Titration Experiments.** The spectra were collected at room temperature ( $\sim 298\text{ K}$ ) on a Nicolet Nexus FT-IR spectrometer with  $2\text{ cm}^{-1}$  resolution and 200 scans. The spectrometer was purged with dry-air. Cells with barium fluoride windows and an optical path of  $\sim 30\text{ }\mu\text{m}$  were used. The cells were loaded in the inert atmosphere glovebox and carried to the spectrometer with a sealed transport. Quantitative measurements were made with a single cell, the exact thickness of which was determined by the interference fringe method.<sup>44</sup>

Two different sets of FT-IR measurements were performed. The first set of experiments has been carried out to obtain information about the coordination mode of acetate. To this purpose, the spectrum of pure DMSO and the spectra of a series of DMSO solutions containing  $50.0\text{ mmol dm}^{-3}$  U(VI) and variable acetate with  $R_{\text{Ac}}$  ranging from 0 to 4 were collected. The recorded spectra were converted to absorbance units, and then the spectrum of pure DMSO was numerically subtracted from the spectra of U(VI) acetate solutions. The second set of experiments was carried out to calculate the average number of DMSO molecules ( $\text{NC}_{\text{DMSO}}$ ) coordinated to the uranyl ion in the complexation reactions. In this case, the spectra of a series of binary AN/DMSO mixtures containing U(VI) ( $\sim 33\text{ mmol dm}^{-3}$ ) with a constant quantity of DMSO ( $\text{C}_{\text{DMSO}}/\text{C}_{\text{U}} = 15.0$ ) and increasing amounts of acetate ( $R_{\text{Ac}}$  from 0 to 6) were recorded. Stock solutions containing U(VI) and DMSO in different ratios were prepared by adding calculated amounts of DMSO to solutions of the adduct  $[\text{UO}_2(\text{DMSO})_3](\text{ClO}_4)_2$  in AN. The net spectra were obtained by a subtraction procedure similar to that previously described.<sup>28</sup>

Quantitative analysis of the spectra were described in detail previously.<sup>45</sup> A Marquardt nonlinear regression program was used to deconvolute the spectra to individual line bands, assuming Lorentzian line shapes. The peak absorbance at  $1060\text{ cm}^{-1}$ , characteristic of free DMSO, was calculated by spectral deconvolution for each of the solutions analyzed. Calibration curves were obtained by plotting the absorbance at  $1060\text{ cm}^{-1}$  vs the DMSO concentration in the mixtures of AN/DMSO (in the absence of U(VI) and acetate). Free DMSO concentrations in the U(VI)/DMSO or U(VI)/DMSO/acetate systems were obtained with the calibration curves and the values of absorbance at  $1060\text{ cm}^{-1}$ .

**Crystallography.** The  $(\text{UO}_2\text{Ac}_2\text{DMSO}_2)_2$  crystals were obtained by slow evaporation, in an anhydrous environment, of an acetonitrile solution of anhydrous  $\text{UO}_2\text{Ac}_2$  in the presence of about three equivalents of DMSO. Prior to the evaporation, the solution was heated to the temperature near the boiling point for several hours. The crystal was mounted in a Lindemann glass capillary and centered on a four circle Philips PW1100 diffractometer using graphite monochromated Mo  $K_\alpha$  radiation ( $\lambda = 0.71073\text{ }\text{\AA}$ ), following the standard procedures at room temperature. All intensities were corrected for Lorentz polarization and absorption.<sup>46</sup> The structure was solved by standard direct methods.<sup>47</sup> Refinement was carried out by full-matrix least-squares procedures (based on  $F_o^2$ ) using anisotropic temperature

factors for all non-hydrogen atoms. Hydrogen atoms were placed in a calculated position with fixed isotropic thermal parameters ( $1.2\text{ U}_{\text{equiv}}$ ) of the parent carbon atom. Structure refinement and final geometrical calculations were carried out with SHELXL-97 program,<sup>48</sup> implemented in the WinGX package.<sup>49</sup>

Crystallographic data:  $\text{C}_{12}\text{H}_{24}\text{O}_{14}\text{S}_2\text{U}_2$ , MW =  $932.49\text{ g/mol}$ , monoclinic, space group  $P2_1/n$ ,  $a = 7.914(2)$ ,  $b = 13.354(3)$ ,  $c = 11.792(3)\text{ }\text{\AA}$ ,  $\beta = 103.46(3)^\circ$ ,  $V = 1212\text{ }\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 2.522\text{ g/cm}^3$ . Final  $R_1 = 0.0478$ ,  $wR_2 = 0.1081$ , goodness of fit =  $1.328$ , 3203 unique reflections [ $R(\text{int}) = 0.0413$ ] of which 2947 with  $I > 2\sigma(I)$ , max positive and negative peaks in  $\Delta F$  map:  $1.529$  and  $-1.374\text{ e-}\text{\AA}^{-3}$ .

**Computational Methods.** Density functional theory calculations were performed on the uranyl-acetate complexes using Gaussian09.<sup>50</sup> The three-parameter hybrid functional B3LYP<sup>51,52</sup> was employed, due to its acceptable performance in describing dissociation energies in uranyl complexes when compared to correlated wave function methods.<sup>53</sup> The Stuttgart-Dresden small core potential for uranium<sup>54</sup> was employed because, in combination with B3LYP functional, it previously provided good agreement with experimental values for reaction energies and vibrational frequencies of U(VI) complexes.<sup>55–58</sup> The other elements were treated using a triple- $\zeta$  basis type plus polarization functions.<sup>59</sup> Solvent effects were taken into account by using the IEF-PCM method<sup>60</sup> with DMSO as solvent and using the UFF radii for the spheres centered on each atom of the solute. Complexes containing 1 to 3 mono- (m) and bidentate (b) acetate ligands and 0 to 5 DMSO molecules were geometry optimized to a minimum. Vibrational frequency calculations confirmed that the structures obtained were minima. Reaction energies in the gas phase were computed using the electronic energy for each reactant and product with the zero point energy and thermal corrections, which comprise electronic, vibrational, rotational, and translational contributions to the internal energy. For the calculation of the reaction free energy in solvent we adopted the procedure proposed by Martin et al.<sup>61</sup> and already applied to the study of hydrated actinyls and their complexes with crown ethers.<sup>62,63</sup> This consists in a correction accounting for the reduction in translational entropy of the DMSO molecule in the condensed phase by setting the DMSO pressure to  $344\text{ atm}$  (value derived from the liquid density of  $1095.8\text{ kg/m}^3$  at  $298\text{ K}$ ) instead of  $1\text{ atm}$  used as default in thermochemical analysis.

