How Important Is the Coordinating Atom In Controlling Magnetic Anisotropy in Uranium(III) Single-Ion Magnets? A Theoretical Perspective

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Table S1: Continuous Shape Measures (CShMs) around Uranium center of complex **1**.

Structure	Point group	Full name	Deviation parameter
JPPY-6	C_{5v}	Johnson pentagonal pyramid J2	20.838
TPR-6	D_{3h}	Trigonal prism	0.678
OC-6	O_h	Octahedron	15.925
PPY-6	C_{5v}	Pentagonal pyramid	16.618
HP-6	D_{6h}	Hexagon	36.100

Table S2: Continuous Shape Measures (CShMs) around the uranium centre of complex **2**.

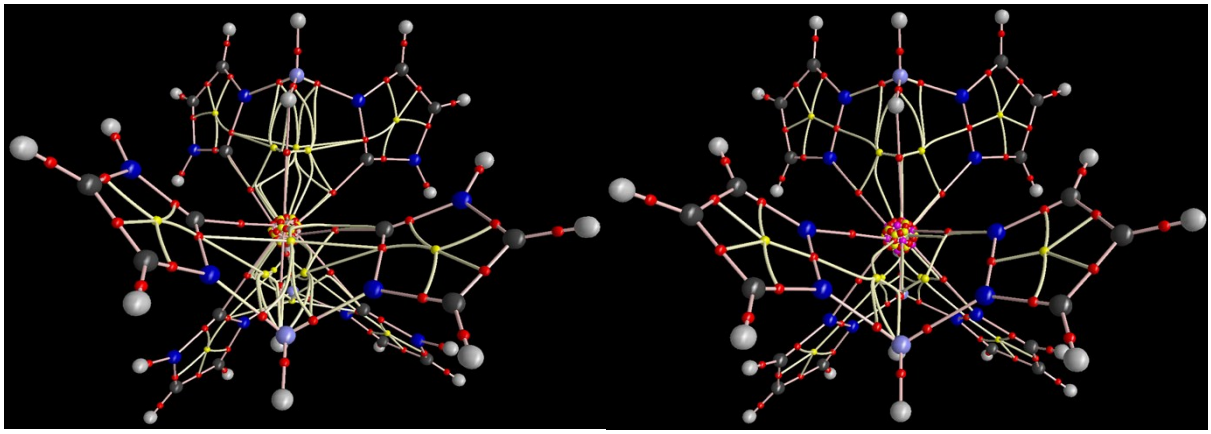
Structure	Point group	Full name	Deviation parameter
JPPY-6	C_{5v}	Johnson pentagonal pyramid J2	20.804
TPR-6	D_{3h}	Trigonal prism	0.236
OC-6	O_h	Octahedron	15.783
PPY-6	C_{5v}	Pentagonal pyramid	16.658
HP-6	D_{6h}	Hexagon	36.088

Table S3: The composition of U-C bonding as computed using NBO analysis.

Bond	Contribution from Carbon and Uranium	Orbital composition of Uranium
U-C1	81.48% C+18.52% U	s(15.16%)+p(27.25%)+d(47.85%)+f(9.73%)
U-C2	81.77% C+18.23% U	s(14.18%)+p(27.75%)+d(50.25%)+f(7.82%)
U-C3	81.48% C+18.52% U	s(15.16%)+p(27.24%)+d(47.84%)+f(9.75%)
U-C4	81.76% C+ 18.24% U	s(14.19%)+p(27.72%)+d(50.21%)+f(7.88%)
U-C5	81.48% C+ 18.52% U	s(15.16%)+p(27.25%)+d(47.88%)+f (9.71%)
U-C6	81.76% C+18.24% U	s(14.18%)+p(27.74%)+d(50.19%)+ f(7.89%)

Table S4: The composition of U-N bonding as computed using NBO analysis.

