Elucidation of the inverse *trans* influence in uranyl, its imido and carbene analogues via quantum chemical simulation

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Electronic Supplementary Information

1. Data Tables

Table S1. Calculated uranium-ligand delocalisation indices, obtained using electron densities calculated in the following ways: UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell electronic structure at frozen 6p shell-optimised geometry.

			$\delta(U,L)$				
Complex	Method	ρ	Total	σ_u	σ_g	π_u	π_g
UO_2^{2+}	PBE0	UU	2.292	0.582	0.328	0.832	0.550
		FU	2.387	0.646	0.333	0.844	0.564
		FF	2.373	0.637	0.326	0.846	0.564
	CASSCF	UU	1.822	0.448	0.294	0.588	0.492
		FU	1.904	0.492	0.308	0.596	0.508
		FF	1.837	0.464	0.297	0.576	0.500
$U(NH)_2^{2+}$	PBE0	UU	2.370	0.525	0.291	0.912	0.642
		FU	2.450	0.561	0.309	0.922	0.658
		FF	2.443	0.543	0.302	0.936	0.662
	CASSCF	UU	1.850	0.396	0.262	0.624	0.568
		FU	1.892	0.410	0.278	0.626	0.578
		FF	1.798	0.367	0.265	0.594	0.572
$U(CH_2)_2^{2+}$	PBE0	UU	1.974	0.490	0.410	0.575	0.499
		FU	1.983	0.475	0.425	0.575	0.508
		FF	1.957	0.484	0.410	0.563	0.500
	CASSCF	UU	1.445	0.356	0.363	0.331	0.395
		FU	1.440	0.341	0.371	0.330	0.398
		FF	1.345	0.323	0.353	0.292	0.377

Table S2. Calculated uranium-ligand ρ_{BCP} values, obtained using electron densities calculated in the following ways: UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell electronic structure at frozen 6p shell-optimised geometry.

			ρ_{BCP}		
Complex	Method	ρ	Total	u	g
UO_2^{2+}	PBE0	UU	0.386	0.225	0.161
		FU	0.395	0.228	0.167
		FF	0.348	0.200	0.148
	CASSCF	UU	0.367	0.209	0.158
		FU	0.375	0.212	0.163
		FF	0.323	0.181	0.142
$U(NH)_2^{2+}$	PBE0	UU	0.318	0.186	0.132
		FU	0.321	0.183	0.138
		FF	0.282	0.161	0.121
	CASSCF	UU	0.289	0.165	0.124
		FU	0.295	0.165	0.130
		FF	0.239	0.134	0.105
$U(CH_2)_2^{2+}$	PBE0	UU	0.259	0.134	0.125
		FU	0.252	0.123	0.129
		FF	0.230	0.113	0.117
	CASSCF	UU	0.234	0.118	0.116
		FU	0.227	0.110	0.117
		FF	0.191	0.093	0.098

Table S3. ITI-induced energy stabilisation obtained at geometries optimised using a fully relaxed electronic structure.

Complex	Method	$\Delta E_{ITI}\,(eV)$
UO_2^{2+}	PBE0	2.58
	CASSCF	2.75
$U(NH)_2^{2+}$	PBE0	1.90
	CASSCF	2.46
$U(CH_2)_2^{2+}$	PBE0	1.24
	CASSCF	1.55

Table S4. ITI-induced energy stabilisation obtained at geometries as detailed in Table 5 fo the manuscript.

Complex	Method	$\Delta E_{ITI}\,(eV)$
UO_2^{2+}	PBE0	2.37
	CASSCF	2.51

$U(NH)_2^{2+}$	PBE0	1.75
	CASSCF	2.14
$U(CH_2)_2^{2+}$	PBE0	1.17
	CASSCF	1.38

Table S5. Calculated uranium charges, localisation indices and uranium-ligand delocalisation indices, obtained using electron densities calculated in the following ways: UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell electronic structure at frozen 6p shell-optimised geometry.

Complex	Method	ρ	Q(U)	λ(U)	$\delta(U,L)$
UO_2^{2+}	PBE0	UU	3.270	86.446	2.291
		FU	3.101	86.498	2.388
		FF	3.066	86.549	2.385
	CASSCF	UU	3.328	86.857	1.822
		FU	3.148	86.955	1.904
		FF	2.108	87.060	1.837
$U(NH)_2^{2+}$	PBE0	UU	2.934	86.634	2.371
		FU	2.753	86.726	2.451
		FF	2.748	86.741	2.443
	CASSCF	UU	3.004	87.070	1.850
		FU	2.850	87.270	1.892
		FF	2.786	87.410	1.798
$U(CH_2)_2^{2+}$	PBE0	UU	2.303	87.517	1.975
		FU	2.171	87.638	1.983
		FF	2.190	87.651	1.955
	CASSCF	UU	2.354	88.130	1.445
		FU	2.250	88.230	1.440
		FF	2.284	88.300	1.345

