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Supporting Information for

$[UO_2(NH_3)_5]Br_2 \cdot NH_3$: Synthesis, Crystal Structure, and Speciation in Liquid Ammonia Solution by First-Principles Molecular Dynamics Simulations.

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Additional Computational Details

PCM and NBO calculations

Starting from the gas-phase BLYP/SDD/6-311+G** equilibrium structures, $[UO_2L_5]^{2+}$ (L = H_2O, NH_3) were re-optimised using the polarisable continuum model in its integral equation formalism (IEF-PCM),[1] as implemented in Gaussian 09.[2] For L = H_2O, standard solvent parameters of water were used, for ammonia we employed the static dielectric constant of liquid ammonia at 20ºC (ε = 16.6),[3] the same dynamic dielectric constant as water,[4] and a solvent radius of 2.5 Å.[5] Natural bond orbital analyses[6] employed the Gaussian NBO version 3.1 as implemented in Gaussian 09.

CPMD simulations

The same methods and basis sets as in our previous studies of uranyl complexes[7] were employed. Car-Parrinello molecular dynamics (CPMD)[8] simulations were performed using the BLYP functional[9] and norm-conserving pseudopotentials that had been generated according to the Troullier and Martins procedure[10] and transformed into the Kleinman-Bylander form.[11] For uranium, the semicore (or small-core) pseudopotential was employed that had been generated and validated in reference 12. Periodic boundary conditions were imposed using cubic supercells with a lattice contant of 13.22 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 and and a total of 42 ammonia molecules, affording a density of 0.71. The system has two positive charges, neutralised by a uniform background charge. 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.

Constrained CPMD simulations were performed along a predefined reaction coordinate ξ (a single U-N bond distance r), starting from the respective mean values for the five-coordinate minumum in gas and solution (as obtained from the unconstrained simulations. Changes in the Helmholtz free energes were evaluated by pointwise thermodynamic integration[13] of the mean constraint force $\langle f \rangle$ along this coordinate via

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

At each point, the system was propagated until $\langle f(\xi) \rangle$ was sufficiently converged (usually within 2 - 2.5 ps after 0.5 ps of equilibration, similar to the degree of convergence documented in Figure S1 of the supporting information for reference 6 (see Table S1 for the resulting numbers). 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 *r*. According to the root-mean-square displacement along the trajectories, the solutions remained liquid-like throughout.

Selected conformers were optimised in the gas phase until the maximum gradient was less than $5 \cdot 10^{-4}$ a.u. (denoted CP-opt).

Table S1: Values for ξ (the constrained U-N distance) and $\langle f(\xi) \rangle$ [in a.u].

ξ	$\langle f(\xi) \rangle^{(a)}$
4.9443	-0.00100(42)
5.3223	-0.00992(24)
5.7002	-0.01127(17)
6.0782	-0.01101(14)
6.4561	-0.00966(12)
6.8341	-0.00409(26)
7.2120	0.00076(59)
7.5900	0.00402(51)
7.9679	0.00175(16)
8.3458	0.00173(17)
8.7238	-0.00040(9)

$^{(a)}$In parentheses: standard deviation of the running average of $\langle f(\xi) \rangle$ over the last picosecond.

Optimised Cartesian Coordinates (in Å, xyz format, BLYP/SDD level)

23
[UO2(NH3)5]2+ (gas)
U,0,0.0024748419,-0.0047799334,0.0009541113
O,0,0.0116837247,-0.0027229327,1.7892135068
O,0,0.0227797756,-0.0094267655,-1.787362502
N,0,2.624595126,0.4278250851,0.0462686629
N,0,0.4108716074,2.6151862988,-0.2044371345
N,0,-2.3444612369,1.2208152089,0.2764777872
N,0,-1.9049286088,-1.8429187343,-0.2571724845
N,0,1.1929440315,-2.380805787,0.1265978163
H,0,3.0110858751,0.7012915997,-0.8670362137
H,0,2.8998112353,1.1683295672,0.7048617399
H,0,3.1881385228,-0.3813558691,0.3356941769
H,0,-0.3221220665,3.0884573287,-0.7488511565

H,0,0.4687131671,3.1275438105,0.6858433926
H,0,1.2744806693,2.8508647306,-0.7098659462
H,0,-2.8694032165,1.4089894783,-0.5881732518
H,0,-2.9858148534,0.6913801985,0.8816212161
H,0,-2.2637915082,2.1302570111,0.7492930426
H,0,-1.6491333521,-2.5658697933,-0.9425003562
H,0,-2.1687654573,-2.3466123111,0.6002045725
H,0,-2.7854358657,-1.4625676917,-0.6274227724
H,0,1.7693775024,-2.6106100349,-0.6939109066
H,0,1.8110780453,-2.4653308665,0.9442273515
H,0,0.5497292567,-3.1766964041,0.2230853549