Bond	Contribution from Nitrogen and Uranium	Orbital composition of Uranium
U-N1	90.15% N+9.85% U	s(13.31%)+p(27.19%)+d(48.67%)+f(10.82%)
U-N2	89.50% N+10.50% U	s(13.32%)+p(24.64%)+d(42.61%)+f(19.52%)
U-N3	89.48% N+10.52% U	s(13.50%)+p(24.63%)+d(42.54%)+f(19.32%)
U-N4	89.96% N+ 10.04% U	s(13.49%)+p(28.29%)+d(45.41%)+f(12.79%)
U-N5	90.50% N+ 9.50% U	s(13.34%)+p(27.77%)+d(51.67%)+f (7.20%)
U-N6	89.75% N+10.25% U	s(13.43%)+p(24.63%)+d(44.79%)+ f(17.44%)



(1) **(2)**

Figure S1. Molecular graphs of the chosen complex **1-2** showing bond paths, bond critical points in red (BCPs), ring critical points (RCPs) in yellow and cage critical points (CCPs) in green.

Table S5. Mulliken charges and spin densities of complexes of selected atoms in complexes **1** and **2** (see Figure **2** for atom labels).

1	Mulliken charges	Spin density	**2**	Mulliken charges	Spin density
C1	-0.1568	-0.014	N1	-0.2010	-0.011
C2	-0.1571	-0.019	N2	-0.1929	-0.018
C3	-0.1577	-0.014	N3	-0.1948	-0.017
C4	-0.1566	-0.019	N4	-0.1960	-0.013
C5	-0.1560	-0.014	N5	-0.2039	-0.008
C6	-0.1562	-0.019	N6	-0.1974	-0.013
U1	0.5068	3.020	U1	1.4031	3.046

Table S6: Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre using MD-I in complex **1**.

States	**Energy**	g_x	g_y	g_z
KD1	0.00	2.586	2.532	2.000
KD2	102.6	0.011	0.036	4.499
KD3	318.5	2.970	2.926	0.017
KD4	409.8	3.160	3.064	0.192
KD5	448.1	0.024	0.102	0.763

Table S7: Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre using MD-I in complex **2**.

States	**Energy**	g_x	g_y	g_z
KD1	0.0	2.636	2.610	1.973
KD2	165.9	0.007	0.025	3.779
KD3	398.9	3.422	3.366	0.705
KD4	495.9	2.886	2.745	0.535
KD5	541.6	0.017	0.091	0.490

