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Supporting Information for

Binding modes of oxalate in UO_2(oxalate) in aqueous solution studied with first-principles molecular dynamics simulations. Implications for the chelate effect.

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Additional Computational Details

The same methods and basis sets as in our previous studies of uranyl complexes[1] were employed. Car-Parrinello molecular dynamics (CPMD)[2] simulations were performed using the BLYP functional[3] and norm-conserving pseudopotentials that had been generated according to the Troullier and Martins procedure[4] and transformed into the Kleinman-Bylander form.[5] For uranium, the semicore (or small-core) pseudopotential was employed that had been generated and validated in reference 6. Periodic boundary conditions were imposed using cubic supercells with a lattice contant of 13 Å. Kohn-Sham orbitals were expanded in plane waves at the Γ-point up to a kinetic energy cutoff of 80 Ry. Simulations were performed in the NVT ensemble using a single Nosé-Hoover thermostat set to 300 K (frequency 1800 cm^{-1}), a fictitious electronic mass of 600 a.u., and a time step of 0.121 fs. The boxes contained uranyl, one oxalate and a total of 56 water molecules, affording a density of ca. 1.0. In order to maintain the time step, hydrogen was substituted with deuterium. Long-range electrostatic interactions were treated with the Ewald method. No electrostatic decoupling between replicated cells was included. Starting structures were generated from previous well-equilibrated simulations from reference 1 by manually changing ligands or replacing water molecules with the appropriate number of ammonium ions.

The initial configuration for aqueous **1a** had been prepared from a well-equilibrated snapshot of a previous uranyl nitrate simulation,[7] manually replacing nitrate and the appropriate number of water molecules with oxalate and equilibrating the system for 2 ps. The orientation of the complex was chosen such that its longer axis (passing through U and the CC midpoint) was roughly aligned along the space diagonal of the cubic box. For the "most oblate" complex of this study, **1c**, the mutual orientation of the mirror images in illustrated in Figure S1. Selected conformers were reoptimised in the gas phase until the maximum gradient was less than $5 \cdot 10^{-4}$ a.u. (denoted CP-opt), followed by unconstrained CPMD simulations for 2.5 ps (the first 0.5 ps of which were discarded as equilibration), denoted CPMD(g).

Constrained CPMD simulations were performed along predefined reaction coordinates ξ (bond distances r or differences in bond distances Δr) connecting complexes with different coordination numbers, in order to evaluate the change in the Helmholtz free energy by pointwise thermodynamic integration[8] of the mean constraint force $\langle f \rangle$ along these coordinates via

$$\Delta A_{a \to b} = -\int_a^b \langle f(\xi) \rangle \mathrm{d}r \qquad (1).$$

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At each point, the system was propagated until $\langle \xi \rangle$ was sufficiently converged (usually within 1.5 - 2 ps after 0.5 ps of equilibration, similar to the degree of convergence documented in Figure S1 of the supporting information for reference 6. Each new point was continued from the final, equilibrated configuration of the previous one, using 2000 steps of continuous slow growth to increase the constrained distance. According to the root-mean-square displacement along the trajectories, the solutions remained liquid-like throughout.

Additional static PCM computations were performed using the M06L functional.[9] Electronic energies for complex **1d** in Table S1 are corrected for basis-set superposition error (BSSE) of the uranium-water bond using the Counterpoise method,[10] and enthalpies and free energies are evaluated at a pressure of 1354 atm to mimic a condensed phase.[11] Full citation of Gaussian 09 is provided in reference [12].

