Electronic Supplementary Information for Dalton Transactions

Supplementary Information

Structures, Equilibria and Ligand Exchange Dynamics in the Binary and Ternary Dioxouranium(VI)-Ethylenediamine-N-N'-diacetic acid – Fluoride system. A Potentiometric, Multinuclear NMR and X-Ray Crystallographic Study.

The protolytic equilibria in EDDA solutions were investigated varying the proton concentration stepwise by coulometric reduction of H^+, in a known volume of TS containing H_0, M H^+, A, M EDDA in 1 M $NaClO_4$ using the circuit (I)

$$(+)\ \text{AE} \mid \text{TS} \mid \text{Pt}\ (-) \qquad \text{(I)}$$

In the coulometric cell Pt is a platinum electrode and AE an external auxiliary electrode in contact with the test solution through a salt bridge:

$$\text{AE} = 1\ \text{M}\ NaClO_4 / 0.010\ \text{M}\ Hg_2(ClO_4)_2, (0.980)\ \text{M}\ NaClO_4, \text{Hg}$$

After each addition the $[H_3O^+]$ was determined from the emf, E_I (in mV), of the cell (I)

$$\text{GE} \mid \text{TS} \mid \text{RE} \qquad (2)$$

by using the Nernst equation (1)

$$E_I = E^0 + 59.16\log[H_3O^+] + E_j \qquad (1)$$

In Eq. (1) the cell constant E^0 was determined in a separate experiment, while the liquid junction potential E_j was evaluated as described elsewhere [1]. (Ag/AgCl, 6.0726.100) electrode from Metrohm was used as the reference electrode.

The $Z(\log h)$ data are plotted in Fig. ESI 1 where the full drawn curve have been calculated using the chemical model and the corresponding protonation constant given in Table 1

[1] G. Biedermann, G. Douhéret, *Chem. Scripta;* 1980, **16**, 144-153.

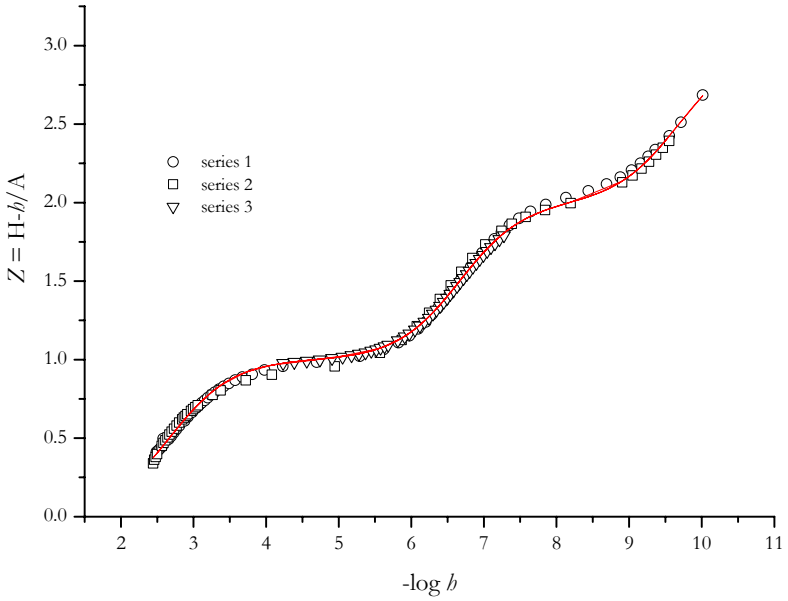


Figure S1

The experimental values of Z, the average number of proton released from H_4EDDA^{2+}, plotted against – log h. The full-drawn curve has been calculated using the protonation constant reported in Table 1

Table S1: Survey of stability constant in the ternary UO_2^{2+} - EDDA – F^- system deduced from the potentiometric data and their standard deviation using different speciation models. σ is the standard deviation in the error carrying variable, in this case the total concentration of protons H_{tot} and U is the error-square sum.