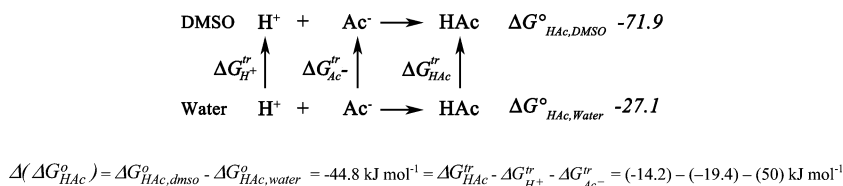
The reaction energy for the formation of the 1:2 complex (D–G in Table 5) has been calculated using the most energetically favored product of the first substitution reaction (in DMSO), and the same was done for the formation of a third complex (H and I in Table 5). The optimization of the  $[\text{UO}_2(\text{DMSO})_4(\text{Ac})]^+$  (b) and  $[\text{UO}_2(\text{DMSO})_3(\text{Ac})_2]$  (m,b) complexes produced the dissociation of one DMSO molecule, so they were considered no further.

## RESULTS AND DISCUSSION

**Protonation of Acetate in DMSO.** Polar aprotic solvents<sup>34</sup> like DMSO can strongly solvate cations but not anions, especially those anions with a localized charge, such as the carboxylates. For this reason the acetate ion is a very strong base in DMSO and tends to bind both metal cations and hydrogen ion strongly.<sup>33</sup> Moreover, acetate can also interact with hydrogen bond donors such as acetic acid (HAc) in DMSO, forming the  $\text{HAc}_2^-$  species<sup>33,64,65</sup> according to reaction 1 where  $j = 1$  and  $2$ .



Scheme 1. Transfer of Acetate from Water to DMSO



The combined analysis of the potentiometric and calorimetric data for the protonation of acetate in DMSO (see the Supporting Information, SI and Figure S1) provided evidence for both the formation of the homoconjugate species and the very strong basicity of acetate. The values of the overall stability constants obtained for reaction 1 ( $\log \beta_{\text{HAc}_j^{(j-1)-}}$ :  $11.59 \pm 0.06$ ,  $14.14 \pm 0.12$ , for  $j = 1$  and  $2$ , respectively) are in good agreement with the literature data. [ $\log \beta_{\text{HAc}_j^{(j-1)-}}$ :  $11.75$  and  $13.93$  at  $I = 0.01 \text{ M}$  in ref 65 and  $12.6$  and  $14.1$  at  $I = 0$  in ref 64 for  $j = 1$  and  $2$ , respectively.] The thermodynamic functions for the protonation of acetate in DMSO are summarized in Table 1 where the corresponding data for the protonation in water are also included for comparison.<sup>66</sup>

The first protonation constant of acetate ( $j = 1$ ) is about 7 orders of magnitude higher in DMSO than in water. Accordingly, the difference between the free energies of protonation in the two media [ $\Delta(\Delta G_{\text{HAc}}^\circ)$ ] is strongly negative (Scheme 1 and Table 2). [Data in Table 2 are taken from refs

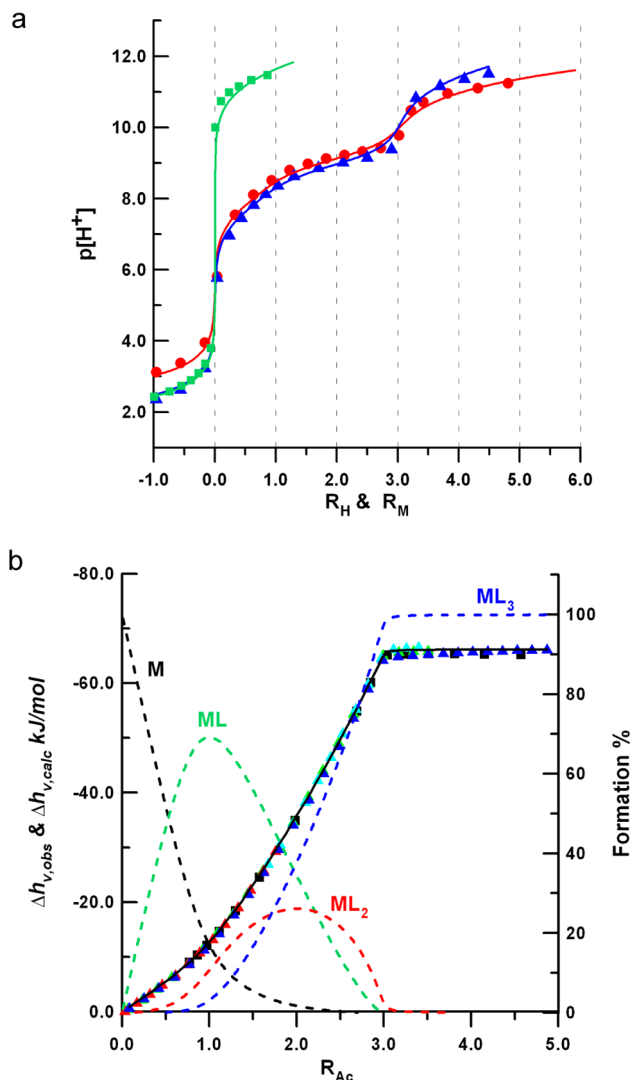
Table 2. Transfer Parameters of Acetic Acid, Proton, and Acetate between Water and DMSO<sup>a</sup>

	$\Delta G$	$\Delta H$	$T\Delta S$
$\Delta X_{\text{HAc,DMSO}}^\circ$	-71.9 <sup>a</sup>	-44.8 <sup>b</sup>	27.1
$\Delta X_{\text{HAc,water}}^\circ$	-27.147 <sup>c</sup>	0.41 <sup>c</sup>	27.56
$\Delta(\Delta X_{\text{HAc}}^\circ)$	-44.8	-45.2	-0.5
$\Delta X_{\text{HAc}}^{\text{tr}}$	-14.2 <sup>d</sup>	-7.2 <sup>f</sup>	7
$\Delta X_{\text{H}^+}^{\text{tr}}$	-19.4 <sup>e</sup>	-27.4 <sup>f</sup>	-8.0
$\Delta X_{\text{Ac}^-}^{\text{tr}}$	50 <sup>e,g</sup>	65.4 <sup>f</sup>	15

<sup>a</sup>From  $\log K = 12.6$  in ref 64. <sup>b</sup>Reference 67. <sup>c</sup>Reference 68,  $\mu = 0.0 \text{ mol dm}^{-3}$ . <sup>d</sup> $\Delta(\Delta G_{\text{HAc}}^\circ) = \Delta G_{\text{HAc,DMSO}}^\circ - \Delta G_{\text{HAc,water}}^\circ = \Delta G_{\text{HAc}}^{\text{tr}} - \Delta G_{\text{H}^+}^{\text{tr}} - \Delta G_{\text{Ac}^-}^{\text{tr}}$ ;  $-44.8 = \Delta G_{\text{HAc}}^{\text{tr}} - (-19.4) - (50 \pm 4) = -14.2 \pm 4$ . <sup>e</sup>Reference 69. <sup>f</sup>Reference 33. <sup>g</sup>This value has a large uncertainty ( $\pm 4 \text{ kJ mol}^{-1}$ ) as it is a weighed average of three measurements which span from  $53.7$  to  $46.4 \text{ kJ mol}^{-1}$ . <sup>h</sup> $\Delta G$ ,  $\Delta H$ , and  $T\Delta S$  in  $\text{kJ mol}^{-1}$ .  $\Delta(\Delta X_{\text{HAc}}^\circ) = \Delta X_{\text{HAc,DMSO}}^\circ - \Delta X_{\text{HAc,water}}^\circ = \Delta X_{\text{HAc}}^{\text{tr}} - \Delta X_{\text{H}^+}^{\text{tr}} - \Delta X_{\text{Ac}^-}^{\text{tr}}$ .