Table S1. Relative energies (kJ/mol) of uranyl-oxalate complexes with respect to **1a** from PCM calculations.[a]

Level[a]	**1b**	**1c**	**1d**[b]	
ΔE (BLYP)[c]	30.5	67.8	22.3	(-8.2)
ΔH^0 (BLYP)[c]	27.0	67.0	21.9	(-5.1)
ΔG^0 (BLYP)[c,d]	30.0	62.9	57.9	(27.9)
ΔA (CPMD-BLYP)[e]	*39.0*	*16.1*	*26.7*	*(-12.3)*
ΔE (B3LYP)	35.6	68.3	18.5	(-17.1)
ΔH^0 (B3LYP)	33.5	68.3	26.0	(-7.5)
ΔG^0 (B3LYP)[d]	30.5	64.7	60.4	(29.9)
B3LYP	33.6	65.1	13.1	(-20.5)
B3LYP-D3	32.5	68.4	-4.5	(-37.0)
M06	48.9	68.5	1.8	(-47.1)
M06-L	47.3	74.5	2.3	(-45.0)
HF	41.4	58.2	32.5	(-8.9)
MP2	58.3	70.2	13.8	(-44.5)

[a]B3LYP(PCM) optimised geometries employed, except where otherwise noted; ΔE, ΔH and ΔG data fully