23
[UO2(NH3)5]2+ (PCM)
U,0,-0.0088999002,-0.0155191276,-0.0002002519
O,0,-0.0145994738,-0.0248319424,-1.8011988124
O,0,-0.0281391617,-0.029924582,1.8005508602
N,0,-2.4377994143,0.9609848947,-0.0828247345
N,0,0.1419280118,2.5924726377,0.2168352827
N,0,2.4939476059,0.7049972438,-0.2567115364
N,0,1.4885262134,-2.1520939586,0.2119823235
N,0,-1.6521430303,-2.0554536756,-0.0807246668
H,0,-2.7838982935,1.2486972072,0.8396085373
H,0,-2.519369873,1.7824087031,-0.6922995288
H,0,-3.1330929817,0.2975741335,-0.441278915
H,0,0.9879969266,2.904643891,0.7060967572
H,0,0.1374590841,3.0809212846,-0.6861267914
H,0,-0.6325821701,2.9903554229,0.7590057259
H,0,2.9989812333,0.8161837127,0.6302747987
H,0,3.0351575798,0.0352306484,-0.8145327684
H,0,2.5926058835,1.5961710217,-0.7549051604
H,0,1.1159010423,-2.8312759525,0.8845968804
H,0,1.618041093,-2.6579907404,-0.6715134584
H,0,2.431279085,-1.9403013585,0.5561998348
H,0,-2.2494486052,-2.1167576518,0.751781032
H,0,-2.2810633321,-2.0256809417,-0.8909526404
H,0,-1.182631523,-2.9651368701,-0.1476447677

23
[UO2(NH3)4]2+.NH3 (gas)
U,0,-0.3463849321,0.1269615719,0.0124167552
O,0,-0.3722153038,0.1169545901,-1.7753951625
O,0,-0.331642986,0.1340068025,1.8004291598
N,0,1.8360007471,1.4512237041,-0.017350086
N,0,1.3501087829,-1.7987864789,0.0000244774
N,0,4.293238925,-0.4694457397,-0.0275284462
N,0,-2.4049346107,-1.4766880985,0.0635250897
N,0,-1.8087047168,2.2860111675,0.0006778225
H,0,2.6480018764,0.7861845222,-0.0192815434
H,0,1.966495322,2.0457737312,-0.8467181779
H,0,1.9783240877,2.0581611458,0.8010893446
H,0,1.3209182554,-2.4110234698,0.8261039323
H,0,1.2984613704,-2.4151474293,-0.821933598
H,0,2.308923367,-1.3908680586,-0.0131775495
H,0,4.6203656906,-0.9895664338,0.7965213123
H,0,4.6084752039,-1.01637558,-0.8387760151
H,0,4.885254965,0.3713188939,-0.0460061914
H,0,-3.1023958986,-1.2303877045,0.7799180514
H,0,-2.9162953086,-1.5284430783,-0.828138616
H,0,-2.1498105616,-2.4507414672,0.282027035
H,0,-1.9773877799,2.6764729166,0.9377165598
H,0,-1.4001154772,3.0523278122,-0.5529801436

H,0,-2.7419660179,2.1476766809,-0.4130620105

18
[UO2(H2O)5]2+ (gas)
U,0,-0.002477717,-0.0002392622,-0.0017956205
O,0,-0.0107764303,-0.0017312009,-1.7844106415
O,0,0.001515436,-0.0063654446,1.780797122
O,0,0.1723044836,2.5047265918,-0.0146898226
O,0,-2.3285880996,0.9426657519,-0.0141563534
O,0,2.4298974387,0.6231355485,0.037417893
O,0,-1.6065050874,-1.9291831829,0.0371779059
O,0,1.3348455703,-2.1240705609,-0.0489937459
H,0,-0.0837151541,3.0977109947,-0.7488745424
H,0,0.5075924078,3.0663600877,0.7122090272
H,0,-2.96261166,0.9085384123,-0.7578959182
H,0,-2.7726440081,1.3980043571,0.7287075228
H,0,2.9391013407,1.0298602277,-0.6916937321
H,0,3.0468586422,0.4836326576,0.7832022578
H,0,-1.7909600164,-2.5469408887,-0.6981258968
H,0,-2.1663140122,-2.1976819624,0.7927407445
H,0,1.8562291376,-2.4583986807,-0.8057656223
H,0,1.4311227283,-2.7682674462,0.6804014225

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