33, 64, and 67–69.] This is due: i), mainly, to the highly unfavorable free energy of transfer of acetate from water to DMSO ( $+50 \text{ kJ mol}^{-1}$ ) and ii), in part, to the favorable energy of transfer of acetic acid from water to DMSO ( $-14.2 \text{ kJ mol}^{-1}$ ).<sup>33,67</sup> The former contribution is due to the poor solvation of acetate in DMSO and essentially determined by the unfavorable transfer enthalpy which is a consequence of the large energy ( $\Delta H_{\text{Ac}}^{\text{tr}} = 65.4 \text{ kJ mol}^{-1}$ , Table 2) required to break the water hydrogen-bonding-network when acetate is transferred from water to DMSO.<sup>33</sup>

**Complexation of  $\text{UO}_2^{2+}$  with Acetate in DMSO.** The titration curves in Figure 1a show that the presence of uranyl ion in solution brings about large changes in the protonation profiles of acetate in DMSO. In particular, titration curves show



**Figure 1.** Selected potentiometric (1a) and calorimetric (1b) titrations for the  $\text{UO}_2^{2+}/\text{H}^+/\text{acetate}$  system in DMSO. (1a)  $\text{C}^\circ_{\text{U}}, \text{C}^\circ_{\text{H}}$  mmol  $\text{dm}^{-3}$ : (■, green) 0.0, 3.71,  $R_{\text{H}}$ ; (▲, dark blue) 0.96, 2.93,  $R_{\text{M}}$ ; (●, red) 3.35, 4.56,  $R_{\text{M}}$ , titrant TBAAc  $100.3 \text{ mmol dm}^{-3}$ ; (1b)  $\text{C}^\circ_{\text{U}}, \text{C}^\circ_{\text{Ac}}$  mmol  $\text{dm}^{-3}$ : (▲, red) 16.30, 0.0; (▲, green) 8.62, 0.0; (▲, dark blue) 5.23, 0.0; (▲, light blue) 16.30, 26.7, titrant TBAAc  $101.5 \text{ mmol dm}^{-3}$ ; (■) 0.0, 51.65, titrant  $\text{UO}_2^{2+}$   $51.6 \text{ mmol dm}^{-3}$ . Full lines in 1a and 1b: calculated with the stability constants and reaction enthalpies of Tables 1 and 3. Dashed lines in part b: % distribution of  $\text{UO}_2^{2+}$  (black),  $\text{UO}_2\text{Ac}^+$  (green),  $\text{UO}_2(\text{Ac})_2$  (red) and  $\text{UO}_2(\text{Ac})_3^-$  (blue).

that the affinity of acetate for protons is much higher than that for uranyl ions and that uranyl(VI) can successfully compete with the protons for binding acetate only when the concentration of  $\text{H}^+$  is drastically reduced in solution.

The abscissa in Figure 1a is the ratio between the difference (moles of acetate – moles of protons) and either the number of moles of protons ( $R_H$ ) or the number of moles of metal ion

**Table 3. Stepwise Thermodynamic Parameters for the Formation of U(VI)–Acetate Complexes in DMSO and Water According to the Reaction:  $\text{UO}_2\text{Ac}_j^{(2-j)+} + \text{Ac}^- \rightleftharpoons \text{UO}_2(\text{Ac})_{j+1}^{(2-j-1)+}$  ( $j = 0-2$ )<sup>a</sup>**

	complex	$\log K_j$	$-\Delta G_j^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H_j^\circ$ (kJ mol <sup>-1</sup> )	$T\Delta S_j^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S_j^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
DMSO	$\text{UO}_2\text{Ac}^+$	$6.63 \pm 0.05$	$37.8 \pm 0.3$	$-11.2 \pm 0.3$	$26.6 \pm 0.4$	$89 \pm 1$
	$\text{UO}_2\text{Ac}_2$	$5.21 \pm 0.10$	$29.8 \pm 0.6$	$-15.3 \pm 1.8$	$14.5 \pm 1.9$	$51 \pm 7$
	$\text{UO}_2\text{Ac}_3^-$	$5.49 \pm 0.11$	$31.3 \pm 0.6$	$-39.6 \pm 1.8$	$-8.3 \pm 2.0$	$-30 \pm 7$
water <sup>6</sup>	$\text{UO}_2\text{Ac}^+$	2.58	14.7	10.6	25.3	85
	$\text{UO}_2\text{Ac}_2$	1.79	10.2	9.4	19.6	66
	$\text{UO}_2\text{Ac}_3^-$	2.49	14.2	-2.5	11.7	39

<sup>a</sup>Errors: three times the standard deviation.

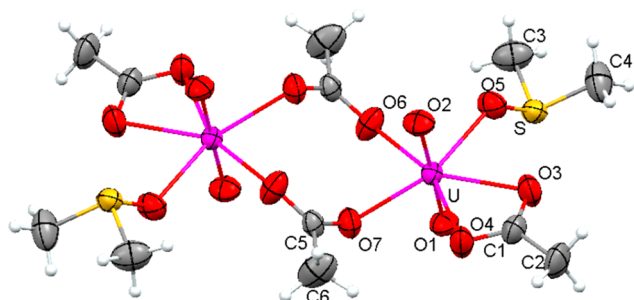
( $R_M$ ) in solution. Then, the first equivalent point in titrations 1, 2, and 3 occurs when  $R_H$  and  $R_M$  are equal to zero, whereas the second equivalent point at  $R_M = 3$  in the titrations 2 and 3 reflects formation of at least three successive uranyl–acetate complexes.

In agreement with this qualitative result, the potentiometric data fitting indicated that  $\text{UO}_2^{2+}$  ion forms three mononuclear successive complexes. The results of data analysis allowed to calculate with satisfactory accuracy the overall stability constants for the formation of the first and third complex but produced only an estimate for  $\beta_2$ . [ $\log \beta_1 = 6.60 \pm 0.09$ ;  $\log \beta_3 = 17.14 \pm 0.18$ . See also the comment on the calculation procedure in the SI, page 3.]

The successive elaboration of the calorimetric data allowed to define with a better precision the value for the formation constant of the second complex (see the Experimental Section and Table 3).

In Figure 1b, selected data points of the calorimetric titrations are reported as  $\Delta h_v$  (total reaction enthalpy per mole of titrant) vs  $R_{Ac}$  ( $R_{Ac} = C_{Ac}/C_U$ , the ligand to metal molar ratio). The overlapping of the  $\Delta h_v$  values on increasing  $R_{Ac}$  and the clear reaction end point at  $R_{Ac} = 3$  in the figure confirm the formation of three stable mononuclear complexes.

