DALTON
FULL PAPER

Structure, equilibrium and ligand exchange dynamics in the binary and ternary dioxouranium(VI)–glyphosate–fluoride system. A multinuclear NMR study †

Zoltán Szabó *

Inorganic Chemistry, Department of Chemistry, Royal Institute of Technology (KTH), S-10044 Stockholm, Sweden. E-mail: zoltan@kth.se

Received 26th June 2002, Accepted 26th September 2002
First published as an Advance Article on the web 14th October 2002

Complex formation in the binary and ternary uranium(VI)–glyphosate–fluoride systems was investigated with the aid of multinuclear NMR spectroscopy. The stoichiometry and the equilibrium constants of the different complexes in both systems are based on the integral values of the coordinated and free ligands in the ^{1}H-, ^{19}F-, ^{31}P- and ^{17}O-NMR spectra. These were measured at different uranium(VI) concentrations, varying the total ligand concentrations (glyphosate and/or fluoride) in the pH range of 7–10 using a $NaClO_4$ medium at constant sodium concentration, $[Na^+] = 1.00$ M. Tridentate and monodentate coordination has been found for the glyphosate ligand. The proposed structures are based on other spectral parameters (chemical shifts, homo- and heteronuclear couplings) and confirmed by two-dimensional homo- and heteronuclear correlation spectra. The spectra indicate the formation of several isomers for complexes **2** and **4**, which differ from one another in the position of the non-chelated glyphosate. The numerical value of the stepwise stability constants for the non-chelated glyphosates in the binary complexes **4** ($\log K$=12) and **5** ($\log K$=11) falls between the formation constants for U(VI) with PO_4^{3-} and HPO_4^{2-}, that is an independent confirmation of the magnitude of the latter, but also a strong indication that complex formation with phosphate/phosphonate through a single oxygen bond is very strong. The line widths of the fluoride signals in the ternary complexes are independent of the free ligand concentrations, and from these similar external fluoride exchange rate, k_{obs1}=10 ± 2 s^{-1} can be calculated as observed for other U(VI) ternary complexes. The exchange between the coordinated and the free glyphosate was studied by 1D ^{1}H magnetization transfer experiments. From these an *inter*-molecular ligand exchange rate, k_{obs2}= 0.69 ± 0.03 s^{-1}, and a faster *intra*-molecular exchange rate for the methylene protons can also be calculated, k_{obs3} = 2.00 ± 0.21 s^{-1}. The latter is probably a result of consecutive ring openings/chelate formation prior to the dissociation of the ligand.

Introduction

Recently, we have studied the structure and the ligand substitution reactions in binary and ternary uranium(VI)-α-hydroxycarboxylate/glycine–fluoride systems, which provided insight on isomer formation and *inter*- and *intra*-molecular ligand exchange mechanisms.[1] As a continuation of this project, we have investigated the complex formation in the binary and ternary uranium(VI)–glyphosate–fluoride systems by multinuclear NMR spectroscopy. Glyphosate (*N*-(phosphonomethyl)glycine) is a commercial herbicide, which exists in the zwitterionic form and its introduction has been described as a revolutionary advance in agriculture. A significant increase of interest in aminophosphonic acids (which contain a direct carbon-to-phosphorus (C–P) bond) arose at the beginning of the 1970s when the compounds turned out to have various important biological properties. Soil glyphosate is regarded as being "relatively persistent" in some soils, with a half-life varying from less than a week to several months, depending on the extent of soil binding and microbial breakdown. The more sand in a soil the greater the persistence; cooler climates also tend to increase persistence—in Sweden, residues have been found up to three years after application.[2]

The coordination chemistry of glyphosate has been studied towards various di- and trivalent metal ions. Most work has focused on the determination of equilibrium data,[3] however several studies using different spectroscopic methods have recently been published on the structure of various complexes both in the solid[4–6] and aqueous phase.[6,7–12] From a coordination chemical point of view, glyphosate could be very effective ligand towards certain metal ions and also a potent inhibitor of metalloenzymes by blocking active metal centers. Beside the structure, the ligand exchange dynamics of the complexes certainly play a role in the potency of glyphosate, in addition to easy transport within the plant and immobilization and degradation in the soil.

The study of the complex formation of uranium(VI) offers not only the possibility to address its behavior in nature, but also to obtain new fundamental information through comparison with other elements. This depends partly on the unique coordination chemistry of the linear UO_2^{2+} ion. This is the first report on the structure, equilibrium and ligand exchange dynamics of dioxouranium(VI)–glyphosate complexes formed in aqueous solution.