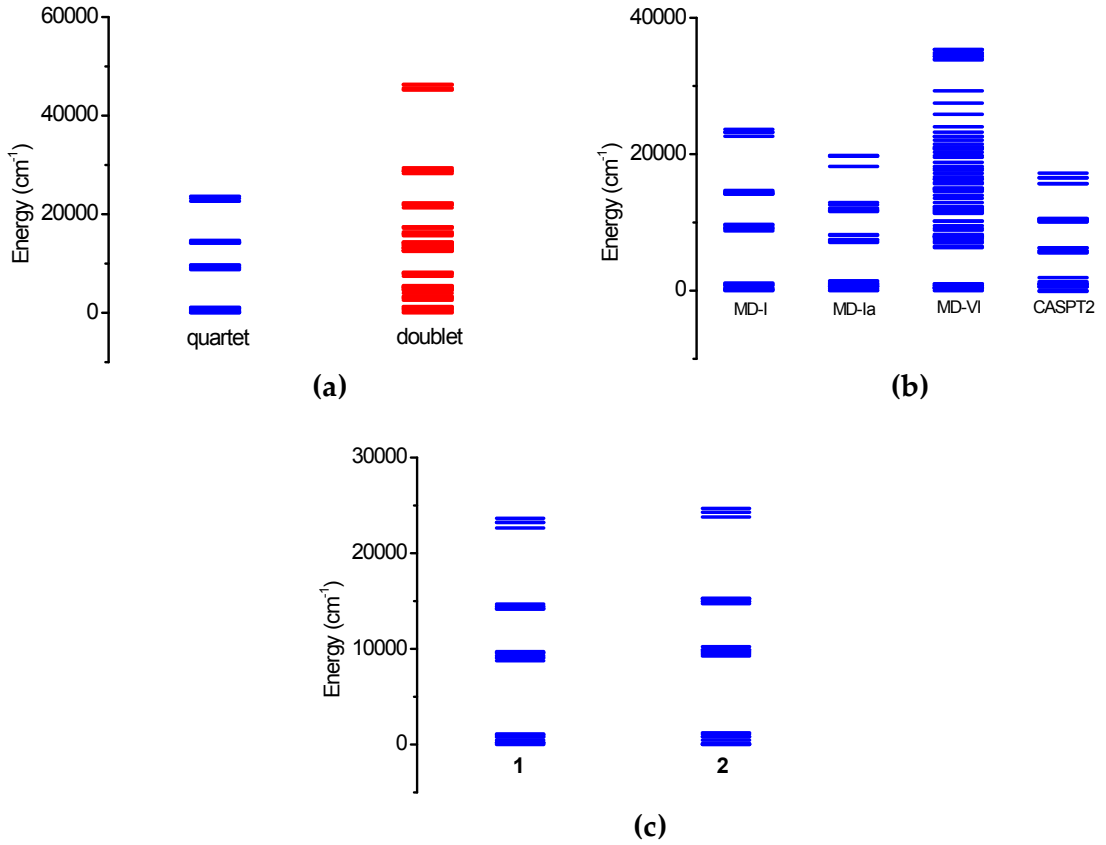


Figure S2. (a) Energy comparison of quartet and doublet states of **1.** (**b**) Energy comparison of quartet states of **1** with varying the size of active space and here CASPT2 denote CASPT2 calculations performed on MD-I reference space (**c**) Energy comparison of 35 quartet states computed for complexes **1** and **2** using MD-I.

Table S8: Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre using MD-Ia in complex **1**.

States	Energy	g_x	g_y	g_z
KD1	0.00	2.588	2.553	0.552
KD2	220.1	0.083	0.130	4.540
KD3	306.6	2.884	2.530	1.050
KD4	548.9	0.063	0.153	2.141
KD5	708.7	3.441	3.401	0.594

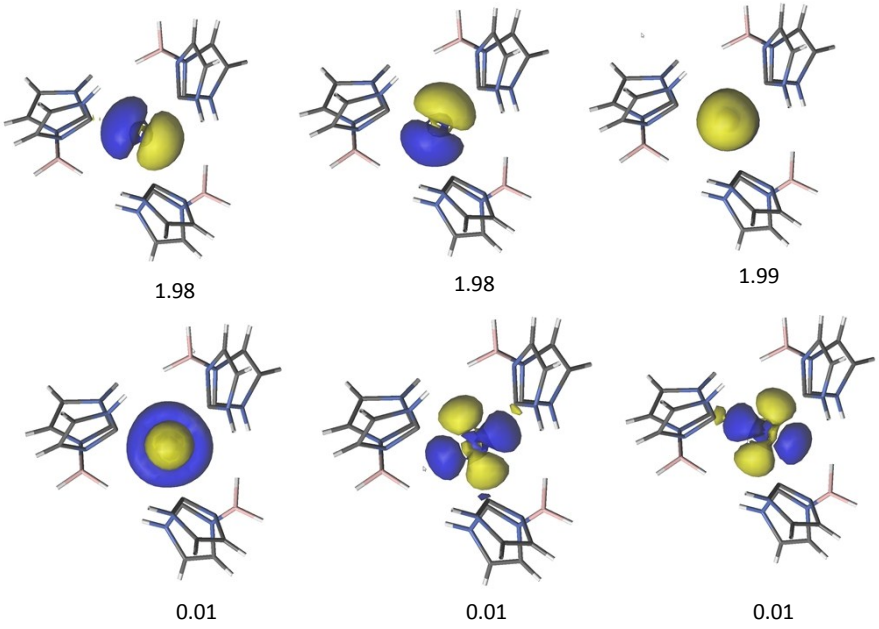


Figure S3. The three bonding orbitals in RAS1 and their corresponding antibonding orbitals in RAS3. The number below each orbitals denote their occupation number.

