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Supporting Information

Magnetic Relaxation in Single-Electron Single-Ion Cerium(III) Magnets: Insights from Ab Initio Calculations

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Supplementary Information

Computational Details:

Table S1. Contractions of the employed ANO-RCC basis sets at three different basis set levels.

Basis Sets	Small (BS1)	Medium (BS2)	Large (BS3)
Elements	(931 basis functions)	(1010 basis functions)	(1255basis functions)
Ce	7s6p4d2f1g	8s7p5d3f2g1h	8s7p5d3f2g1h
Zn	5s4p2d1f	5s4p2d	5s4p2d1f
I	6s5p2d	6s5p2d	6s5p2d
C	3s2p1d (close atoms) 3s2p (distant atoms)	3s2p	3s2p1d (close atoms) 3s2p (distant atoms)
N	3s2p	4s3p2d	3s2p
O	3s2p1d	4s3p2d	4s3p2d1f
H	2s	2s	2s

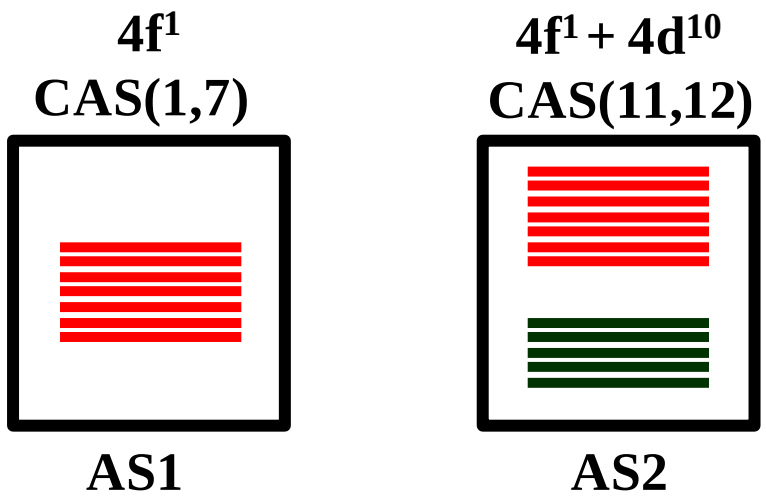

Figure S1. Pictorial Scheme of two different active spaces considered in the computational approximations. AS1: CAS(1,7) one electron in the seven active 4f based orbitals; AS2: CAS(11,12) Eleven active electrons in 12 active orbitals.

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Table S2. CASSCF+RASSI computed spin-orbit states of complex **1** at three different levels of basis sets with two different levels of active spaces.

AS1			AS2		
BS1	BS2	BS3	BS1	BS2	BS3
0.000	0.000	0.000	0.000	--//--	0.000
175.835	179.575	196.916	179.027		202.505
487.196	488.325	527.562	490.362		518.562
2326.713	488.325	2329.809	2683.560		2716.751
2477.312	2485.755	2485.740	2824.001		2866.708
2714.523	2711.089	2747.628	3061.877		3112.500
3107.786	3107.852	3145.089	3424.311		3471.357
Main values of the g-tensor in the ground doublet state					
0.3769 0.5275 4.0530	0.3311 0.4826 4.0631	0.3484 0.5021 4.0661	0.4108 0.5315 4.0943		0.3370 0.4560 4.1256

Table S3. CASSCF+RASSI calculated energies of the low-lying spin-orbit Kramers doublets (cm^{-1}) along with main values of g-tensors in the ground state doublet of Complex **1** with experimental geometry + 4 layers of point charges.

AS1		AS2	
BS1	BS3	BS1	BS3
0.000	0.000	0.000	0.000
175.835	196.916	179.027	202.505
487.196	527.562	490.362	518.562
2326.713	2329.809	2683.560	2716.751
2477.312	2485.740	2824.001	2866.708
2714.523	2747.628	3061.877	3112.500
3107.786	3145.089	3424.311	3471.357
Main values of the g-tensor in the ground doublet state			
0.3802 0.5250 4.0571	0.3344 0.4827 4.0767	0.3958 0.5136 4.1021	0.3121 0.4284 4.1357

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Table S4. SINGLE_ANISO computed crystal field parameters of Complex **1** along with experimental geometry + 4 layers of point charges on Complex **1**.