Experimental

The NMR spectra were recorded on a Bruker DMX500 spectrometer at −5 °C, either in D_2O or H_2O, using 5% D_2O solutions to achieve a locked mode. We used a $NaClO_4$ ionic medium at constant sodium concentration, $[Na^+] = 1.00$ M, with the exception of samples where the total concentrations of ligands were higher than 1 M. The temperature was checked using the chemical shift of methanol.[13] The test solutions were

† Electronic supplementary information (ESI) available: Figs. S1–13: additional NMR spectra. See http://www.rsc.org/suppdata/dt/b2/b206175a/

 DOI: 10.1039/b206175a

Table 1 Equilibrium constants, $\log\beta$, for the binary and for the ternary uranium(VI)–glyphosate–fluoride systems. The values refer to the following reactions: $UO_2^{2+} + pL^{3-} + qH^+ \rightleftharpoons UO_2H_qL_p^{2-3p+q}$ and $UO_2^{2+} + pL^{3-} + qH^+ + rF^- \rightleftharpoons UO_2H_qL_pF_r^{2-3p+q-r}$ where L^{3-} is deprotonated glyphosate ($OOCCH_2NHCH_2PO_3^{3-}$). The values in parantheses reflect the errors originating from spectrum processing, integration of the signals, pH measurements and the linear regression of the data. The protonation constants for glyphosate refer reaction $L^{3-} + nH^+ \rightleftharpoons LH_n^{(3-n)+}$ and were determined by potentiometry in a 1.00 M $NaClO_4$ ionic medium at 25 °C. Their uncertainty is equal to three times the estimated standard deviation in the least-squares refinement of the experimental data

Complex	Logβ
LH^{2-}	9.75 ± 0.04
LH_2^-	14.92 ± 0.07
LH_3	17.02 ± 0.07
$UO_2LF_2^{3-}$ (**1**)	16.10 (± 0.05)
$UO_2L_2HF^{4-}$ (**2**)	26.75 (± 0.07)
UO_2L^- (**3**)	13.65 (± 0.2)
$UO_2L_2H^{3-}$ (**4**)	25.62 (± 0.15)
$UO_2L_3H_2^{5-}$ (**5**)	36.62 (± 0.05)

measured using 5 mm inverse (for ^{1}H and ^{19}F), or 5 mm normal (for ^{17}O, ^{31}P and ^{13}C), broadband NMR probe heads. The NMR spectra were referenced as follows, ^{1}H- and ^{13}C-NMR spectra (recorded at 500.1 and 125.7 MHz, respectively) to the methyl signal of external TMS, the ^{19}F-spectra (470.5 MHz) to an aqueous solution of NaF (pH = 12) at 25 °C, the ^{17}O-spectra (67.8 MHz) to water at 25 °C, and the ^{31}P-NMR spectra (202.4 MHz) to 85 % H_3PO_4 at 25 °C. ^{17}O-NMR measurements were performed using ^{17}O-enriched samples. The enrichment of the "-yl" oxygens of the uranyl-ion was accomplished by a procedure described previously[14] using ^{17}O-enriched water. Magnetization transfer experiments were performed using Gaussian pulses. The proton concentration was calculated from the measured $-\log[H^+]$ corrected for the "Irving factor" in the working media;[15] $-\log[D^+]$ in pure D_2O solvent was calculated as described before.[16]

In order to calculate the stability constant for the different complexes one has to know the concentration of the free deprotonated glyphosate $[L^{3-}]$, in which the deprotonated nitrogen atom provides a free electron pair for coordination. Hence, the protonation constants of glyphosate were determined by potentiometry at 25 °C in 1 M $NaClO_4$. These are given in the Table 1 and practically identical with the ones reported in 1 M NaCl at the same temperature.[8]

Results and discussion

The constitution and the structure of the complexes identified in the ternary (**1**, **2**) and the binary (**3**–**5**) systems are given in Schemes 1 and 2. Both the stoichiometry and the equilibrium constants of the complexes given in the Table 1 are based on the integral values of the coordinated and free ligands (fluoride and glyphosate) in the ^{1}H-, ^{19}F-, ^{31}P- and ^{17}O-NMR spectra, which allow a direct determination of the concentrations of the complexes (including isomers) and non-coordinated ligands. The proposed structures are based on other NMR spectral parameters (chemical shifts, homo- and heteronuclear couplings) and confirmed by two-dimensional homo- and heteronuclear correlation spectra. The spectra were measured at different uranium(VI) concentrations, varying the total ligand concentrations (glyphosate and/or fluoride) in the pH range of 7–10.

Equilibrium and structure in the ternary system

The formation of two ternary species (**1**, **2**) was observed in the NMR spectra measured at various uranium(VI) and ligand concentrations. Fig. 1 shows the ^{19}F-NMR peaks for the complexes. In complex **1** the two fluoride signals have very different

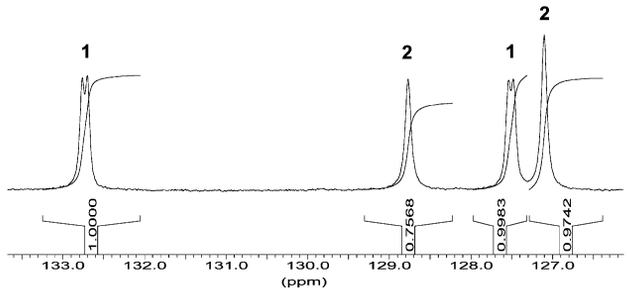


Fig. 1 ^{19}F-NMR spectrum in the ternary uranium(VI)–glyphosate–fluoride system showing couplings between the signals in complex **1** and two signals for the isomers in complex **2**. The spectrum was recorded at −5 °C using $[UO_2^{2+}]_{tot}$= 20 mM, $[H_3L]_{tot}$ = 80 mM and $[F^-]_{tot}$ = 190 mM at pH = 9.0.

chemical shift and they are coupled to one another with 27 Hz coupling. This was confirmed by a ^{19}F–^{19}F COSY spectrum (ESI, Fig. S1 †). For the other ternary complex (**2**) the ^{19}F-NMR spectra also show two signals and the ratio of the signals is the same (1:0.75) in all the spectra. This indicates the formation of two isomers with different thermodynamic stability, by the coordination of a glyphosate in two possible positions, as shown in Scheme 1.

