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Complexation of Uranium(VI) with Glutarimidoxioxime: Thermodynamic and Computational Studies

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Supplementary Information

NMR Analysis of Glutarimidoxioxime (HC)

The ^{1}H-NMR spectrum of HC is characterized by a defined quintet signal at 1.66 ppm, indicating the absence of byproducts. The $^{13}C\{^{1}H\}$-NMR spectrum is indicative of the purity of the product: five unique and distinct peaks are detectable at 18.7, 24.6, 32.2, 145, 170 ppm (see Figure S1). This latter signal in particular is related to the unique C=O group of HC, lacking instead in H_2A and H_2B.

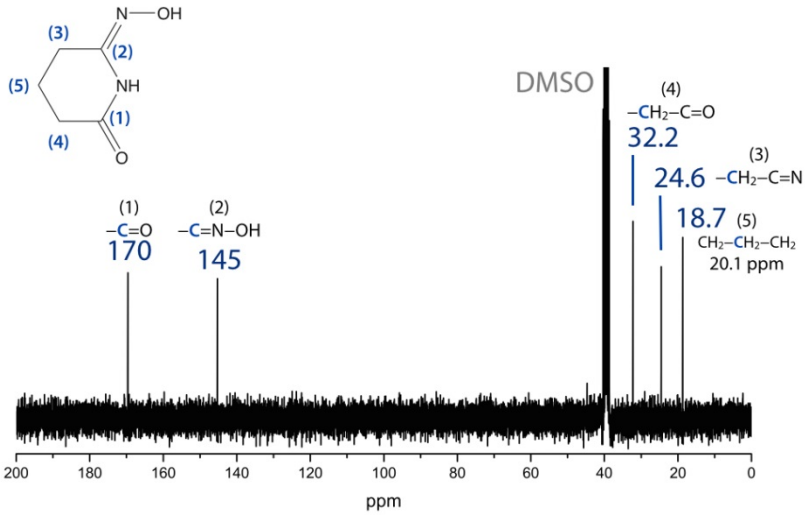

Figure S1 $^{13}C\{^{1}H\}$-NMR spectrum of Glutarimidoxioxime in DMSO-d_6

Table S1 Protonation of HL^{III}. Analytical data of the potentiometric and microcalorimetric experiments. Negative H^+ concentrations mean the total concentration of OH^-.

Potentiometric experiments					
Titration n.	C_H^0, mM	C_L^0, mM	$C_H^{tit.}$, mM	$C_L^{tit.}$, mM	V^0, mL
1 (Fig. 1a)	20.3	7.20	-101.6	-	19.03
2 (Fig. 1b)	27.7	15.8	-101.6	-	20.84
3	23.3	7.79	-101.6	-	16.04
4	-1.69	6.02	495.5	-	19.78
Microcalorimetric experiments					
Titration n.	C_H^0, mM	C_L^0, mM	$C_H^{tit.}$, mM	$C_L^{tit.}$, mM	V^0, mL
1 (Fig. 2a)	490	0.251	19.2	19.2	0.770
2 (Fig. 2b)	19.2	19.2	99.9	-	0.750

3 (Fig. 2c)	3.86	3.86	-101.6	-	0.757
4 (Fig. 2d)	19.1	19.1	-101.6	-	0.756
5	100	-	19.2	19.2	0.750

Table S2 Potentiometric titrations for the complexation of U(VI) with HL^{III}. Analytical data of the potentiometric experiments. Negative H^+ concentrations mean the total concentration of OH^-.

Titration n.	$C^0_{UO_2}$, mM	C^0_H, mM	C^0_L, mM	C^0_{edta}, mM	$C^{tit.}_H$, mM	V^0, mL
1 (Fig. 3a)	0.460	4.82	1.95	0.230	-20.0	10.8
2 (Fig. 3b)	0.410	3.75	1.21	0.210	-20.0	12.3
3	0.470	2.93	-	0.240	-20.0	10.6
4	0.820	18.9	3.14	3.33	-102.1	12.3

Table S3 Selected bond distances (Å) for the gas-phase optimized structures. The U-Owater average bond distance is reported (standard deviation in parenthesis).

	A	b	c	d	e	f	g	h	i	j	k	l
U-O_{oxime}	2.037	2.312	2.138	2.147	2.177	2.176	2.306	2.336	2.346	2.215	2.240	2.268
U-N_{oxime}	-	-	2.303	-	-	-	-	-	-	2.357	2.342	2.329
U-N_{ring}	-	2.306	-	-	-	-	2.623	2.644	2.673	-	-	-
U-O_{carb}		2.561	-	-	-	-	3.73	3.77	3.82	-	-	-
U-O_{water}	-	-	-	2.49(0.03)	2.56(0.03)	2.55(0.05)	2.51(0.07)	2.49(0.06)	2.46(0.03)	2.54(0.01)	2.65(0.05)*	2.51(0.04)

*one water 2.72Å

Complete reference to Gaussian09 program

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