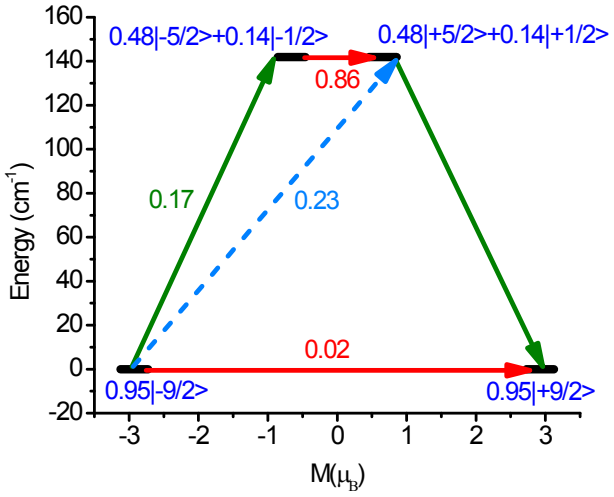


Figure S4. The CASPT2 computed magnetic relaxation pathways of **1**. The Blackline indicates the KDs as a function of magnetic moments. The red line represents QTM via ground states and TA-OTM via excited states. The dashed line indicates possible Orbach process. The olive line indicates possible pathways of magnetic relaxation. The blue characters indicate the m_J composition of the Kramer doublet (KD).

Table S9: Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre by CASPT2 calculation of **1**.

States	Energy	g_x	g_y	g_z
KD1	0.0	0.017	0.095	5.852
KD2	141.9	2.768	2.055	1.330
KD3	295.3	1.025	1.669	3.442
KD4	339.9	1.619	1.163	0.323
KD5	499.3	0.702	0.924	1.961

Table S10. SINGLE_ANISO computed crystal field parameters for the uranium center with varying active space size and CASPT2 results (MD-I). The crystal field Hamiltonian:

$$\hat{H}_{CF} = \sum_{k=-q}^{q} \sum B_k^q \tilde{O}_k^q$$

Where $\tilde{O}_k^q$ and B_k^q are the computed extended Stevens operator and crystal field (CF) parameter, respectively. Quantization axis is considered as the main magnetic axis of the KD1

k	q	B_k^q			
		Set 1	Set 2	Set 3	CASPT2
2	-2	-5.73E-02	-4.02E-03	-3.49E-02	-9.80E-01
	-1	2.84E-01	-4.59E-01	-5.92E-01	-1.94E-01
	0	**-3.99E+00**	**-3.64E+00**	**-5.51E+00**	**-5.21E+00**
	1	1.70E-01	-1.67E-01	1.13E+00	7.83E-01
	2	-3.18E-02	-2.61E-02	1.27E-01	2.27E-01
4	-4	-3.07E-03	-4.61E-03	1.92E-03	2.78E-02
	-3	1.62E-01	1.83E-01	-1.04E-01	2.85E-01