Complex **1** has four NMR signals for the methylene protons with very different chemical shifts (Fig. 2(a)), indicating a tridentate coordination of the glyphosate ligand. The chemical shift difference and the multiplet structure of the signals indicate the formation of a rigid ring system. ^{1}H–^{1}H, ^{1}H–^{13}C and ^{1}H–^{31}P two-dimensional correlation spectra show (ESI, Fig. S2–S4 †), that the proton signals at 3.58 and 4.39 ppm are coupled to one another and belong to the methylene group next to the carbonyl carbon. Consequently, the signals appearing at 2.90 and 3.61 ppm are from the methylene protons next to the phosphono group. These signals are coupled both to one another and to the phosphorus atom. In the ^{17}O-NMR spectrum, two peaks with the same intensity can be observed for the uranyl-oxygens (Fig. 2(b)). The appearance of these signals

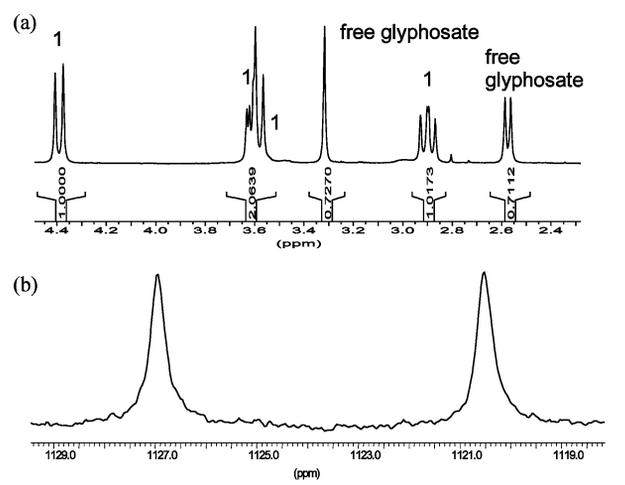
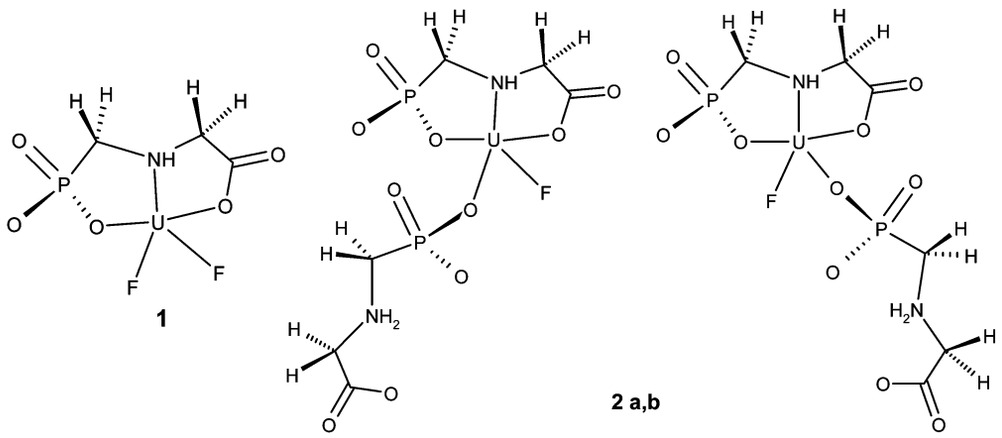
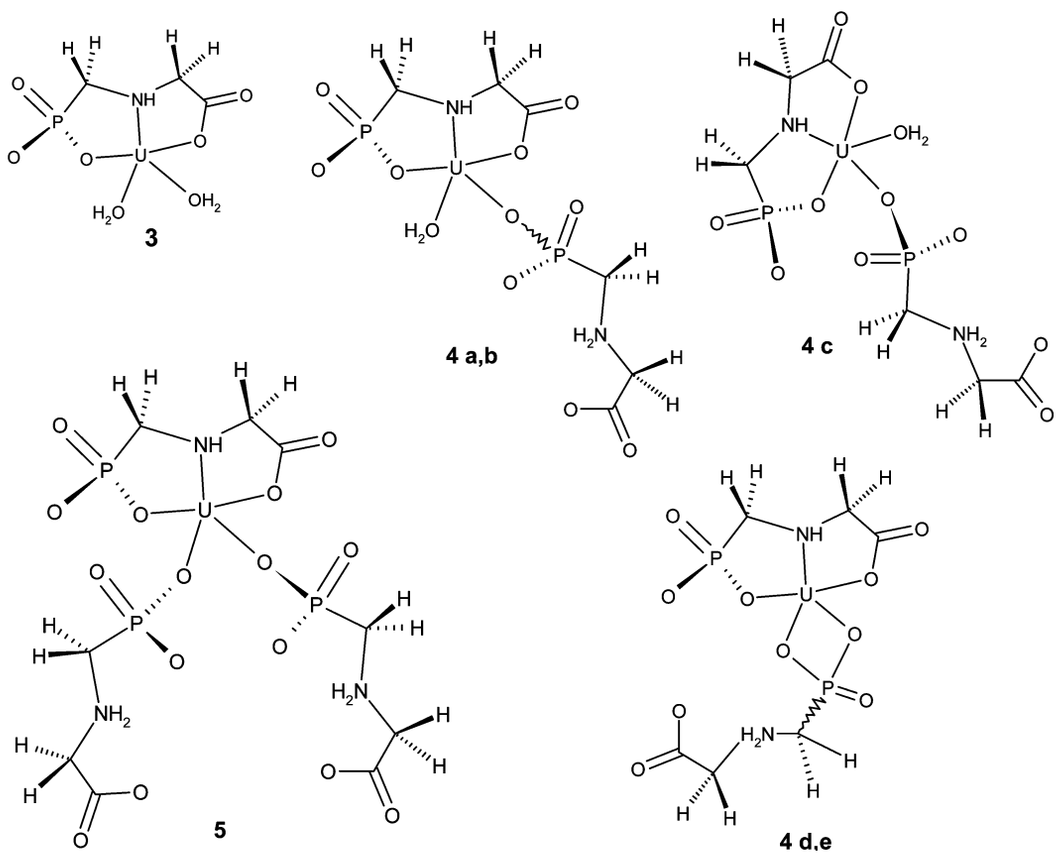