optimised at SDD/6-311+G*, other entries denote SDD(g)/auc-cc-pVTZ single-point electronic energies (i.e. ΔE) at the level indicated.
[b]Relative to **1a** + H_2O including corrections for BSSE (16 kJ/mol for SDD/6-311+G* basis (BLYP and B3LYP), 13 kJ/mol for MP2/SDD(g)/auc-cc-pVTZ, 1 - 2 kJ/mol for all other levels); in parentheses: relative to **1b** + H_2O. [c]BLYP(PCM) optimised structures. [d]Including pressure correction for condensed phase. [e]Constrained CPMD/PTI results (cf. Figure 1), estimated numerical uncertainty at least ±7.0 kJ/mol.

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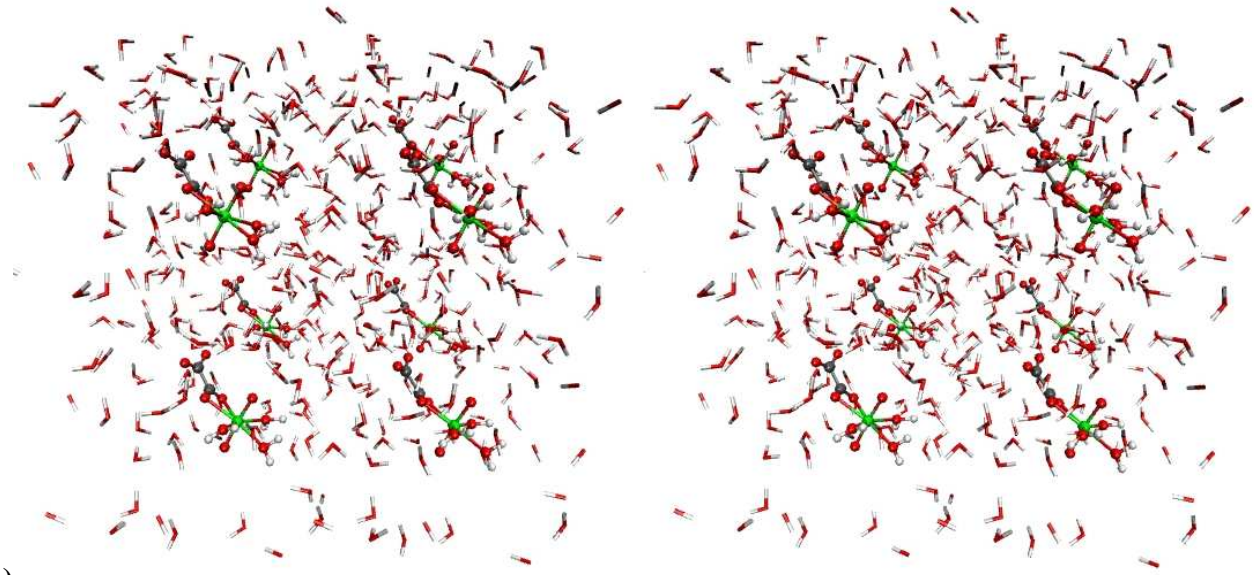
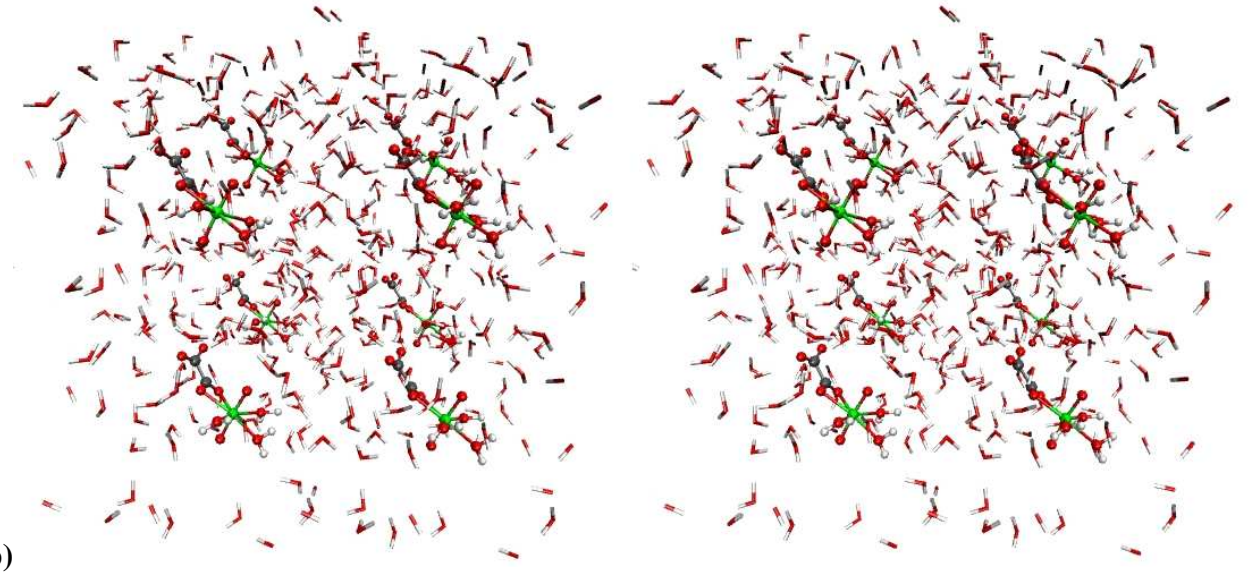