	-2	4.05E-03	-8.70E-04	-8.94E-04	2.52E-02
	-1	-9.78E-03	-2.15E-03	1.69E-02	5.58E-03
	0	**3.51E-02**	**-1.47E-03**	**1.10E-01**	**-2.35E-02**
	1	-6.21E-03	-1.40E-03	-2.55E-02	-2.81E-02
	2	6.01E-04	-5.20E-05	5.48E-04	-1.18E-03
	3	6.10E-03	-1.97E-01	1.54E-01	-9.52E-02
	4	4.09E-03	6.21E-04	-4.28E-04	-1.03E-02
6	-6	3.52E-02	9.05E-03	2.44E-02	-4.35E-03
	-5	1.73E-03	-1.19E-03	2.19E-03	-2.80E-03
	-4	-8.37E-05	4.56E-06	5.20E-04	9.36E-04
	-3	-8.00E-03	5.66E-03	-2.48E-02	-6.07E-03
	-2	-1.54E-04	-1.66E-04	-2.58E-04	-7.22E-04
	-1	-1.74E-04	6.12E-05	-8.65E-04	-5.19E-06
	0	**4.99E-04**	**1.99E-04**	**-1.30E-03**	**-2.32E-04**
	1	-1.31E-04	5.49E-05	1.47E-03	1.50E-03
	2	3.30E-06	-6.97E-05	4.37E-04	-4.39E-04
	3	8.04E-03	-2.82E-03	1.01E-02	8.60E-03
	4	1.66E-04	-6.24E-05	-6.33E-06	-1.86E-03
	5	3.40E-03	-1.67E-04	-2.55E-04	1.52E-03
	6	6.21E-03	-1.81E-02	1.89E-02	4.84E-03

Table S11. m_J compositions of KD1 derived from $^4I_{9/2}$ with varying the size of the active space.

KD1 of all possible roots	**Composition of m_J**
MD-I	0.46|±7/2>+0.24|±5/2>
MD-II	0.55|±7/2>+0.35|±5/2>
MD-III	0.47|±7/2>+0.05|±5/2>
MD-IV	0.89|±9/2>+0.09|±3/2>
MD-V	0.41|±9/2>+0.23|±5/2>+0.14|±7/2>
MD-VI	0.93|±9/2>+0.04|±3/2>

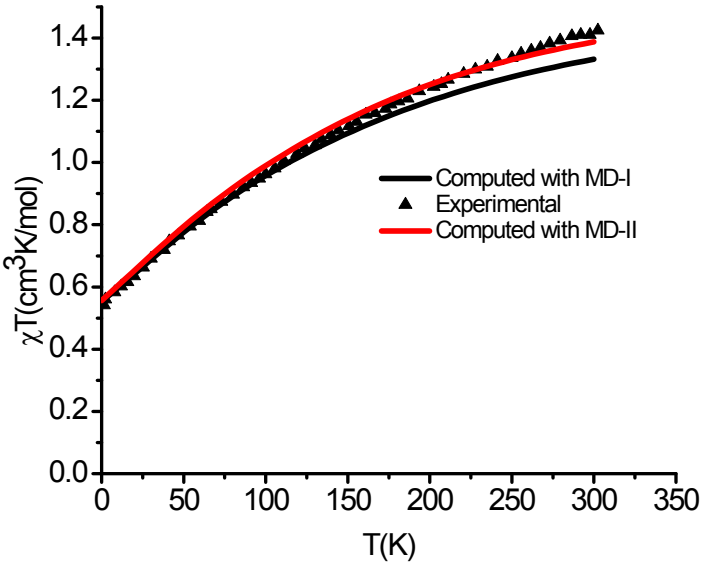


Figure S5. Comparison of the magnetic susceptibility computed for complex **2** using CAS(3,8) active space.

Table S12. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of complex **2** using MD-II.

States	Energy	g_x	g_y	g_z
KD1	0.0	2.725	2.699	1.756
KD2	169.2	0.006	0.020	2.882
KD3	329.2	3.513	3.475	0.732
KD4	478.6	3.055	2.759	0.359
KD5	499.0	0.107	0.158	1.372

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Table S13. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of the model complex using MD-II.

States	Energy	g_x	g_y	g_z
KD1	0.0	2.212	1.946	0.250
KD2	372.9	0.036	0.184	2.444
KD3	1266.9	3.236	1.997	0.328
KD4	1319.2	0.174	0.924	4.134
KD5	1523.9	2.941	2.196	1.126

Magneto-structural correlation

Table S14. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at *r* = 2.46 Å.