Fig. 2 (a) ^{1}H- and (b) ^{17}O-NMR peaks for complex **1** recorded at −5 °C using pH = 8.8, $[UO_2^{2+}]_{tot}$ = 20 mM, $[F^-]_{tot}$ = 800 mM and $[H_3L]_{tot}$ = 20 mM.

and their chemical shift difference can be explained by the steric interaction of the closely spaced oxygen atoms in the phosphono group and one of the uranyl oxygens, as can be seen in the perspective view of this complex (Fig. 3). According to the best of our knowledge this is the first observation of two different ^{17}O-NMR peaks for the "yl"-oxygens in the uranyl ion. Both the ^{13}C- and the ^{31}P-NMR signals appear at much higher field in the coordinated ligands than those in the free



Scheme 1 Constitution and the structure of the complexes in the ternary uranium(VI)–glyphosate–fluoride system (U = UO_2^{2+}, charges are neglected for simplicity).



Scheme 2 Constitution and the structure of the complexes in the binary uranium(VI)–glyphosate system (U = UO_2^{2+}, charges are neglected for simplicity).

ligand. The spectra with the peak assignments are shown in the ESI (Figs. S5–S6). †

Using less than 25 mM glyphosate in test solutions with a total concentration of 20 mM for uranium(VI) and 800 mM for fluoride at pH = 8.8, the main components are $UO_2F_4^{2-}$, $UO_2F_5^{3-}$ and $UO_2LF_2^{3-}$ (**1**) (L = *N*-(phosphonomethyl)glycine), hence the formation constant for complex **1** can be calculated using the integrals of the ^{31}P- and ^{19}F-NMR spectra (ESI, Figs. S6, S7 †). The equilibrium between $UO_2F_4^{2-}$ and complex **1** and their equilibrium constant (K_1) can be given by eqns. (1) and (2)

$$UO_2F_4^{2-} + L^{3-} \rightleftharpoons UO_2LF_2^{3-} + 2F^- \quad (1)$$

$$K_1 = \frac{\beta_1}{\beta_{4,F}} = \frac{[UO_2LF_2]}{[UO_2][L][F]^2} \times \frac{[UO_2][F]^4}{[UO_2F_4]} = \frac{[UO_2LF_2][F]^2}{[UO_2F_4][L]} \quad (2)$$

where, $\beta_{4,F}$ is the stability constant for $UO_2F_4^{2-}$, [L] is the concentration of the free depronated glyphosate ($OOCCH_2NHCH_2PO_3^{3-}$). The latter can be calculated by eqn. (3)

$$[L] = \frac{C_{HL}}{1 + K_{HL}[H^+]} \quad (3)$$

where C_{HL} is the concentration of the free glyphosate, K_{HL} is the first protonation constant of glyphosate and [H^+] is the equilibrium hydrogen ion concentration. The concentration of the free glyphosate (C_{HL}) was calculated using the integrals in the ^{31}P-NMR spectra (see ESI, Fig. S6 †). The ratio between the complexes, as well as the free fluoride concentration is based on the ^{19}F integrals. Then using eqn. (2), $\log\beta_1 = 16.10$ (± 0.05) can be calculated for complex **1**.