The good agreement between the experimental and calculated  $\Delta h_v$ 's (solid lines in Figure 1b) implies that only mononuclear U(VI) species are formed in solution, despite a dinuclear 1:2 uranyl:acetate complex with two bridging acetates in a  $((\text{UO}_2)_2(\text{DMSO})_2(\text{Ac})_4)$  crystal is identified in the present study and polynuclear solid adducts are not uncommon in the literature.<sup>70</sup>

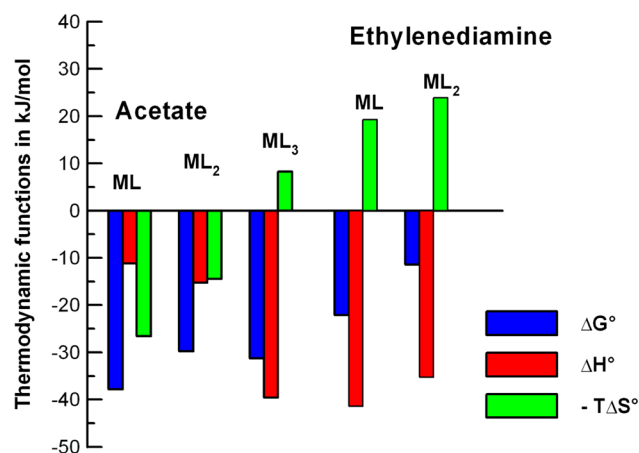


**Figure 2.** The crystal structure of  $[(\text{UO}_2)_2(\text{DMSO})_2(\text{Ac})_4]$ .

Thermodynamic parameters in Table 3 show that the three mononuclear complexes of uranyl with acetate are stabilized in DMSO both by the entropy [except for the third stepwise entropy] and enthalpy terms which follow the trends:  $-\Delta H_1^\circ < -\Delta H_2^\circ \ll -\Delta H_3^\circ$  and  $\Delta S_1^\circ > \Delta S_2^\circ \gg \Delta S_3^\circ$ . The enthalpy and entropy of complexation result from the combination of contributions associated with three main events: i) the

formation of the metal–ligand coordination bonds; ii) the desolvation/solvation processes of reactants and products; and iii) the changes in the bulk of the solvent due to the complex formation.

The exothermic enthalpies associated with the formation of all the uranyl–acetate complexes indicate that the substitution of the neutral solvent molecules by negatively charged ions in the coordination sphere of the metal ion is an enthalpy-favored process, as expected on the basis of the mainly electrostatic character which governs these interactions. As far as point ii) is concerned, it is reasonable to assume that the enthalpy and entropy terms associated with the acetate desolvation are modest (see above) when compared with those for the uranyl desolvation in DMSO and solvent reorganization. The positive reaction entropies which accompany the complex formation can be due to both the reorganization of the bulk solvent and the release of solvent molecules from the first coordination sphere of the metal ion. However, the comparison of the thermodynamic functions for the formation of uranyl–acetate and uranyl–ethylenediamine complexes in DMSO (Figure 3) suggests that solvent reorganization should play the most relevant role.

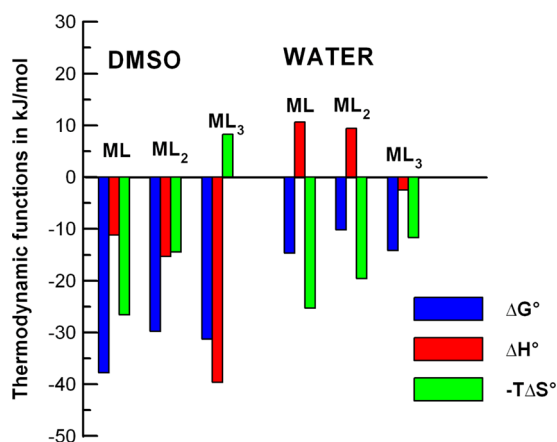


**Figure 3.** Stepwise thermodynamic functions for the formation of uranyl(VI)–acetate and uranyl(VI)–ethylenediamine complexes (ref 22) in DMSO. Ionic medium  $\mu = 0.1 \text{ mol dm}^{-3}$  and  $T = 298 \text{ K}$ .

As previously found,<sup>22</sup> ethylenediamine (en) forms two successive mononuclear chelate complexes with uranyl(VI) according to a reaction that occurs without charge neutralization. In that case, the formation of  $\text{UO}_2(\text{en})_j^{2+}$  ( $j = 1, 2$ ) complexes is only driven by the highly favorable reaction enthalpy. The chelation of uranyl by en is expected to be accompanied by a desolvation of the first coordination sphere of the metal ion similar to that due to the acetate coordination.

In addition, ethylenediamine, as hydrogen bond donor, should be more solvated than acetate in DMSO. All this, in the absence of solvent reorganization upon charge neutralization, should result in thermodynamic parameters for the two systems having, at least, the same sign. The entropy terms relative to the formation of  $\text{UO}_2(\text{en})_j^{2+}$  and  $\text{UO}_2(\text{Ac})_j^{(2-j)+}$  ( $j=1, 2$ ) complexes have opposite sign, and the enthalpy terms for  $\text{UO}_2^{2+}$ –acetate complexes are less favorable than those for the formation of en complexes. This finding is quite unexpected on the basis of the stronger interaction between  $\text{UO}_2^{2+}$  and a charged species and can be considered a clear indication of the prominent role played by the enthalpy and entropy contributions related to the solvent reorganization in the reactions between charged species. Possibly, the endothermic process<sup>71</sup> associated with solvent destructuring promoted by the charge neutralization may overcome the higher heat released by the formation of the uranyl–acetate bonds.

**Role of the Ligand Solvation in the Complexation Reactions.** The stability of uranyl–acetate complexes differs significantly in different solvents, with the stability in water much weaker than that in DMSO. The most relevant differences between the thermodynamic data for the formation of the acetate complexes in the two solvents (Table 3 and Figure 4) are the shift toward the endothermicity of the

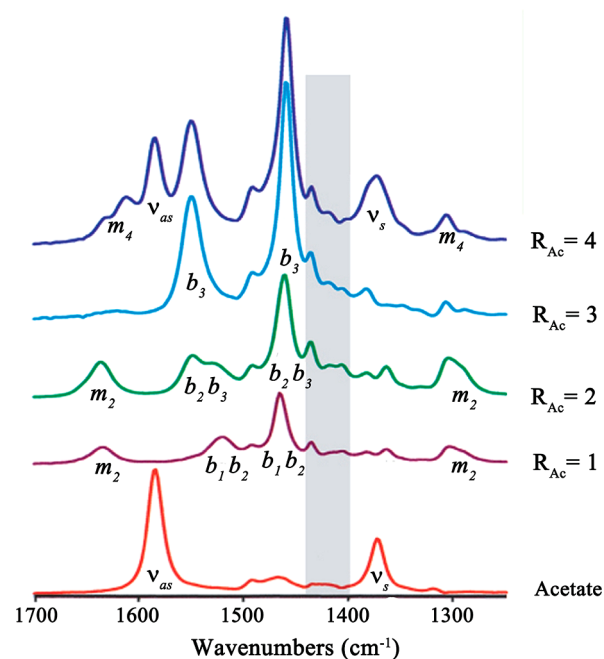


**Figure 4.** Stepwise thermodynamic functions for the formation of uranyl(VI)–acetate complexes in DMSO and in water. For DMSO  $\mu = 0.1 \text{ mol dm}^{-3}$ , for water  $\mu = 1 \text{ mol dm}^{-3}$ ,  $T = 298 \text{ K}$  (ref 6).

enthalpies of formation and the larger entropies of complexation in water. Since the metal cations are generally more solvated in DMSO than in water,<sup>72</sup> the above trends are the result of a much higher degree of solvation of acetate in water than in DMSO (Table 2). [This implies that the desolvation enthalpy of uranyl(VI) is larger in DMSO than in water.]