States	Energy	g_x	g_y	g_z
KD1	0.0	2.522	2.339	0.016
KD2	17.1	0.035	0.083	4.487
KD3	172.2	2.615	2.530	1.386
KD4	262.3	0.007	0.063	1.150
KD5	341.3	3.122	3.059	0.736

Table S15. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at *r* = 2.56 Å.

States	Energy	g_x	g_y	g_z
KD1	0.0	2.678	2.617	1.132
KD2	46.9	0.021	0.021	4.074
KD3	213.2	3.039	3.013	0.500
KD4	281.3	0.029	0.164	0.675
KD5	295.3	3.068	2.947	0.489

Table S16. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at *r* = 2.66 Å.

States	Energy	g_x	g_y	g_z
KD1	0.00	2.735	2.667	1.596
KD2	84.1	0.025	0.033	3.735
KD3	218.9	3.311	3.247	0.502
KD4	292.7	3.349	2.493	0.043
KD5	297.7	0.895	0.641	0.061

Table S17. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at *r* = 2.76 Å.

States	Energy	g_x	g_y	g_z

KD1	0.0	2.760	2.711	1.803
KD2	107.3	0.001	0.021	3.412
KD3	214.3	3.409	3.367	0.528
KD4	283.9	3.148	2.730	0.176
KD5	300.3	0.133	0.249	1.058

Table S18. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at *r* = 2.86 Å.

States	Energy	g_x	g_y	g_z
KD1	0.0	2.768	2.727	1.942
KD2	118.8	0.002	0.017	3.252
KD3	210.6	3.345	3.416	0.503
KD4	271.8	3.090	2.829	0.276
KD5	297.7	0.108	0.148	1.270

Table S19. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at θ = 63°.

States	Energy	g_x	g_y	g_z
KD1	0.0	1.743	1.824	2.178
KD2	33.7	0.039	0.064	1.267
KD3	243.1	3.462	3.444	0.648
KD4	451.2	0.007	0.035	5.382
KD5	626.4	1.935	1.955	3.704

Table S20. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at θ = 68°.

States	Energy	g_x	g_y	g_z
KD1	0.0	2.308	2.169	1.415
KD2	66.5	0.014	0.052	0.420
KD3	223.1	3.432	3.380	0.804
KD4	321.9	0.010	0.074	4.203
KD5	415.1	2.387	2.452	2.772

Table S21. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at θ = 73°.

States	Energy	g_x	g_y	g_z
KD1	0.00	2.735	2.667	1.596
KD2	84.1	0.025	0.033	3.735
KD3	218.9	3.311	3.247	0.502
KD4	292.7	3.349	2.493	0.043
KD5	297.7	0.895	0.641	0.061

Table S22. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at θ = 78°.

States	Energy	g_x	g_y	g_z
KD1	0.0	1.434	1.441	4.199
KD2	142.5	0.001	0.007	5.683
KD3	336.1	3.252	3.217	0.543
KD4	412.6	1.628	1.664	2.622
KD5	486.3	0.010	0.047	1.717

Table S23. Calculated KDs energies (cm^{-1}) along with g factors of the uranium centre of **1** using MD-II at θ = 83°.

States	Energy	g_x	g_y	g_z

KD1	0.0	0.690	0.702	4.557
KD2	233.9	0.003	0.012	6.137
KD3	468.8	3.415	3.322	0.866
KD4	668.6	0.753	0.797	3.316
KD5	734.3	0.034	0.074	2.192

Table S24. Deviation from the ideal trigonal prismatic geometry with ligand bite angle for complex **1** using CShM measurements.

Angle(°)	Deviation from trigonal prism geometry
63	2.608
68	1.458
73	0.678
78	0.275
83	0.252