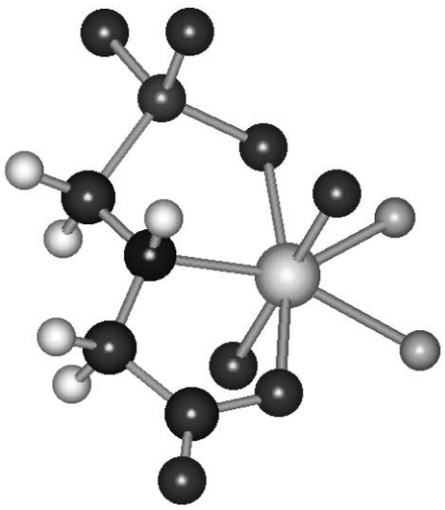


Fig. 3 Perspective view for complex **1**.

At increased glyphosate concentration one fluoride in complex **1** is replaced by HL forming two isomers of $UO_2L_2HF^{4-}$ (**2a**,**b**) as indicated by the NMR spectra (ESI, Figs. S6, S8, S9†). The ^1H and ^{31}P chemical shifts for the chelated ligand in this complex are almost identical with those in complex **1**. However, the very different chemical shifts and the exchange averaged CH_2 proton signals for the second glyphosate indicate its different coordination mode through one oxygen atom of the phosphono group. The two ^{31}P signals recorded for both the chelated and for the monodentatly coordinated glyphosates in this complex are in accordance with the ^{19}F-NMR spectra and confirm the formation of two structural isomers. Similarly to complex **1**, two ^{17}O-NMR peaks can be observed for these isomers, (ESI, Fig. S9†).

The equilibrium between complexes **1** and **2a**,**b** and their equilibrium constant (K_2) can be described by eqns. (4) and (5), and K_2 can be calculated using the NMR integrals measured at various ligand concentrations,

$$UO_2LF_2^{3-} + L^{3-} + H^+ \rightleftharpoons UO_2L_2HF^{4-} + F^- \quad (4)$$

$$K_2 = \frac{[UO_2L_2HF][F]}{[UO_2LF_2][L][H^+]} = \frac{\beta_2}{\beta_1} \quad (5)$$

Eqn. (5) can be rearranged to eqn. (6),

$$\frac{[UO_2L_2HF][F]}{[UO_2LF_2]} = K_2[L][H^+] \quad (6)$$

hence K_2 can be calculated from the slope of a linear plot of the product of the ratio between the complexes ($R_1 = [UO_2L_2HF^{4-}]/[UO_2LF_2^{3-}]$) and the free fluoride concentration against $[L][H^+]$. The ratio between the complexes and the free fluoride concentration are based on the integrals of the ^{19}F-NMR spectra recorded at different total glyphosate concentrations. The concentration of the free deprononated glyphosate, [L] is calculated by eqn. (3), as described above. The total fluoride and the equilibrium hydrogen-ion concentration were kept constant in these experiments, so the ratio between the complexes is determined mainly by [L]. Linear regression of the data (Fig. 4) resulted in $\log K_2 = 10.65$, from which $\log\beta_2$, can be calculated for complex **2**, *cf.* Table 1. Characteristic distribution diagrams calculated by the equilibrium constants are given as ESI, Fig. S10.†

Equilibrium and structure in the binary system

The ^1H spectra are less informative than in the ternary system because of the overlapping signals of the different complexes.

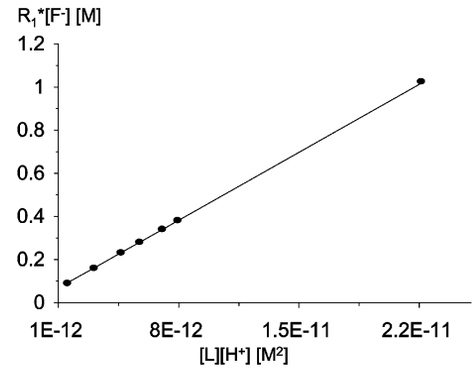


Fig. 4 Linear plot of the product of the ratio of the concentrations for complexes **2** and **1** ($R_1 = [UO_2L_2HF^{4-}]/[UO_2LF_2^{3-}]$) and the free fluoride concentration against $[L][H^+]$. (See text for details.)

Nevertheless, both the ^1H- and the ^{31}P-NMR spectra indicate the formation of three complexes (**3**–**5**) with the coordination of up to three glyphosates. The ^{31}P-NMR spectra measured at various ligand concentrations and the peak assignments are given as ESI (Figs. S11 and S12).†

The spectra show that, similarly to the ternary complexes, one glyphosate is chelated, while the second and third glyphosates are monodentately coordinated in complexes **4** and **5**. For complex **5**, the signal of chelated glyphosate is located at 24.2 ppm; two ^{31}P-peaks for the additional glyphosates are observed at 12.1 and 12.4 ppm (Fig. 5(a)). The much lower