Model (H,F,U,L)	log K (0,1,1,1)	log K (-1,0,1,1)	log K (3,1,1,1)	log K (3,2,1,1)	log K (3,3,1,1)
1	15.11 ± 0.1				
2	15.38 ± 0.03	5.98 ± 0.05			
3	15.37 ± 0.02	5.90 ± 0.04	27.2 ± 0.2		
4	15.38 ± 0.02	5.92 ± 0.04	----------	29.8 ± 0.2	
5	15.40 ± 0.03	5.94 ± 0.04	----------	----------	32.3 ± 0.2
Model →	1	2	3	4	5
σ, mM	0.68651	0.20118	0.14869	0.14838	0.15093
$U = \Sigma(H_{calc} - H_{exp})^2$	35.3475	2.99489	1.61384	1.60721	1.66283

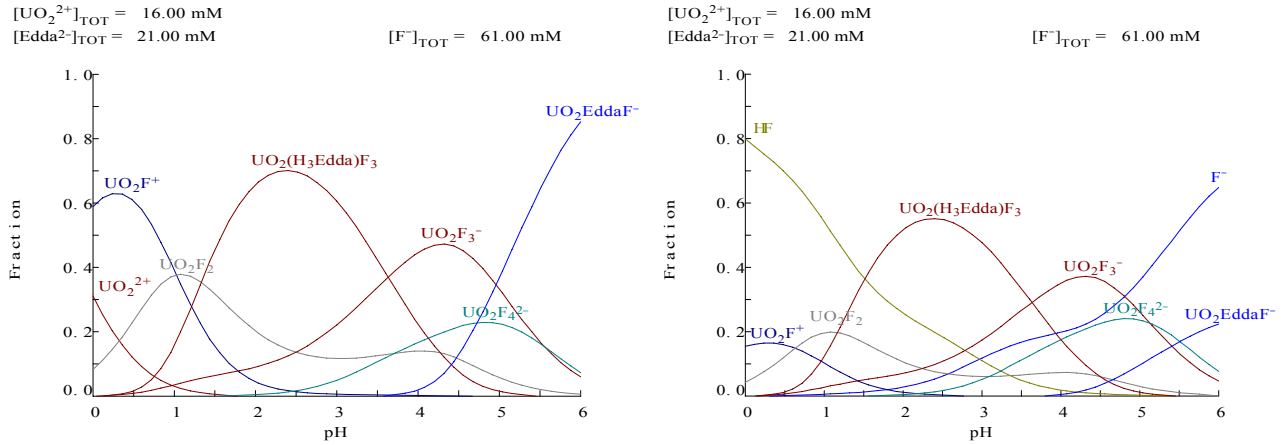


Figure S2 a, b.

Uranium(VI) and fluoride distribution diagrams of a solution containing: U(VI) 16 mM, EDDA 21 mM, fluoride 61 mM calculated by the following potentiometric stability constants:

logβ(HF)= 2.97, logβ (HF_2^-)=3.56; logβ (UO_2F^+)= 4.56; logβ (UO_2F_2)=7.99; logβ($UO_2F_3^-$)=10.41; logβ ($UO_2F_4^{2-}$)= 11.90; logβ ($UO_2(H_3Edda)$) = 20.80; logβ (UO_2Edda) = 11.63; logβ (UO_2EddaF) = 15.46, logβ ($UO_2H_3EddaF_3$) = 32.3.