The difference in the energetics of acetate solvation overrides the difference in the energetics of uranyl solvation in the two solvents, so that the complexation of uranyl with acetate in water requires more desolvation energy (mainly for acetate) and releases more solvent molecules. Consequently, both the enthalpies and entropies of complexation in water are more positive. This comparison underlines the important, often underestimated, role of ligand solvation in the energetics of complexation reactions.

**Coordination Modes of Acetate.** In Figure 5, the vibrational spectra of solutions containing acetate and uranyl(VI) in different ratios ( $R_{\text{Ac}} = 1\text{--}4$ ) are shown in the range of



**Figure 5.** The FT-IR spectra of a  $100 \text{ mmol dm}^{-3}$  tetrabutylammonium acetate solution and those of uranyl(VI)–acetate solutions at different ligand to metal ratios,  $R_{\text{Ac}} = 1\text{--}4$ .  $[\text{UO}_2^{2+}] = 50 \text{ mmol dm}^{-3}$ .  $b_j$  and  $m_j$  stand for  $\nu_s$  or  $\nu_{\text{as}}$  of bidentate and monodentate acetates in  $\text{UO}_2(\text{Ac})_j^{(2-j)+}$  complexes. In the shadowed area the DMSO absorbance is very high, so the subtraction of the absorption spectrum of the solvent is difficult in this region and the spectra after subtraction can be somewhat undefined in this area. See the SI for experimental details and Table S1 for the peak labels and corresponding wavenumber values.

$1700\text{--}1250 \text{ cm}^{-1}$ , where the symmetric ( $\nu_s$ ) and asymmetric ( $\nu_{\text{as}}$ ) stretching modes of the carboxyl group appear. For comparison, the spectrum of a tetrabutylammonium acetate solution is also reported in the same figure.

It is well-known that the difference ( $\Delta\nu = \nu_s - \nu_{\text{as}}$ ) is diagnostic of the type of acetate coordination. Compared with the  $\Delta\nu$  for the free acetate ( $211 \text{ cm}^{-1}$ ),  $\Delta\nu$  becomes larger for the monodentate acetate but smaller for the bidentate acetate.<sup>73</sup> The complex features of the spectra in Figure 5 reflect the presence of different uranyl–acetate complexes and ligand coordination modes in the solutions with different  $R_{\text{Ac}}$ .

For the solution with  $R_{\text{Ac}} = 1$ ,  $\text{UO}_2\text{Ac}^+$  is the dominant species [ $\text{UO}_2^{2+}$  17.0%;  $\text{UO}_2\text{Ac}^+$  69.2%;  $\text{UO}_2(\text{Ac})_2$  10.7%;  $\text{UO}_2(\text{Ac})_3^-$  3.1%]. The most relevant peaks in the spectrum can be attributed to  $\nu_s$  ( $1520 \text{ cm}^{-1}$ ) and  $\nu_{\text{as}}$  ( $1465 \text{ cm}^{-1}$ ), and the corresponding  $\Delta\nu$  ( $55 \text{ cm}^{-1}$ ) suggests bidentation of acetate in  $\text{UO}_2\text{Ac}^+$  ( $b_1$ , in Figure 5). The minor bands in the same spectrum (at  $1636$  and  $1305 \text{ cm}^{-1}$ ,  $m_2$ ) can be assigned to the 1:2 complex ( $\text{UO}_2\text{Ac}_2$ ), since they increase in intensity in the spectrum of the solution with  $R_{\text{Ac}} = 2$  and nearly disappear when  $R_{\text{Ac}} = 3$ . The value of  $\Delta\nu = 331 \text{ cm}^{-1}$  for the minor bands suggests that at least one acetate should be monodentate in  $\text{UO}_2\text{Ac}_2$  ( $m_2$ ). Comparable amounts of each of the uranyl–acetate complexes are present in the solution with  $R_{\text{Ac}} = 2$  [ $\text{UO}_2^{2+}$  1.7%;  $\text{UO}_2\text{Ac}^+$  34.4%;  $\text{UO}_2(\text{Ac})_2$  26.1%;  $\text{UO}_2(\text{Ac})_3^-$  37.8%]. Accordingly, the solution spectrum shows both the bands previously assigned to the bidentate and monodentate acetate in  $\text{UO}_2\text{Ac}^+$  and  $\text{UO}_2(\text{Ac})_2$  ( $b_1$  and  $b_2$ , respectively) and two new bands, at  $1549$  and  $1461 \text{ cm}^{-1}$  ( $b_3$ ), which are the main feature of the spectrum collected for the solution with  $R_{\text{Ac}}$

= 3. At  $R_{Ac} = 3$ , the  $UO_2Ac_3^-$  complex is predominant in solution (97.4%) and the observed  $\Delta\nu$  ( $88\text{ cm}^{-1}$ ) agrees with bidentation of all three acetates ( $b_3$ ). As expected from the speciation, the bands characteristic of both the complex 1:3 and the free ligand appear in the spectrum collected for  $R_{Ac} = 4$ . However, in addition to those expected, the spectrum shows a new couple of bands at 1612, with a shoulder at  $\sim 1640\text{ cm}^{-1}$ , and at  $1307\text{ cm}^{-1}$  ( $m_4$ ). The presence of these bands suggests that a small part of the acetate added in excess with respect to the 1:3 stoichiometry may be involved in the formation of a successive complex where it binds uranyl as monodentate.

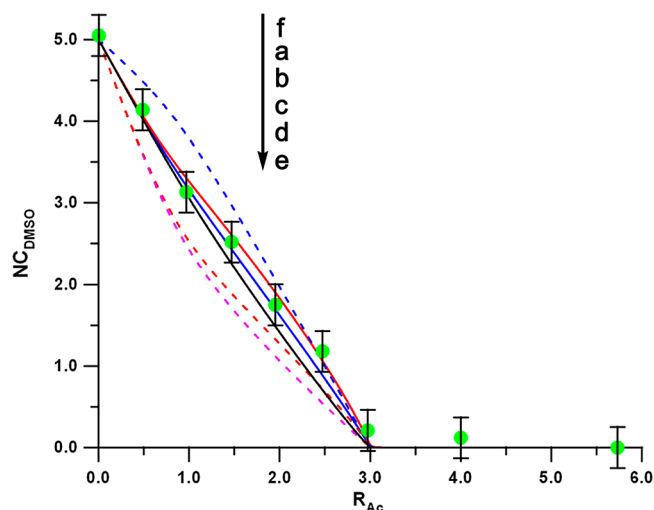
Formation of uranyl–acetate complexes containing more than three acetates per uranyl ion was not observed neither in the potentiometric nor in the calorimetric experiments, where the reagent concentrations were significantly lower. Therefore, the peaks appearing for  $R_{Ac} = 4$  and  $C_M^\circ = 50\text{ mmol dm}^{-3}$  can be assigned to the formation of a weak complex which can form in solution only at high metal ion concentrations.