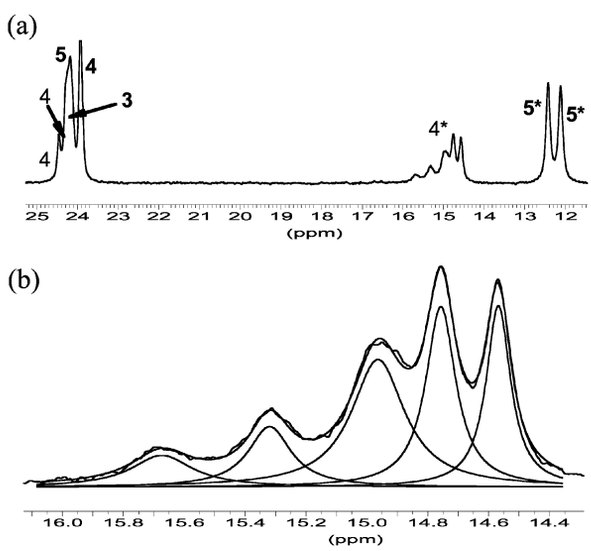


Fig. 5 Proton decoupled ^{31}P-NMR spectrum for the binary uranium(VI)–glyphosate system measured at −5 °C ($[UO_2^{2+}]_{tot}$ = 50 mM, $[H_3L]_{tot}$ = 200 mM, pH = 9.6). (a) The numbers indicate the peaks for complexes **3**, **4** and **5**, peaks marked with stars are from the non-chelated glyphosates. (The peak for the free glyphosate is not shown.) Deconvolution of the peaks for the non-chelated ligands in isomers **4a**–**e** (b).

chemical shifts indicate monodentate coordination of the phosphono groups as for complex **2**. The appearance of two signals reflects the difference in their chemical environment and the dominance of one isomer, in which, for steric reasons the phosphorus atoms are located above and below the equatorial plane perpendicular to the linear UO_2-axis, as shown in Scheme 2.

From the ^{31}P-NMR spectra measured at 20 mM uranium(VI) and 200 mM glyphosate concentrations at pH= 9.5 (ESI, Fig. S11†) it is apparent that complex **5** is the dominant component beside a small amount of complex **4**. Adding fluoride to this solutions the formation of complex **2** can also be observed, and at higher fluoride concentration complexes **2** and **5** are the

main components. Hence, the stability constant for complex **5** can be determined using the integrals in the ^{19}F- and ^{31}P-NMR spectra recorded at various fluoride concentrations. The equilibrium between these complexes and their equilibrium constant can be written by eqns. (7) and (8),

$$UO_2L_2HF^{4-} + L^{3-} + H^+ \rightleftharpoons UO_2L_3H_2^{5-} + F^- \quad (7)$$

$$K_3 = \frac{[UO_2L_3H_2][F]}{[UO_2L_2HF][L][H^+]} = \frac{\beta_5}{\beta_2} \quad (8)$$

Eqn. (8) can be rearranged to

$$\frac{[F]}{[L][H^+]} = K_3 \frac{[UO_2L_2HF]}{[UO_2L_2H_2]} \quad (9)$$

from which, K_3 can be calculated from the slope of a linear plot of $[F^-]/([L][H^+])$ against the quotient of the concentrations of complexes **2** and **5**. The ratio ($R_2 = [UO_2L_2HF^{4-}]/[UO_2L_3H_2^{5-}]$) was calculated using their ^{31}P-peak integrals. The concentration of the free deprononated glyphosate, [L] was calculated from the equilibrium hydrogen ion and the free glyphosate concentrations according to eqn. (3). The free fluoride concentration is based on the ^{19}F-integrals. Then the slope of a linear regression according to eqn. (9) (Fig. 6) resulted in $\log K_3 = 9.87$, and from that, $\log \beta_5$ was calculated. (*cf.* Table 1)

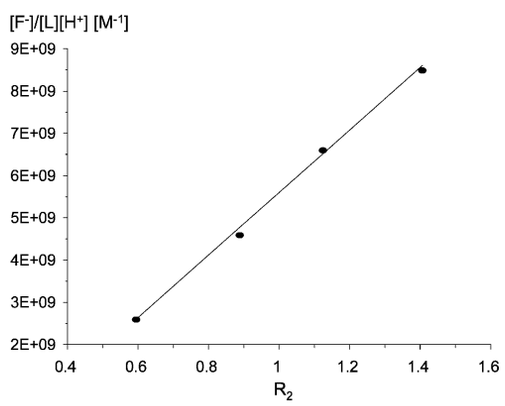


Fig. 6 Linear plot of $[F^-]/([L][H^+])$ against the quotient of the concentrations of complexes **2** and **5**. ($R_2 = [UO_2L_2HF^{4-}]/[UO_2L_3H_2^{5-}]$) (See text for details.)

Varying the total concentration of glyphosate at pH= 9.5 using 50 mM uranium(VI) total concentration, the binary complexes, **3**, **4** and **5** are formed in comparable amount (ESI, Fig. S12†). The coordination of an additional glyphosate resulted in several ^{31}P signals (*cf.* Fig. 5(a)) both at higher and lower fields for complex **4** indicating the presence of structural isomers. Deconvolution of the signals at around 15 ppm allowed us to distinguish five different peaks (Fig. 5(b)), indicating the existence of at least five different isomers (**4a**–**e**). UO_2^{2+} complexes are predominantly five-coordinated in the equatorial plane with some exceptions of four- and six-coordination. Six-coordination is found for chelating ligands with a short ligand bite, such as carbonate, acetate or in the case of some macrocyclic ligands. Assuming five-coordination for these isomers the structures shown in Scheme 2 are suggested. After the tridentate coordination of the first glyphosate, the two remaining coordination sites can be occupied by a bidentate coordination of the phosphono group of the second glyphosate. It can result two isomers (**4d**,**e**), which differ in the steric position of the aminoalkyl-chain relative to the position of the phosphorus atom in the chelated ligand. If the second glyphosate is monodentate, then water can be coordinated and can result in several isomers (**4a**–**c**). These differ from one another not only in the positions of the monodentate glyphosate and water, but also in the spatial position of the phosphono group. From steric considerations, we suggest that when the water is next to the chelated phosphono group, the monodentatly-coordinated glyphosate can be located either on the same or on the opposite side (**4a**,**b**) of the equatorial plane relative to the phosphorus atom in the chelated phosphono group; in **4c** the monodentate glyphosate is preferably on the opposite side of this plane.