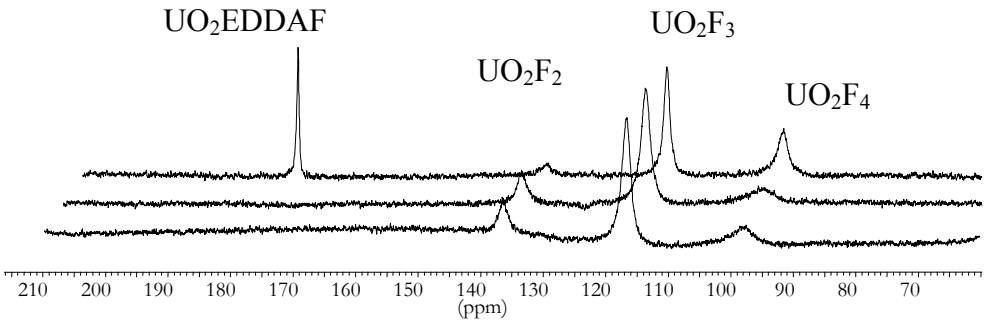
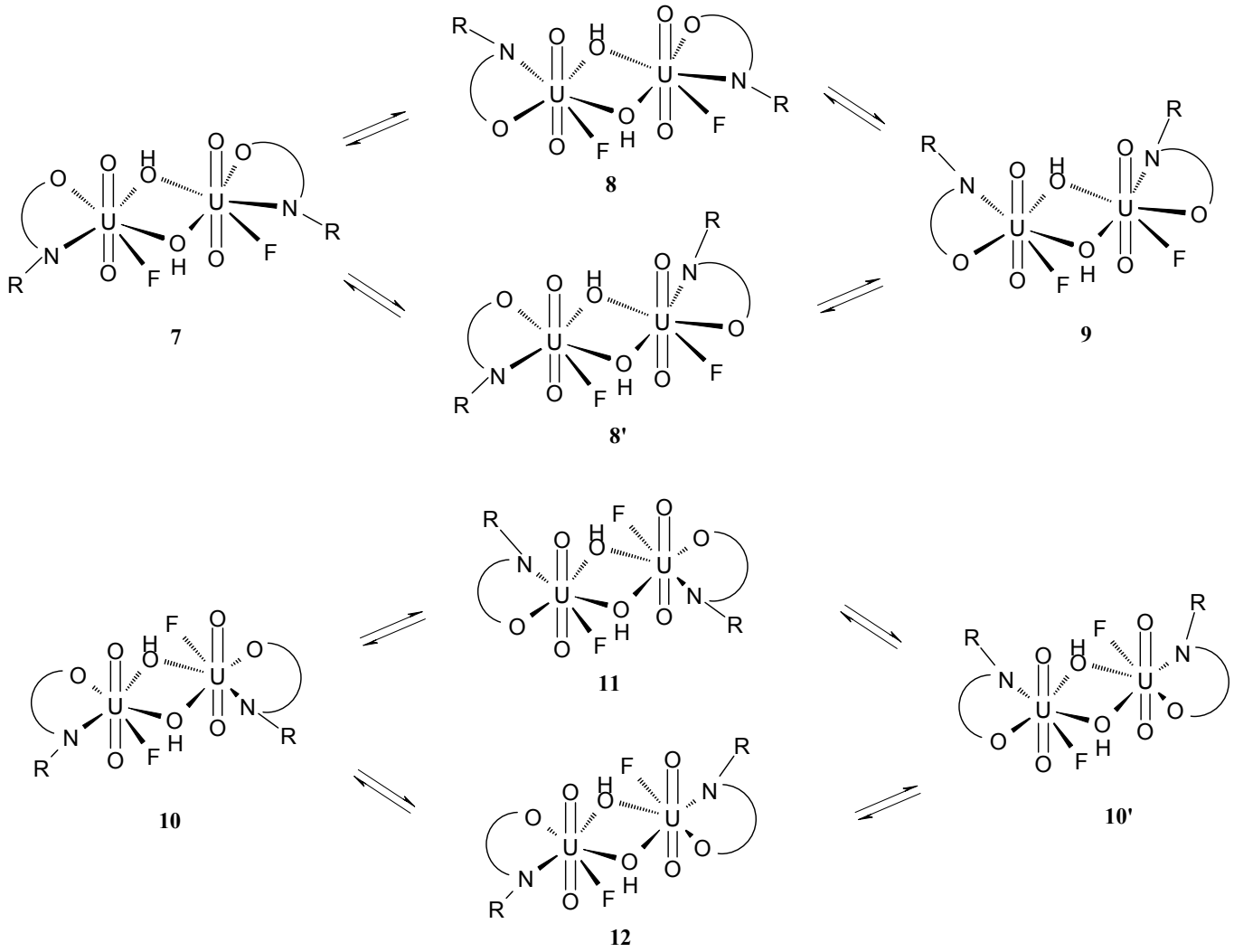


Figure S3

pH dependence of the ^{19}F-NMR spectra measured in the ternary uranium(VI)-EDDA-fluoride system using $[UO_2^{2+}]_{tot}$ = 16 mM, $[EDDA]_{tot}$ = 21 mM, $[F^-]_{tot}$ = 61 mM, T = 268 K. -log$[H^+]$ from top to bottom: 5.24, 3.57 and 2.60.



Scheme S1. The six possible isomers of the complex $(UO_2)_2(\mu\text{-}OH)_2(HEDDA)_2F_2^{2-}$, where $R{\equiv}CH_2CH_2NH_2^+CH_2COO^-$. (8, 8') and (10, 10') are identical.