**Solvation Changes of the Metal Ion upon Complexation.** The FT-IR study discussed in the previous section provided information about the acetate coordination modes in the complexes, but no information was acquired about the changes in the first coordination sphere of the metal ion. A series of FT-IR experiments was therefore carried out to explore the preferential and quantitative solvation of uranyl ion by DMSO in DMSO/acetonitrile mixtures.

When uranyl(VI) perchlorate and an excess of DMSO are dissolved in AN, the anions are completely dissociated to form  $[UO_2(DMSO)_n]^{2+}$  adducts. In experiments preliminary to this study, we have found that the number of DMSO molecules ( $NC_{DMSO}$ ) coordinated to uranyl(VI) in this medium is 5, even in solutions where the ratio  $C_{DMSO}/C_{U(VI)}$  is about 16 (Figure S2). In addition, since the absorption spectra of solutions with different  $R_{Ac}$  in DMSO and in mixed solvent do not differ significantly (Figure S3), it is reasonable to assume quite similar local reaction conditions and formation constants in both the solvent media.

Quantitative analysis of the FT-IR spectra for solutions of uranyl(VI) in AN/DMSO mixtures containing increasing amounts of acetate ( $0 \leq R_{Ac} \leq 4$ ), allowed to determine the mean  $NC_{DMSO}$  in the first coordination sphere of uranyl(VI) on increasing  $R_{Ac}$  (Figure 6). [A detailed description of the experiments and methodological approach followed to obtain these results is provided in the Experimental Section and in the SI.]  $NC_{DMSO}$  (circles in Figure 6) results from the ratio between the difference ( $[DMSO]_{total} - [DMSO]_{free}$ ) and the total metal-ion concentration (See the SI and ref 28 for details.). The decrease of  $NC_{DMSO}$  is nearly linear for  $R_{Ac} \leq 1$ , becomes less steep at higher  $R_{Ac}$ , and reaches zero at  $R_{Ac} = 3$ . This result, in conjunction with the fact that no bands relative to monodentate acetate are visible in the spectrum collected for  $R_{Ac} = 3$  (Figure 5 and Table S1), demonstrates that the coordination number of the metal ion increases from 5 to 6 during complexation.

Lines in Figure 6 represent values of  $NC_{DMSO}$  calculated on the basis of six different desolvation schemes (Table 4). They result from the sum  $\sum_{j=0}^3 n_j \times X_j$ , where  $n_j$  is the number of molecules of DMSO assumed [On the basis of a given model, see Table 4.] to be present in the first coordination sphere of the  $[UO_2(Ac)_j(DMSO)_{n_j}]^{(2-j)+}$ ,  $j = 0-3$ , complexes;  $X_j$  is the mole fraction of the  $j^{th}$  complex, for each value of  $R_{Ac}$  [calculated on the basis of the stability constants in Table 3 and the analytical concentrations of U(VI) and acetate].



**Figure 6.** The mean number of molecules of DMSO coordinated to the uranyl ion (green circles) observed for the formation of uranyl–acetate complexes in the AN/DMSO mixtures as a function of  $R_{Ac}$ . The error bars correspond to an estimated uncertainty in  $NC_{DMSO}$  of  $\pm 0.25$ . The lines a–f have been calculated on the basis of the desolvation sequences in Table 4 and the stability constants in Table 3.

The curves d, e, and f in Figure 6 (dashed lines) correspond to the release of 3, 3, and 1 DMSO molecules, respectively, in the first coordination step. They all lie outside the error bars associated with the values of  $NC_{DMSO}$ . Hence, this treatment suggests that, on forming the 1:1 complex,  $[UO_2(DMSO)_5]^{2+}$  loses two DMSO molecules without any change of the metal-ion coordination number. Therefore, taking into account that all experimental data in Figure 6 can be equally well fitted by curves a, b, and c, it emerges that the change in the coordination number of uranyl ion, from 5 to 6, can occur either in the second or in the third complexation step.

**DFT Calculations on Uranyl–Acetate Complexes.** Generally, theoretical methods have been applied to study the coordination of acetate to uranyl only in the gas phase,<sup>10,11,15</sup> except for one work where water replacement has been considered.<sup>12</sup>

To gain information about the molecular process at the basis of the complex formation in DMSO and relate it to structural information, DFT calculations were used to study the solvent replacement by acetate in the formation of uranyl(VI) complexes having the stoichiometry of  $[UO_2(DMSO)_n(Ac)_m]^{(2-m)+}$  with  $m = 0-3$  and  $n = 0-5$ . Both coordination modes of acetate, mono- and bidentate, have been considered in the DFT calculations.

The optimized structures of these complexes are shown in Figure 7. Selected bond lengths calculated for these complexes are reported in Table S3 and are found to be in good agreement with those of available experimental structures.<sup>74–76</sup> In Table S4 selected bond distances of the structure of  $[(UO_2)_2(DMSO)_2(Ac)_4]$  obtained in this work (Figure 2) are also reported for comparison.

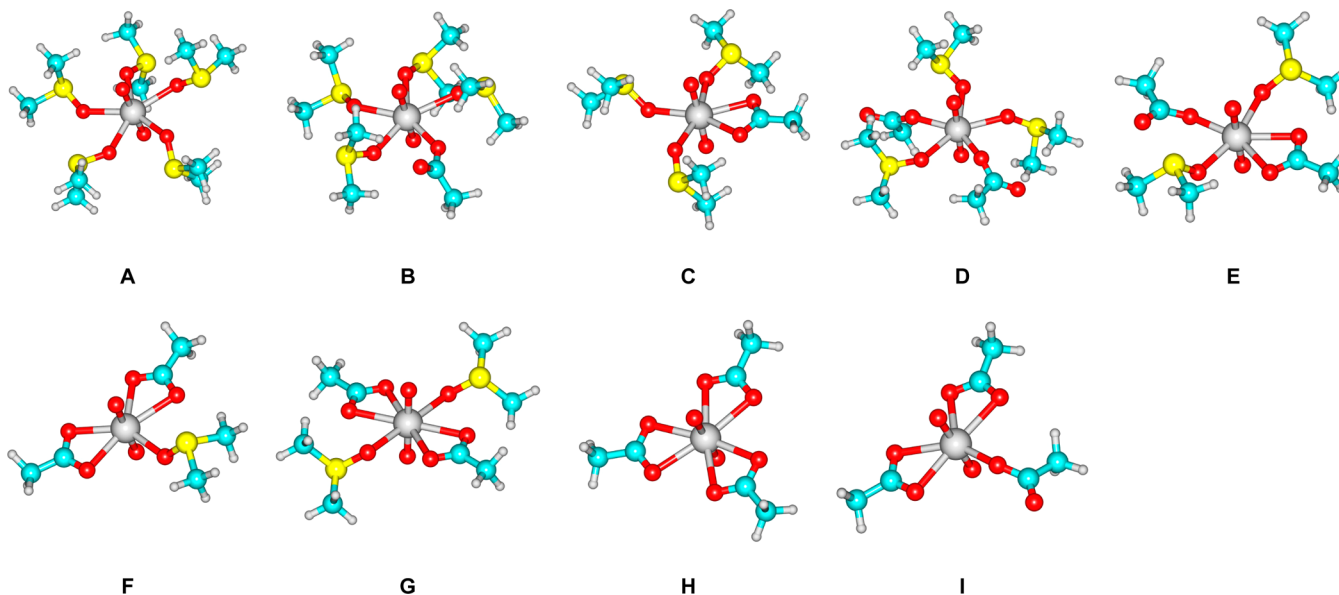
The calculated U–O<sub>ac</sub> bonds lengths are slightly overestimated with respect to the values in the literature<sup>75,76</sup> and to those obtained for the structure in Figure 2 (Table S5). These bonds are found to be longer for bidentate acetate (the average value reported in Table S3 is  $2.50(3)\text{ Å}$ ) than for monodentate (average value  $2.28(4)\text{ Å}$ ). This last result is quite reasonable as the U–O<sub>ac</sub> bonds in the complex in Figure 2 are somewhat