The equilibrium between these complexes and their equilibrium constants (K_3, K_4) can be written by eqns. (10)–(13),

$$UO_2L_2H^{3-} + L^{3-} + H^+ \rightleftharpoons UO_2L_3H_2^{5-} \quad (10)$$

$$UO_2L^- + L^{3-} + H^+ \rightleftharpoons UO_2L_2H^{3-} \quad (11)$$

$$K_3 = \frac{[UO_2L_3H_2]}{[UO_2L_2H][L][H^+]} = \frac{\beta_5}{\beta_4} \quad (12)$$

$$K_4 = \frac{[UO_2L_2H]}{[UO_2L][L][H^+]} = \frac{\beta_4}{\beta_3} \quad (13)$$

From the ^{31}P-NMR integrals measured at different total glyphosate concentrations, the ratio of the complexes and the free glyphosate concentration can be calculated (spectra are given as ESI, Fig. S12†). The concentration of the free deprononated glyphosate, [L], can be calculated as indicated above. Knowing the hydrogen ion concentration, the equilibrium constants for reactions (10) and (11), and from those the stability constants for complexes **3** and **4** were calculated which are given in Table 1. From these one can conclude that the numerical value of the stepwise stability constants for complex **4** ($\log K$=12) and **5** ($\log K$=11) falls between the formation constants for U(VI) with PO_4^{3-} ($\log K$=13.25) and HPO_4^{2-} ($\log K$=7.28).[16] This is an independent confirmation of the magnitude of the latter, but also a strong indication that complex formation with phosphate/phosphonate through a single oxygen bond is very strong, hence these complexes may significantly contribute both to the uptake in plants (the soil-to-plant transfer factors) and to the migration of hexavalent actinides.

Ligand exchange dynamics

The exchange reactions of the coordinated fluoride and glyphosate with the free ligands were studied using different NMR methods that are well documented in the literature.[17]

(i) Fluoride exchange

The line width of the fluoride signals in the ternary complexes is independent of both the concentrations of the free ligands (fluoride and glyphosate) and the complexes. From the line width of the coordinated fluorides approximately the same intermolecular fluoride exchange rate, k_{obs1}=10 ± 2 s^{-1} can be calculated as observed for other U(VI) ternary complexes at the same temperature.

(ii) Glyphosate exchange

The line width of the ^{1}H- and ^{31}P-signals in both the chelated and monodentate glyphosates was also independent from the free ligand concentrations. The glyphosate exchange rate was not fast enough to affect the line width of the NMR signals of the coordinated and the free glyphosate; hence the exchange between them had to be studied by one-dimensional ^{1}H magnetization transfer experiments. The large ^{1}H-NMR chemical shift differences between the signals in the free and the coordinated glyphosate in complex **1** offered an excellent possibility for their selective inversion. First, the signal of the CH_2

protons, which are adjacent to the carboxylate group in the free ligand, was inverted. Then, in a complementary experiment, the corresponding methylene signal in the chelated ligand was inverted (at 4.4 ppm, see Fig. 2(a)). After the selective inversion of these signals, different delays were applied in the pulse sequence and the full spectra were recorded; these are shown as ESI, Fig. S13.† It can be seen, that the inversion of these signals decreased the intensity of the corresponding signals in the coordinated and in the free ligand due to the exchange between them. The time dependence of the signal intensities is determined by both the longitudinal relaxation rate of the exchanging sites and the chemical exchange rate between them. The simultaneous analysis of the experiments proved the existence of two exchange processes for the chelated glyphosate, a slower, intermolecular exchange with the free glyphosate, k_{obs2} = 0.69 ± 0.03 s^{-1}, and a faster intramolecular exchange k_{obs3} = 2.00 ± 0.21 s^{-1}. The latter is the result of the exchange between the spatial positions of the protons in the same CH_2 group. The nitrogen-inversion in the chelated ligand is restricted, hence this exchange can be explained only by a consecutive ring openings/chelate formation prior to the dissociation of the ligand. The relative intensity of the signals against the variable delay and the fitted curves are shown in Fig. 7.