a)



b)

Figure S1: Stereoplots of a supercell from a snapshot of **1c**, with the box length doubled in each direction; a) parallel view, b) cross-eyed view. The longest intramolecular distance is ca. 7.9 Å; because the molecule is roughly aligned along the long diagonal of the box, the shortest intermolecular distance between replicated complexes is ca. 6.9 Å, with at least two shells of water molecules between them.

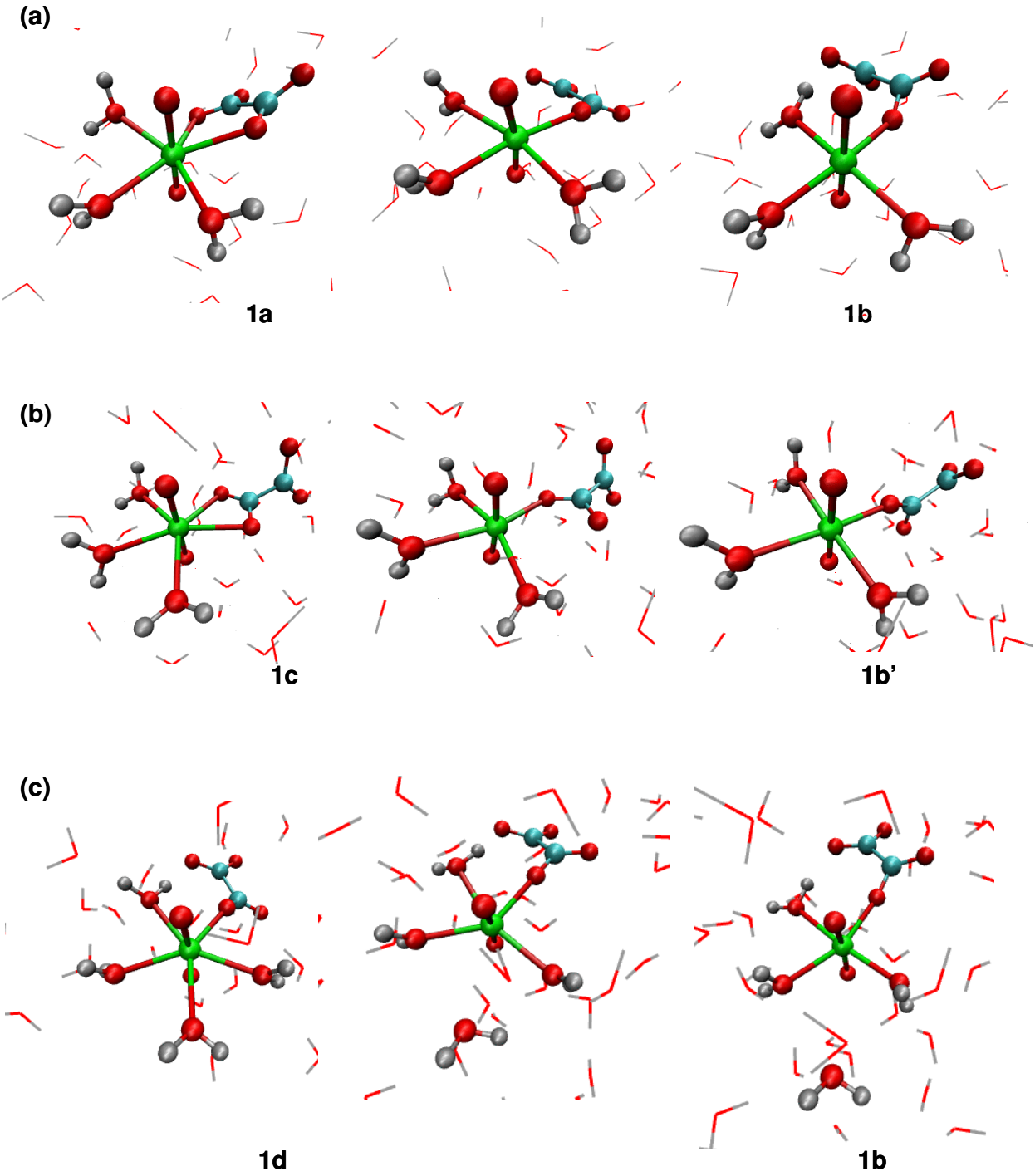


Figure S2: Magnified snapshots from Figure 1 of the main paper. Color code: U green, O red, C cyan; solvent water molecules rendered as wireframe.

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Cartesian coordinates of 1a-1d

xyz format, B3LYP(PCM)/SDD/6-311G**
optimised

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18
1a
 U 0.4604740977 0.0781885852 0.0046154186
 C -2.7010336169 0.7285931031 0.0498153643
 C -2.6345481 -0.8387783474 -0.0244869922
 O 0.519531823 0.0439091169 1.7833025954
 O 0.5199786315 0.1210982428 -1.7737395993
 O -3.7641300475 1.3217278346 0.1022551976
 O -1.5185046602 1.2650155691 0.0480600433
 O 3.0176297049 0.2139403377 -0.0372052904
 O -3.6433575331 -1.5211553674 -0.0590058973
 O -1.4102969552 -1.2716017492 -0.042795469
 O 1.5470342622 -2.1845716479 0.0331589087
 O 1.3063102529 2.441717342 0.0386472073
 H 1.2542579636 3.0142499918 0.8144797454
 H 1.3166821691 3.0081700114 -0.7431678141
 H 3.4832950967 1.0321747348 0.1721539845
 H 3.5732204204 -0.5331974596 0.2142041665
 H 1.6453968721 -2.7433263727 -0.7481465318
 H 1.5445066189 -2.7608209253 0.8078349626