Table 4. Possible Desolvation Sequences (a–f) for the Formation of the Uranyl Complexes<sup>a</sup>

	a	b	c	d	e	f
$[\text{UO}_2(\text{DMSO})_{n_0}]^{2+}$	$n_0 = 5$	5	5	5	5	5
$[\text{UO}_2\text{Ac}(\text{DMSO})_{n_1}]^+$	$n_1 = 3(2)$	3(2)	3(2)	2(3)	2(3)	4(1)
$[\text{UO}_2\text{Ac}_2(\text{DMSO})_{n_2}]$	$n_2 = 1(2)$	2(1)	3(0)	1(1)	2(0)	2(2)
$[\text{UO}_2\text{Ac}_3(\text{DMSO})_{n_3}]^-$	$n_3 = 0(1)$	0(2)	0(3)	0(1)	0(2)	0(2)

<sup>a</sup> $n_j$  is the number of residual molecules of DMSO assumed to be metal-ion coordinated for the calculation of  $\text{CN}_{\text{DMSO}}$  in Figure 6. In parentheses,  $p_i$  the number of molecules of DMSO released according to the equation:  $[\text{UO}_2(\text{Ac})_j(\text{DMSO})_{n_j}]^{(2-j)+} + \text{Ac}^- \rightarrow [\text{UO}_2(\text{Ac})_{j+1}(\text{DMSO})_{n_j-p_i}]^{(2-j-1)+} + p_i \text{DMSO}$  for  $j = 0-2$ .



**Figure 7.** Optimized structures of the uranyl–acetate complexes ( $m$  = monodentate,  $b$  = bidentate): (A)  $[\text{UO}_2(\text{DMSO})_5]^{2+}$  ( $\text{CN}_{\text{eq}} = 5$ ); (B)  $[\text{UO}_2(\text{DMSO})_4(\text{Ac})]^+$ ,  $\text{CN}_{\text{eq}} = 5$ , ( $m$ ); (C)  $[\text{UO}_2(\text{DMSO})_3(\text{Ac})]^+$ ,  $\text{CN}_{\text{eq}} = 5$ , ( $b$ ); (D)  $[\text{UO}_2(\text{DMSO})_3(\text{Ac})_2]$ ,  $\text{CN}_{\text{eq}} = 5$ , ( $m,m$ ); (E)  $[\text{UO}_2(\text{DMSO})_2(\text{Ac})_2]$ ,  $\text{CN}_{\text{eq}} = 5$ , ( $b,m$ ); (F)  $[\text{UO}_2(\text{DMSO})_2(\text{Ac})_2]$ ,  $\text{CN}_{\text{eq}} = 6$ , ( $b,b$ ); (G)  $[\text{UO}_2(\text{DMSO})(\text{Ac})_2]$ ,  $\text{CN}_{\text{eq}} = 5$ , ( $b,b$ ); (H)  $[\text{UO}_2(\text{Ac})_3]^-$ ,  $\text{CN}_{\text{eq}} = 6$ , ( $b,b,b$ ); (I)  $[\text{UO}_2(\text{Ac})_3]^-$ ,  $\text{CN}_{\text{eq}} = 5$ , ( $b,b,m$ ).  $\text{CN}_{\text{eq}}$  coordination number of uranyl ion in the equatorial plane.

Table 5. Theoretical Reaction Enthalpies and Free Energies for the Sequential Substitution of Coordinated DMSO by Acetate<sup>a</sup>

	product	$\text{CN}_{\text{eq},i}$	$\text{CN}_{\text{eq},f}$	$\Delta H$ (kJ mol <sup>-1</sup> )		$\Delta G$ (kJ mol <sup>-1</sup> )	
				vacuum	DMSO	vacuum	DMSO
$[\text{UO}_2(\text{DMSO})_5]^{2+} + \text{Ac}^- \rightarrow [\text{UO}_2(\text{DMSO})_4(\text{Ac})]^+ (m) + \text{DMSO}$	B	5	5	-595.6	-31.8	-577.8	-0.4
$[\text{UO}_2(\text{DMSO})_5]^{2+} + \text{Ac}^- \rightarrow [\text{UO}_2(\text{DMSO})_3(\text{Ac})]^+ (b) + 2\text{DMSO}$	C	5	5	-580.2	-44.2	-617.1	-52.1
$[\text{UO}_2(\text{DMSO})_3(\text{Ac})]^+ (b) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{DMSO})_3(\text{Ac})_2] (m,m)$	D	5	5	-373.3	-23.4	-322.4	+27.5
$[\text{UO}_2(\text{DMSO})_3(\text{Ac})]^+ (b) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{DMSO})_2(\text{Ac})_2] (b,m) + \text{DMSO}$	E	5	5	-373.8	-46.5	-369.1	-27.3
$[\text{UO}_2(\text{DMSO})_3(\text{Ac})]^+ (b) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{DMSO})(\text{Ac})_2] (b,b) + 2\text{DMSO}$	F	5	5	-326.7	-14.9	-371.6	-30.8
$[\text{UO}_2(\text{DMSO})_3(\text{Ac})]^+ (b) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{DMSO})_2(\text{Ac})_2] (b,b) + \text{DMSO}$	G	5	6	-360.8	-34.6	-357.8	-17.2
$[\text{UO}_2(\text{DMSO})_2(\text{Ac})_2] (b,m) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{Ac})_3]^- (b,b,b) + 2\text{DMSO}$	H	5	6	-88.0	-30.8	-139.2	-53.1
$[\text{UO}_2(\text{DMSO})_2(\text{Ac})_2] (b,m) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{Ac})_3]^- (b,b,m) + 2\text{DMSO}$	I	5	5	-87.3	-14.0	-136.4	-34.1
$[\text{UO}_2(\text{DMSO})(\text{Ac})_2] (b,b) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{Ac})_3]^- (b,b,b) + \text{DMSO}$	H	5	6	-135.1	-62.4	-136.7	-49.6
$[\text{UO}_2(\text{DMSO})(\text{Ac})_2] (b,b) + \text{Ac}^- \rightarrow [\text{UO}_2(\text{Ac})_3]^- (b,b,m) + \text{DMSO}$	I	5	5	-134.4	-45.0	-133.9	-30.6