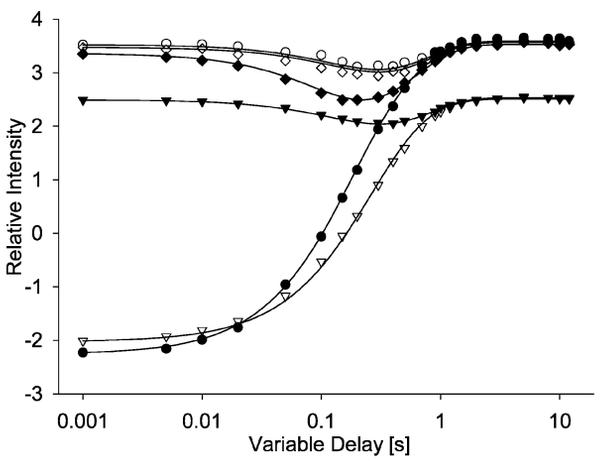


Fig. 7 Data from the ^{1}H-NMR magnetization transfer experiments between complex **1** and free glyphosate. First the methylene signal at 3.32 ppm (see Fig. 2(a)) in the free ligand (▽) was inverted (intensity change in the methylene signals at 4.39 (○) and 3.58 (□) ppm in the coordinated glyphosate) and then the methylene signal at 4.39 ppm in the chelated glyphosate (●) was inverted (intensity change in the methylene signals in the free ligand at 3.32 ppm (▼) and in the coordinated glyphosate at 3.58 ppm (◆). The solid lines are generated by a simultaneous analysis of the data from both experiments (see text for details).

The ligand exchange reaction for the monodentate glyphosates cannot be studied by magnetization transfer experiments because of the overlapping signals or the small chemical shift difference. However, the ^{31}P-NMR signals of the non-chelated glyphosates have the same line width as the chelated ones, indicating similar exchange rate with the free glyphosate. Therefore, a common rate-determining step can be suggested for the dissociation of the glyphosates, that is the U–O(P) bond breaking. It worth noting, that the relatively sharp ^{31}P signals for the non-chelated glyphosates in isomers **4a**–**c** indicate slow exchange between them. Therefore the water exchange rate for the isomers must be slow, several order of magnitude slower that that for the aqua ion, 1.6×10^4 s^{-1}, at the same temperature.[18]

From these experimental data one can conclude that the intermolecular fluoride and glyphosate exchange reactions take place along two parallel pathways as has been found for other ternary systems.[19] The reactions follow I_D or D mechanisms with U–F and U–O(P) bond breaking as the rate determining steps for the fluoride and the glyphosate exchange, consequently.

Acknowledgements

This study has been supported by Sveriges Civilingenjörsförbund (Miljöfonden) and the European Community through contract FIKW-CT-2000–00035 (ACTAF). The author thanks Professor Ingmar Grenthe for his helpful comments and the valuable discussions.

References

1 Z. Szabó and I. Grenthe, *Inorg. Chem.*, 2000, **39**, 5036.
2 P. Eberbach and L. Douglas, *Soil Biol. Biochem.*, 1983, **15**, 485.
3 R. M. Smith, A. E. Martell and R. J. Motekaitis, Critically Selected Stability Constants of Metal Complexes, NIST Standard Reference Database 46; Version 6.0 for Windows.
4 E. Galdecka, Z. Galdecki, P. Gawryszewska and J. Legendziewicz, *New J. Chem.*, 2000, **24**, 387.
5 D. S. Sagatys, C. Dahlgren, G. Smith, R. C. Bott and J. M. White, *J. Chem. Soc., Dalton Trans.*, 2000, 2404.
6 T. G. Appleton, K. A. Byriel, J. R. Hall, C. H. L. Kennard, D. E. Lynch, J. A. Sinkinson and G. Smith, *Inorg. Chem.*, 1994, **33**, 444.
7 J. Kobylecka, B. Ptaszynsky and A. Zwolinska, *Monatsh. Chem.*, 2000, **131**, 1.
8 B. C. Barja and M. D. S. Afonso, *Environ. Sci. Technol.*, 1998, **32**, 3331.
9 T. Undabeytia, E. Morillo and C. Maqueda, *J. Agric. Food Chem.*, 2002, **50**, 1918.
10 J. Sheals, P. Persson and B. Hedman, *Inorg. Chem.*, 2001, **40**, 4302.
11 D. Sanna, I. Bódi, S. Bouhsina, G. Micera and T. Kiss, *J. Chem. Soc., Dalton Trans.*, 1999, 3275.
12 M. J. Bojczuk, T. Kiss, H. Kozlowski, P. Decock and J. Barycky, *J. Chem. Soc., Dalton Trans.*, 1994, 811.
13 A. L. V. Geet, *Anal. Chem.*, 1970, **42**, 679.
14 I. Bányai, J. Glaser, K. Micskei, I. Tóth and L. Zékány, *Inorg. Chem.*, 1995, **34**, 3785.
15 H. M. Irving, M. G. Miles and L. D. Pettit, *Anal. Chim. Acta*, 1967, **38**, 475.
16 A. Sandino and J. Bruno, *Geochim. Cosmochim. Acta*, 1992, **56**, 4135.
17 Z. Szabó, J. Glaser and I. Grenthe, *Inorg. Chem.*, 1996, **35**, 2036.
18 I. Farkas, I. Bányai, Z. Szabó, U. Wahlgren and I. Grenthe, *Inorg. Chem.*, 2000, **39**, 799.
19 Z. Szabó and I. Grenthe, *Inorg. Chem.*, 1998, **37**, 6214.