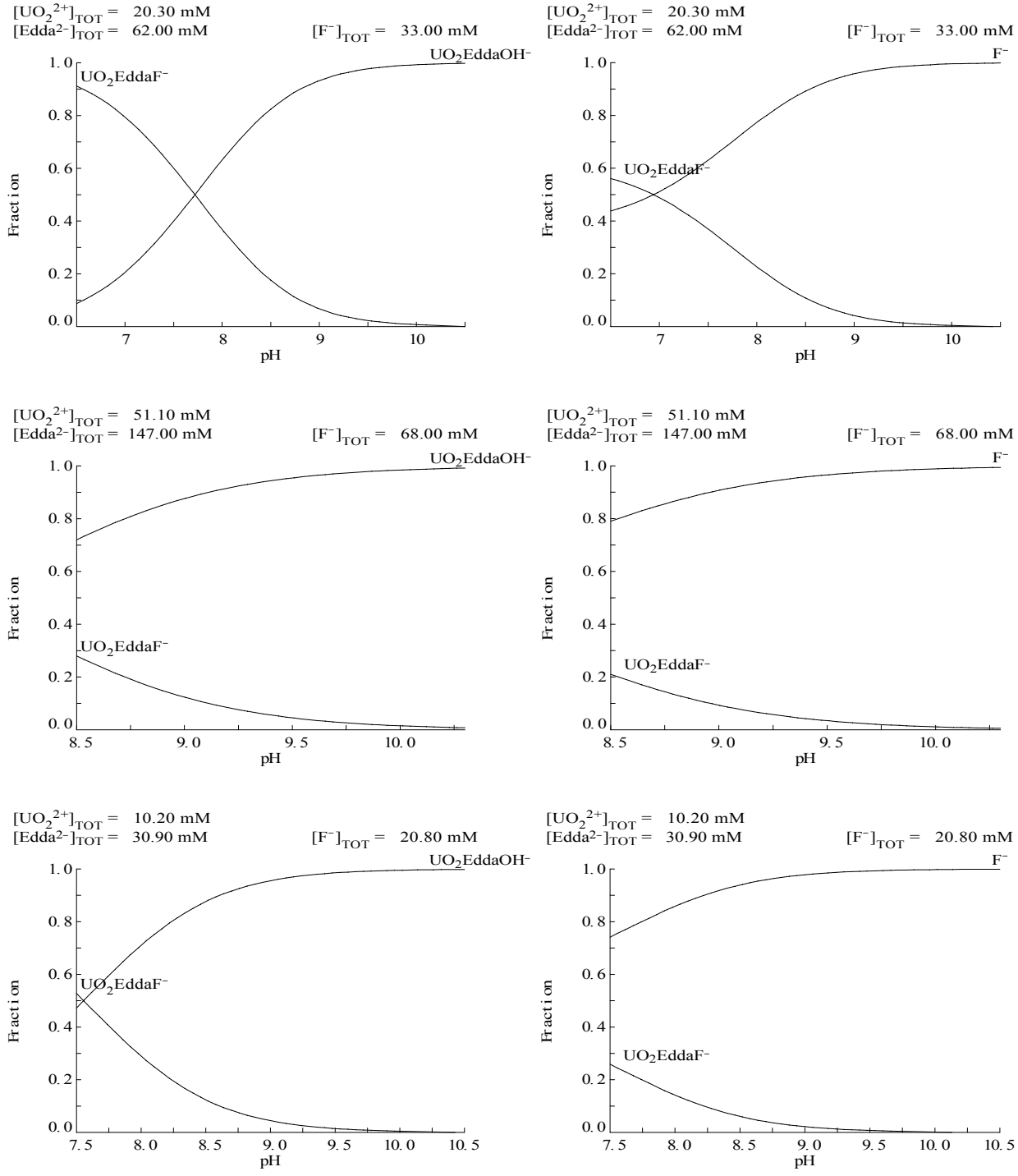


Figure S4
pH dependence of the uranium(VI) (left) and fluoride (right) distribution diagrams for some of the test solutions using various total concentration of uranium(VI) and the ligands.