<sup>a</sup>The free energy in solution has been calculated with the correction taking into account the reduced translational entropy of DMSO.<sup>61–63</sup> Letters refer to the complexes in Figure 7,  $\text{CN}_{\text{eq},i/f}$  = initial/final coordination number of uranyl ion in the equatorial plane,  $b$  = bidentate  $m$  = monodentate.

shorter for the bis-monodentate acetates with respect to the bidentate ones (Table S4). In addition, these structural results are in good agreement with the EXAFS experiments in aqueous solution where two types of coordinated oxygens were observed in the equatorial plane when  $R_{\text{Ac}} = 3$  (four oxygens at  $\text{U}-\text{O}_{\text{ac}} 2.34 \text{ \AA}$  and one at  $2.48 \text{ \AA}$  from uranium).<sup>6</sup>

Vibrational analysis carried out for the optimized structures gives a result coherent with the experimental spectra. The  $\Delta\nu_{\text{calc}}$  values calculated for the structures in which acetate is bidentate fall in the range  $51-146 \text{ cm}^{-1}$  (Table S5), in qualitative

agreement with the experimental results of Figure 5 ( $\Delta\nu_{\text{exp}} = 65-88 \text{ cm}^{-1}$ ). Accordingly,  $\Delta\nu_{\text{calc}}$  becomes larger with respect to that of free acetate when acetate is assumed to be monodentate ( $\Delta\nu_{\text{calc}} = 319-412 \text{ cm}^{-1}$ ).

The values of the reaction enthalpies ( $\Delta H$ ) associated with the replacement of the DMSO coordinated to metal ion in the sequential formation of uranyl(VI)–acetate complexes (Table 5) show a marked medium effect. In vacuum, monodentate acetate coordination ( $m$  in Table 5) has similar or more negative  $\Delta H$  values with respect to bidentate for the formation

of the 1:1 and 1:2 complexes, while the 1:3 species they are quite similar. The reaction free energies (Table 5) in vacuum are very negative as expected for gas-phase reactions.

When the solvent effect is considered, the calculated  $\Delta H$  gives a clear indication that the formation of complexes with bidentate acetate (C in Table 5) and the release of two DMSO molecules are favored for the first complexation step. The calculated  $\Delta G$  for the formation of C is also strongly negative indicating that the 1:1 complex with bidentate acetate with three coordinated DMSO molecules is largely the most stable species. This result is compatible with the a–c desolvation sequences in Table 4 and in agreement with the calculated curves in Figure 6.

The most negative  $\Delta H$  for the formation of the 1:2 species in DMSO is that obtained for the complex E (Figure 7), where one acetate is bidentate and the other monodentate. However, the associated  $\Delta G$  values show that the complexes E and F are the most thermodynamically favored species with rather similar stability. This results from the theoretical gas-phase free energy contribution, which is much more favorable for the formation of F (two solvent molecules are released instead of one). This implies that a consistent fraction of coordinated acetate is monodentate, as also suggested by the IR spectra in Figure 5. In addition, the formation of D can be excluded (positive  $\Delta G$ ). In conclusion, DFT calculations for the formation of the 1:2 complex exclude the simultaneous release of three DMSO molecules and are compatible only with the a and b desolvation models in Table 4.

Finally, we obtain that the formation of the  $[\text{UO}_2(\text{Ac})_3]^-$  complex where all acetates are bidentate (H) is always favored in DMSO with respect to the complex I (Table 5 and Figure 7) either if the reacting species is E or F. This result is also in agreement with the spectra in Figure 5 which show that at  $R_{\text{Ac}} = 3$  no monodentate acetate is present. EXAFS experiments in aqueous solution<sup>6</sup> showed clearly that monodentate acetate is present in the  $[\text{UO}_2(\text{Ac})_3]^-$  complex. This was explained by the stabilization of the monodentate bonding through the formation of an hydrogen bond between the free oxygen and water hydrogen.<sup>6</sup> Previous experiments and theoretical results in the gas phase also indicated that at least one acetate is monodentate in the  $[\text{UO}_2(\text{Ac})_3]^-$  species and that the energy difference with the tris-bidentate complex is negligible (as also found here, Table 5).<sup>10</sup> Therefore our theoretical and experimental evidence show that DMSO stabilizes the tris-bidentate complex with respect to both water and gas phase.

Direct comparisons between experimental and calculated thermodynamic parameters are quite difficult since the latter refer to individual microscopic processes and affected by the approximations of the method. However, we find that both calculated  $\Delta G$  and  $\Delta H$  values relative to the most stable species (C, E/F, and H) become markedly less negative from the first to the second complexation step. This trend seems to be more similar to that experimentally found for ethylenediamine than for acetate (Figure 3) and may be another (indirect) indication of the importance of the reorganization of the solution due to complexation occurring with charge neutralization.

## CONCLUSIONS

A comparison of the thermodynamic and structural data on the complexation of U(VI) with acetate in DMSO and water has demonstrated the importance of the medium effect on the complexation. In contrast with water, which is both acceptor and donor of hydrogen bonds, DMSO is a solely hydrogen

bonds acceptor. Therefore, DMSO does not strongly solvate anionic ligands such as acetate, which results in much higher basicity of acetate in DMSO than in water. Uranyl(VI), on the contrary, is more solvated in DMSO. Consequently, the higher stability of U(VI)–acetate complexes in DMSO is a good example of formation of complexes whose stability is uniquely due to the solvent effect on the anion properties.

In addition, comparison of the thermodynamic parameters for the complex formation of U(VI) with acetate and ethylenediamine in DMSO indicates that the changes in solvent bulk, associated with the reactions where charge neutralization occurs, give important contributions to both the enthalpy (less favorable for the charged ligand) and the entropy of complexation (always negative for the neutral ligand).

The combination of theoretical calculations and IR spectroscopy shows that the predominant scheme for the formation of the 1:1 U(VI)–acetate complex in DMSO is described by a reaction where two solvent molecules are released. In the second complexation step the release of one or two DMSO molecules leads to the formation of solvated complexes of comparable stability, where acetate is mono- and bidentate. Both DFT calculations and IR experiments agree that in the third complex all acetate ions are bidentate. This is different from what has been found previously in water and in the gas phase evidencing a strong medium effect on the type of coordination of acetate to uranyl(VI) ion.

## ASSOCIATED CONTENT

### Supporting Information

Tables S1–S5, Figures S1–S3, coordinates of the final structures of complexes after geometry optimization, and cif files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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