18
1b
 U 6.8326337007 6.6156598686 7.2362395459
 C 8.6999769457 8.4189028606 9.4706002947
 C 8.2861987879 8.2619047301 10.9833581933
 O 7.6759098468 5.0531183815 7.2318836935
 O 5.9011897307 8.126036134 7.2256122006
 O 9.3802661561 9.3515662673 9.0857148336
 O 8.2695774866 7.4583501061 8.6855609165
 O 4.6957805795 5.3663597268 6.9915621062
 O 8.951607422 8.9014493292 11.8059113576
 O 7.301255224 7.4981615763 11.2217437388
 O 6.0171990993 6.1497178922 9.4699043546
 O 7.8536291081 7.2917254513 5.0532263517
 H 8.4451016236 6.753649079 4.5130244239
 H 7.661588902 8.105700011 4.5718489452
 H 3.8172139771 5.7512619991 6.8841976692
 H 4.6051185934 4.4055267448 7.0055233418
 H 5.0808609438 6.0937941946 9.6893406947
 H 6.5152452027 6.6846490075 10.1866227382

18
1c
 U  -3.5025801983 -3.0133756683 -0.1725428669
 C  -1.7052253144 -1.2494050463 1.0880725685
 C  -0.7154096766 -0.2963437762 1.775994271
 O  -2.2946869595 -4.3069941809 -0.1837490045
 O  -4.7796150906 -1.7889179528 -0.2105375357
 O  -1.7765297424 -1.321920784 -0.1843315742
 O  -2.483191536 -1.9979348671 1.7691119678
 O  -5.1018870071 -4.5631370356 -1.2864096432
 O  0.4091194548 -0.7873464781 2.0120485036
 O  -1.16156129 0.8468650838 2.0110903434
 O  -4.6166377498 -4.0670402325 1.7516833689
 O  -3.0607209552 -2.5770697328 -2.5533255679
 H  -2.3473111356 -2.9665403364 -3.0743764971
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 H  -4.922780506 -5.4776713299 -1.5382494787
 H  -5.3760635586 -3.7035069114 2.2239773432
 H  -4.2751937117 -4.8126385236 2.2612028079

21
1d
 U  5.909229663 6.1660452145 6.7497707717
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 C  8.2733903742 7.1686678167 10.2187115419
 O  6.3722722553 4.5285937263 6.2349936315
 O  5.2551205978 7.729327209 7.2711256278
 O  8.8736664653 8.2745249085 8.1008574453
 O  7.7578085856 6.3542743519 8.0004763386
 O  3.5888580741 5.306966982 6.8513018216
 O  9.1704809577 7.7136015059 10.8752568584
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 O  5.5023283942 5.3991659988 9.0606275949
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 O  5.0635893889 6.6829845904 4.4592984729
 H  8.1831674502 8.1253696981 6.3283197771
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 H  3.3165495957 4.4016026353 6.6575371531
 H  4.6258294899 5.4133586367 9.4608340725
 H  6.1741174617 5.7956237676 9.702579604
 H  4.7706858747 7.5534594582 4.163423171
 H  4.993610179 6.0731991391 3.714654578

21
1a.H2O
 U  0.7317991427 0.0079609362 0.0207852646
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 C  -1.8174351248 -2.009258825 0.297804246
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 O  0.3087302667 0.4432117177 -1.6507023551
 O  -3.5142206858 -0.4943239062 1.1640070114
 O  -1.4617766133 0.3089487498 0.7311785698
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 O  -0.5612702165 -1.9525210581 -0.04563758
 O  1.2023787029 -4.0393982939 -0.46181513
 O  0.2531615677 2.3859063964 0.7264649604
 O  2.8207498331 1.3358271342 -0.3008853457
 H  -0.5957644096 2.5029713418 1.1726044235
 H  0.8914904826 3.0000618629 1.1083500487
 H  2.721452328 -1.5631113302 -1.7446331063
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 H  1.1067549823 -4.6879907935 -1.1686928865
 H  0.3404661199 -3.5950439317 -0.3402009764
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