Supplementary Materials: Decomposition of d- and f-shell contributions to uranium bonding from the quantum theory of atoms in molecules: application to uranium and uranyl halides

Jonathan Tanti, Meghan Lincoln and Andy Kerridge

Table S1. Decomposed QTAIM metrics of the U–O bond in $[UO_2X_4]^{2-}$ complexes, obtained from B3LYP-derived densities. All values are in a.u.

Complex	$\rho_{BCP}(U,O)$			$\delta(U,O)$				
	Total	5f	6d	Total	$5f_\sigma$	$5f_\pi$	$6d_\sigma$	$6d_\pi$
$[UO_2F_4]^{2-}$	0.271	0.160	0.111	1.766	0.553	0.596	0.252	0.365
$[UO_2Cl_4]^{2-}$	0.305	0.181	0.124	1.899	0.562	0.655	0.263	0.419
$[UO_2Br_4]^{2-}$	0.310	0.184	0.126	1.927	0.564	0.663	0.268	0.432
UO_2^{2+}	0.377	0.224	0.153	2.252	0.580	0.830	0.310	0.532

Table S2. Decomposed QTAIM metrics of the U–X bond in $[UO_2X_4]^{2-}$ and UX_6 complexes, obtained from B3LYP-derived densities. All values are in a.u.

Complex	$\rho_{BCP}(U,X)$			$\delta(U,X)$				
	Total	5f	6d	Total	$5f_\sigma$	$5f_\pi$	$6d_\sigma$	$6d_\pi$
$[UO_2F_4]^{2-}$	0.089	0.051	0.038	0.547	0.189	0.120	0.154	0.084
$[UO_2Cl_4]^{2-}$	0.054	0.028	0.026	0.535	0.173	0.105	0.190	0.067
$[UO_2Br_4]^{2-}$	0.047	0.024	0.023	0.545	0.173	0.105	0.203	0.064
UF_6	0.155	0.090	0.065	0.960	0.358	0.255	0.188	0.159
UCl_6	0.100	0.054	0.046	1.093	0.365	0.308	0.251	0.169
UBr_6	0.085	0.044	0.041	1.134	0.363	0.329	0.270	0.172

Table S3. Decomposed QTAIM metrics of the U–O bond in $[UO_2X_2Y_2]^{2-}$ complexes, obtained from B3LYP-derived densities. All values are in a.u.

X	Y	$\rho_{BCP}(U,O)$			$\delta(U,O)$				
		Total	5f	6d	Total	$5f_\sigma$	$5f_\pi$	$6d_\sigma$	$6d_\pi$
F	F	0.271	0.160	0.111	1.766	0.553	0.596	0.252	0.365
F	Cl	0.289	0.171	0.118	1.833	0.559	0.628	0.254	0.392
F	Br	0.292	0.173	0.119	1.849	0.560	0.634	0.257	0.398
Cl	Cl	0.305	0.181	0.124	1.899	0.562	0.655	0.263	0.419
Cl	Br	0.308	0.183	0.125	1.916	0.563	0.660	0.267	0.426
Br	Br	0.310	0.184	0.126	1.927	0.564	0.663	0.268	0.432

Table S4. Decomposed QTAIM metrics of the equatorial bonds in $[UO_2X_2Y_2]^{2-}$ complexes, obtained from B3LYP-derived densities. All values are in a.u.

Complex		$\rho_{BCP}(U,X/Y)$			$\delta(U,X/Y)$				
		Total	5f	6d	Total	$5f_\sigma$	$5f_\pi$	$6d_\sigma$	$6d_\pi$
$[UO_2F_2Cl_2]^{2-}$	F	0.103	0.059	0.044	0.643	0.220	0.151	0.165	0.106
	Cl	0.044	0.023	0.021	0.417	0.139	0.068	0.166	0.043
$[UO_2F_2Br_2]^{2-}$	F	0.106	0.060	0.045	0.667	0.227	0.158	0.169	0.112
	Br	0.036	0.018	0.017	0.394	0.130	0.058	0.170	0.036
$[UO_2Cl_2Br_2]^{2-}$	Cl	0.056	0.030	0.027	0.567	0.181	0.114	0.197	0.074
	Br	0.043	0.022	0.021	0.507	0.164	0.093	0.195	0.055

Table S5. Decomposed QTAIM metrics of the axial U–F bond in $UF_2X_2Y_2$ complexes, obtained from B3LYP-derived densities. All values are in a.u.

X	Y	$\rho_{BCP}(U,F)$			$\delta(U,F)$				
		Total	5f	6d	Total	$5f_\sigma$	$5f_\pi$	$6d_\sigma$	$6d_\pi$
F	F	0.155	0.090	0.065	0.960	0.358	0.255	0.188	0.159
F	Cl	0.157	0.091	0.066	0.974	0.357	0.259	0.190	0.168
F	Br	0.157	0.091	0.066	0.973	0.353	0.258	0.191	0.171
Cl	Cl	0.160	0.093	0.067	0.991	0.354	0.266	0.193	0.178
Cl	Br	0.160	0.093	0.067	0.992	0.354	0.263	0.194	0.181
Br	Br	0.160	0.093	0.067	0.994	0.350	0.265	0.194	0.185

Table S6. Decomposed QTAIM metrics of the axial U–Cl bond in $UCl_2X_2Y_2$ complexes, obtained from B3LYP-derived densities. All values are in a.u.