[UO_2EDDAF] M	[$UO_2EDDAOH$] M	[$UO_2EDDA(H_2O)$] M	[F^-] M	[OH^-] M	$k_{(obs)1}$ s^{-1} (expt.) ($=\pi \times \Delta\nu_{1/2(complex)}$)	$k_{(obs)1}$ s^{-1} (calcd.)	$k_{(obs)2}$ s^{-1} (expt.) ($=\pi \times \Delta\nu_{1/2(F)}$)	$k_{(obs)2}$ s^{-1} (calcd.)
Expt. 1 $[UO_2^{2+}]_{tot.}$= 0.0203 M, $[EDDA]_{tot.}$= 0.0620 M, $[F^-]_{tot.}$= 0.0330 M								
0.0196	0.0003	2.94E-04	0.0133	9.55E-08	282.6	277.7	449.0	457.3
0.0189	0.0010	2.69 E-04	0.0140	3.02E-07	288.8	280.3	408.2	421.7
0.0163	0.0038	1.94 E-04	0.0166	9.77E-07	295.1	289.9	298.3	313.2
0.0126	0.0074	1.24 E-04	0.0203	3.55E-06	304.5	303.9	213.5	208.3
0.0087	0.0114	7.15E-05	0.0242	1.26E-05	317.1	323.2	122.4	125.0
0.0025	0.0177	1.64E-05	0.0304	7.24E-05	386.2	381.9	34.5	30.9
Expt. 2 $[UO_2^{2+}]_{tot.}$= 0.0511 M, $[EDDA]_{tot.}$= 0.1475 M, $[F^-]_{tot.}$= 0.0678 M								
0.0207	0.0302	8.79E-05	0.0470	1.07E-05	411.3	400.0	194.6	188.7
0.0131	0.0378	4.79E-05	0.0546	3.01E-05	433.3	438.6	113.0	110.0
0.0087	0.0422	2.96E-05	0.0590	5.75E-05	474.1	470.8	75.3	70.7
0.0045	0.0465	1.41E-05	0.0633	1.12E-04	533.8	519.7	47.1	35.6
0.0030	0.0480	9.25E-06	0.0648	1.73 E-04	568.3	563.2	34.5	24.1
0.0018	0.0492	5.70E-06	0.0659	2.39 E-04	621.7	608.3	18.8	15.6
0	0.0511	0	0.0678	3.31 E-04	656.2	671.8	9.4	1.6
Expt. 3 $[UO_2^{2+}]_{tot.}$= 0.0102 M, $[EDDA]_{tot.}$= 0.0309 M, $[F^-]_{tot.}$= 0.0208 M								
0.0073	0.0028	1.07E-04	0.0135	8.51E-07	273.8	279.0	151.9	166.9
0.0055	0.0045	7.28E-05	0.0152	2.69E-06	285.1	286.0	106.7	115.7
0.0041	0.0061	4.85E-05	0.0167	6.17E-06	279.7	293.4	74.7	78.4
0.0011	0.0090	1.18E-05	0.0196	2.95E-05	313.3	317.9	26.6	19.9
0.0003	0.0099	2.86E-06	0.0205	1.07E-04	351.6	369.4	14.4	5.1

UO_2EDDAF^- (*Site-1*) ⇔ **F^-** (*Site-2*)

Expt. 1		***Expt. 2***		***Expt. 3***	
Rate *(forw.)* M s^{-1} ($=k_{(obs)1} \times [UO_2EDDAF]$)	Rate *(rev.)* M s^{-1} ($=k_{(obs)2} \times [F^-]$)	Rate *(forw.)* M s^{-1} ($=k_{(obs)1} \times [UO_2EDDAF]$)	Rate *(rev.)* M s^{-1} ($=k_{(obs)2} \times [F^-]$)	*Rate (forw.)* M s^{-1} ($=k_{(obs)1} \times [UO_2EDDAF]$)	Rate *(rev.)* M s^{-1} ($=k_{(obs)2} \times [F^-]$)
5.56	5.98	8.55	9.16	2	2.02
5.48	5.72	5.71	6.18	1.59	1.50
4.81	4.98	4.17	4.45	1.14	1.25
3.86	4.34	2.4	2.98	0.37	0.54
2.77	2.97	1.71	2.24	0.1	0.35
0.97	1.05	1.18	1.24	-	-

Table S 2: Comparison of experimental and calculated rate constants for the exchange reactions (15) – (17) in the U(VI) – EDDA – F^- system.