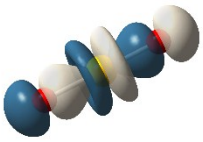
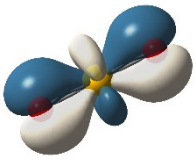
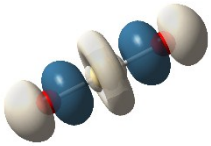
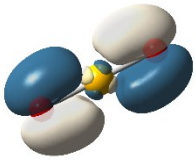
Table S6. Energy differences between electronic structures in which the 6p shell was frozen or unfrozen. UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell electronic structure at frozen 6p shell-optimised geometry.

Complex	Method	E_{FU} - E_{UU} (eV)	E_{FF} - E_{UU} (eV)
UO_2^{2+}	PBE0	2.58	2.38
	CASSCF	2.76	2.51
$U(NH)_2^{2+}$	PBE0	1.90	1.75
	CASSCF	2.45	2.14
$U(CH_2)_2^{2+}$	PBE0	1.24	1.17
	CASSCF	1.55	1.37

Table S7. Uranium and ligand localisation indices, obtained using electron densities calculated in the following ways: UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell electronic structure at frozen 6p shell-optimised geometry.

Complex	Method	ρ	λ(U)	λ(L)
UO_2^{2+}	PBE0	UU	86.446	7.438
		FU	86.498	7.289
		FF	86.549	7.278
	CASSCF	UU	86.857	7.719
		FU	86.955	7.586
		FF	87.060	7.605
$U(NH)_2^{2+}$	PBE0	UU	86.634	7.197
		FU	86.726	7.060
		FF	86.741	7.066
	CASSCF	UU	87.070	7.509
		FU	87.270	7.400
		FF	87.410	7.450
$U(CH_2)_2^{2+}$	PBE0	UU	87.517	6.978
		FU	87.638	6.899
		FF	87.651	6.906
	CASSCF	UU	88.130	7.358
		FU	88.230	7.322
		FF	88.300	7.380

2. Natural Orbital renderings

σ_u	π_u	σ_g	π_g
			
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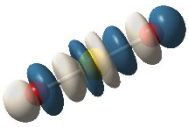	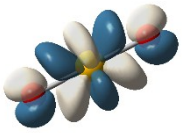	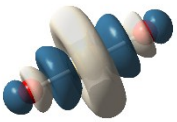	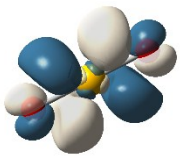
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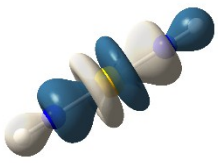
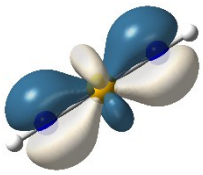
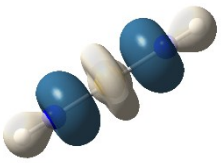
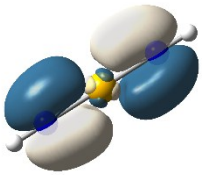
Figure S1. Natural orbitals and natural occupancies from CASSCF(12,12) calculations of UO_2^{2+}, obtained from the following calculations: UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell electronic structure at frozen 6p shell-optimised geometry. Note that natural orbitals are shown for the UU simulation only, but are representative of the active spaces in all calculations.

σ_u	π_u	σ_g	π_g
			
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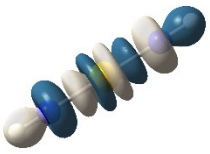	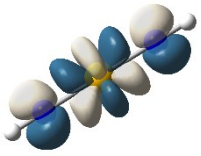	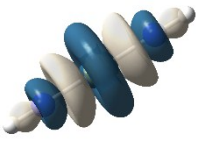	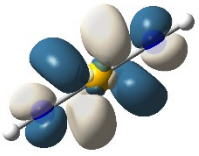
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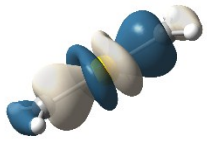
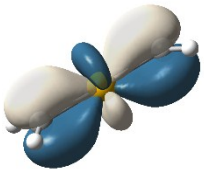
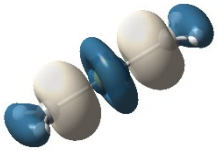
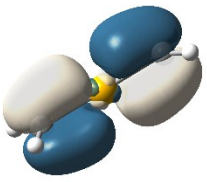
Figure S2. Natural orbitals and natural occupancies from CASSCF(12,12) calculations of $U(NH)_2^{2+}$, obtained from the following calculations: UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell

electronic structure at frozen 6p shell-optimised geometry. Note that natural orbitals are shown for the UU simulation only, but are representative of the active spaces in all calculations.