X	Y	$\rho_{BCP}(U,Cl)$			$\delta(U,Cl)$				
		Total	5f	6d	Total	$5f_\sigma$	$5f_\pi$	$6d_\sigma$	$6d_\pi$
F	F	0.096	0.052	0.044	1.059	0.374	0.297	0.245	0.143
F	Cl	0.098	0.053	0.045	1.078	0.368	0.304	0.248	0.158
F	Br	0.098	0.053	0.045	1.069	0.362	0.299	0.247	0.161
Cl	Cl	0.100	0.054	0.046	1.093	0.365	0.308	0.251	0.169
Cl	Br	0.101	0.054	0.047	1.097	0.361	0.307	0.254	0.175
Br	Br	0.100	0.054	0.046	1.091	0.353	0.306	0.253	0.179

Table S7. Decomposed QTAIM metrics of the axial U–Br bond in $UBr_2X_2Y_2$ complexes, obtained from B3LYP-derived densities. All values are in a.u.

X	Y	$\rho_{BCP}(U,Cl)$			$\delta(U,Cl)$				
		Total	5f	6d	Total	$5f_\sigma$	$5f_\pi$	$6d_\sigma$	$6d_\pi$
F	F	0.082	0.043	0.039	1.100	0.383	0.323	0.260	0.134
F	Cl	0.083	0.043	0.040	1.115	0.377	0.328	0.263	0.147
F	Br	0.083	0.043	0.040	1.116	0.370	0.326	0.266	0.154
Cl	Cl	0.085	0.044	0.041	1.131	0.371	0.334	0.267	0.159
Cl	Br	0.085	0.044	0.041	1.136	0.368	0.331	0.271	0.166
Br	Br	0.085	0.044	0.041	1.134	0.363	0.329	0.270	0.172

Table S8. Binding energies, vibrational frequencies, and axial/equatorial QTAIM metrics of $[UO_2X_2Y_2]^{2-}$ complexes, obtained from B3LYP-derived densities.

Equatorial ligands	E_B (a.u.)	ν_s (cm^{-1})	ν_{as} (cm^{-1})	$\rho_{BCP}(U,O)$ (a.u.)	$\delta(U,O)$	$\bar{\rho}_{BCP}(U,X/Y)$ (a.u.)	$\bar{\delta}(U,X/Y)$
F_4	1.089	793	854	0.271	1.766	0.089	0.547
F_2Cl_2	0.995	828	901	0.289	1.833	0.074	0.530
F_2Br_2	0.979	836	909	0.292	1.849	0.071	0.531
Cl_4	0.883	855	939	0.305	1.899	0.054	0.535
Cl_2Br_2	0.862	861	946	0.308	1.916	0.050	0.537
Br_4	0.841	866	951	0.310	1.927	0.047	0.545
Free UO_2^{2+}	-	1043	1137	0.377	2.252	-	-

Table S9. Binding energies and ρ_{BCP} values of $UX_2Y_2Z_2$ complexes, obtained from B3LYP-derived densities.

Ligands	E_B (a.u.)	$\rho_{BCP}(U,X)$ (a.u.)	$\rho_{BCP}(U,Y)$ (a.u.)	$\rho_{BCP}(U,Z)$ (a.u.)	$\bar{\rho}_{BCP}$ (a.u.)
F_6	7.207	0.155	0.155	0.155	0.155
F_4Cl_2	7.058	0.157	0.157	0.096	0.137
F_4Br_2	7.028	0.157	0.157	0.082	0.132
F_2Cl_4	6.906	0.160	0.098	0.098	0.119
$F_2Cl_2Br_2$	6.876	0.160	0.098	0.083	0.114
F_2Br_4	6.845	0.160	0.083	0.083	0.109
Cl_6	6.752	0.100	0.100	0.100	0.100
Cl_4Br_2	6.721	0.101	0.101	0.085	0.096
Cl_2Br_4	6.689	0.100	0.085	0.085	0.090
Br_6	6.657	0.085	0.085	0.085	0.085

Table S10. Binding energies and delocalisation indices of $UX_2Y_2Z_2$ complexes, obtained from B3LYP-derived densities.

Ligands	E_B (a.u.)	$\delta(U,X)$	$\delta(U,Y)$	$\delta(U,Z)$	$\bar{\delta}$
F_6	7.207	0.960	0.960	0.960	0.960
F_4Cl_2	7.058	0.974	0.974	1.059	1.002
F_4Br_2	7.028	0.973	0.973	1.100	1.015
F_2Cl_4	6.906	0.991	1.078	1.078	1.049
$F_2Cl_2Br_2$	6.876	0.992	1.069	1.115	1.059
F_2Br_4	6.845	0.994	1.116	1.116	1.075
Cl_6	6.752	1.093	1.093	1.093	1.093
Cl_4Br_2	6.721	1.097	1.097	1.131	1.108
Cl_2Br_4	6.689	1.091	1.136	1.136	1.121
Br_6	6.657	1.134	1.134	1.134	1.134

Table S11. Comparison of QTAIM metrics for chloride species obtained with Grimme's D3-dispersion correction or using all-electron scalar-relativistic Hamiltonians, namely, the 2nd order Douglas-Kroll-Hess (DKH), Barysz-Sadlej-Snijders (BSS) and exact two-component (X2C) Hamiltonians. All densities were generated using the B3LYP functional at the B3LYP-optimised geometry.

Complex		ρ_{BCP}				δ			
		D3	DKH	BSS	X2C	D3	DKH	BSS	X2C
$[UO_2Cl_4]^{2-}$	U–O	0.3048	0.3109	0.3109	0.3109	1.899	1.894	1.893	1.893
	U–Cl	0.0539	0.0534	0.0534	0.0534	0.532	0.528	0.528	0.528
UCl_6	U–Cl	0.1000	0.0998	0.0999	0.0999	1.089	1.087	1.087	1.086