σ_u	π_u	σ_g	π_g
			
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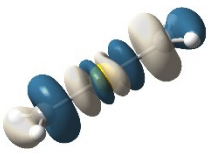	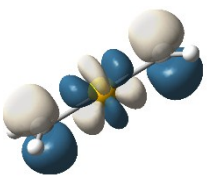	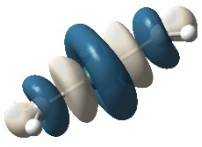	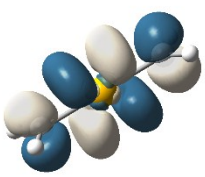
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FU: 0.095 FF: 0.121	FU: 0.134 FF: 0.171	FU: 0.019 FF: 0.023	FU: 0.045 FF: 0.055

Figure S3. Natural orbitals and natural occupancies from CASSCF(8,8) calculations of $U(CH_2)_2^{2+}$, obtained from the following calculations: UU – Fully relaxed electronic structure at fully relaxed geometry; FU – frozen 6p shell electronic structure at fully relaxed geometry; FF – frozen 6p shell electronic structure at frozen 6p shell-optimised geometry. Note that natural orbitals are shown for the UU simulation only, but are representative of the active spaces in all calculations.

3. Optimised structural data

UO_2^{2+}

PBE0/TZVP (6p unfrozen)					PBE0/TZVP (6p frozen)			
U	0.000000	0.000000	0.000000		U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.684254		O	0.000000	0.000000	1.739874
O	0.000000	0.000000	-1.684254		O	0.000000	0.000000	-1.739874

CASSCF(12,12)/TZVP (6p unfrozen)					CASSCF(12,12)/TZVP (6p frozen)			
U	0.000000	0.000000	0.000000		U	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.709039		O	0.000000	0.000000	1.774825

O	0.000000	0.000000	-1.709039		O	0.000000	0.000000	-1.774825

$U(NH)_2^{2+}$

PBE0/TZVP (6p unfrozen)					PBE0/TZVP (6p frozen)			
U	0.000000	0.000000	0.000000		U	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.746131		N	0.000000	0.000000	1.800954
N	0.000000	0.000000	-1.746131		N	0.000000	0.000000	-1.800954
H	0.000000	0.000000	2.778370		H	0.000000	0.000000	2.834617
H	0.000000	0.000000	-2.778370		H	0.000000	0.000000	-2.834617

CASSCF(12,12)/TZVP (6p unfrozen)					CASSCF(12,12)/TZVP (6p frozen)			
U	0.000000	0.000000	0.000000		U	0.000000	0.000000	0.000000
N	0.000000	0.000000	1.783373		N	0.000000	0.000000	1.873370
N	0.000000	0.000000	-1.783373		N	0.000000	0.000000	-1.873370
H	0.000000	0.000000	2.797736		H	0.000000	0.000000	2.888377
H	0.000000	0.000000	-2.797736		H	0.000000	0.000000	-2.888377

$U(CH_2)_2^{2+}$

PBE0/TZVP (6p unfrozen)					PBE0/TZVP (6p frozen)			
U	0.000000	0.000000	0.000000		U	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.904577		C	0.000000	0.000000	1.953594
C	0.000000	0.000000	-1.904577		C	0.000000	0.000000	1.953594
H	0.000000	0.945302	2.471137		H	0.000000	0.946382	2.518224
H	0.000000	-0.945302	2.471137		H	0.000000	-0.946382	2.518224
H	0.000000	0.945302	-2.471137		H	0.000000	0.946382	-2.518224
H	0.000000	-0.945302	-2.471137		H	0.000000	-0.946382	-2.518224

CASSCF(8,8)/TZVP (6p unfrozen)					CASSCF(8,8)/TZVP (6p frozen)			
U	0.000000	0.000000	0.000000		U	0.000000	0.000000	0.000000

C	0.000000	0.000000	1.970008		C	0.000000	0.000000	2.061185
C	0.000000	0.000000	-1.970008		C	0.000000	0.000000	-2.061185
H	0.000000	0.946389	2.509568		H	0.000000	0.943977	2.601462
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H	0.000000	0.946389	-2.509568		H	0.000000	0.943977	-2.601462
H	0.000000	-0.946389	-2.509568		H	0.000000	-0.943977	-2.601462