		Active Space 1					
		Experimental geometry			Experimental geometry + 4 layers of point charges		
		BS1	BS2	BS3	BS1	BS2	BS3
k	q	B_k^q	B_k^q	B_k^q	B_k^q	--//--	B_k^q
2	-2	0.317597265E+00	-0.548361240E+00	0.492680366E+00	-0.574443444E+00	---	-0.738863071E+00
	-1	-0.715490575E+01	-0.670657303E+01	-0.715688972E+01	-0.735184253E+01		-0.689295833E+01
	0	**-0.233590790E+02**	**-0.236424373E+02**	**-0.252802021E+02**	**-0.235596098E+02**		**-0.258282897E+02**
	1	**-0.148869978E+02**	**-0.147599115E+02**	**-0.145201156E+02**	**-0.140408783E+02**		**-0.138047932E+02**
	2	0.615801854E+01	0.758359214E+01	0.673858796E+01	0.758847625E+01		0.835061700E+01
4	-4	-0.567279831E+00	-0.505845098E+00	-0.581997060E+00	-0.202159751E+00	---	-0.350510951E+00
	-3	-0.665558391E+00	-0.823610300E+00	-0.554639714E+00	0.138080769E+00		-0.190497699E-01
	-2	-0.126097365E+00	0.703650691E-02	-0.339339472E+00	-0.317833443E+00		-0.511187332E+00
	-1	**0.176850578E+01**	**0.171352523E+01**	**0.188850957E+01**	**0.202049253E+01**		**0.204116945E+01**
	0	0.295304691E+00	0.298831514E+00	0.320925379E+00	0.319205168E+00		0.355569445E+00
	1	**0.265528808E+01**	**0.264565418E+01**	**0.253894240E+01**	**0.246433632E+01**		**0.238135636E+01**
	2	-0.691252976E+00	-0.785871898E+00	-0.666282650E+00	-0.661457854E+00		-0.622370167E+00
	3	**0.265802267E+01**	**0.278828679E+01**	**0.262491409E+01**	**0.248727377E+01**		**0.247071180E+01**
	4	0.744480751E+00	0.708274010E+00	0.751762401E+00	0.938403908E+00		0.882870254E+00

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		Active Space 2			
		Experimental geometry		Experimental geometry + 4 layers of point charges	
		BS1	BS3	BS1	BS3
k	q	B_k^q	B_k^q	B_k^q	B_k^q
2	-2	-0.608598696E+00	0.152063727E+00	-0.130504424E+01	-0.957844402E+00
	-1	-0.418211744E+01	-0.289448083E+01	-0.467119683E+01	-0.305155293E+01
	0	**-0.239025181E+02**	**-0.252926798E+02**	**-0.240939470E+02**	**-0.258173877E+02**
	1	**-0.134742803E+02**	**-0.141439297E+02**	**-0.128307268E+02**	**-0.138653749E+02**
	2	0.679543859E+01	0.707432272E+01	0.806649711E+01	0.854728389E+01
4	-4	-0.855624085E+00	-0.736992224E+00	-0.596120213E+00	-0.543608989E+00
	-3	-0.625957348E+00	-0.297656357E+00	-0.308342172E-01	0.131817651E-01
	-2	-0.313202999E+00	-0.456284843E+00	-0.485857120E+00	-0.580029460E+00
	-1	**0.125340924E+01**	**0.111230138E+01**	**0.148682426E+01**	**0.125945545E+01**
	0	0.345758006E+00	0.326668589E+00	0.367704818E+00	0.355381820E+00
	1	**0.237827644E+01**	**0.234326121E+01**	**0.222227216E+01**	**0.223888470E+01**
	2	-0.711679823E+00	-0.597372679E+00	-0.647994802E+00	-0.547048008E+00
	3	**0.182570316E+01**	**0.146145446E+01**	**0.176116152E+01**	**0.133064877E+01**
	4	0.361159721E+00	0.468794359E+00	0.708540509E+00	0.663154897E+00

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Table S5. CASSCF computed Mulliken charges on complex **1.**

		CASSCF charges	Atoms		CASSCF charges	Atoms		CASSCF charges
1	Ce	2.5192	47	C	-0.1558	93	C	0.0861
2	Zn	1.4207	48	H	0.1532	94	H	0.1344
3	I	-0.7657	49	C	-0.1449	95	C	-0.1017
4	Zn	1.4195	50	H	0.1568	96	C	-0.1204
5	I	-0.756	51	C	0.1644	97	H	0.1481
6	O	-0.4601	52	C	0.2565	98	C	-0.1617
7	O	-0.8927	53	C	-0.1465	99	H	0.1531
8	O	-0.91	54	H	0.1358	100	C	-0.1546
9	O	-0.4729	55	H	0.1649	101	H	0.1515
10	N	-0.3974	56	H	0.1511	102	C	0.1517
11	N	-0.3886	57	O	-0.47	103	C	0.27
12	C	-0.144	58	O	-0.8994	104	C	-0.1491
13	H	0.1377	59	O	-0.89	105	H	0.1487
14	H	0.1567	60	O	-0.4636	106	H	0.1526
15	H	0.1414	61	N	-0.3915	107	H	0.1393
16	C	0.1624	62	N	-0.3839	108	O	-0.6413
17	C	-0.1533	63	C	-0.1443	109	H	0.3657
18	H	0.1512	64	H	0.1335	110	C	-0.1413
19	C	-0.163	65	H	0.1612	111	H	0.1332
20	H	0.1518	66	H	0.1571	112	H	0.146
21	C	-0.1207	67	C	0.1598	113	H	0.1695
22	H	0.1475	68	C	-0.1444			
23	C	-0.1016	69	H	0.159			
24	C	0.2774	70	C	-0.1596			
25	C	0.0939	71	H	0.1536			
26	H	0.1334	72	C	-0.1227			
27	C	-0.1378	73	H	0.1475			
28	H	0.1173	74	C	-0.107			
29	H	0.1467	75	C	0.263			
30	C	0.0819	76	C	0.0909			
31	C	-0.406	77	H	0.1323			
32	H	0.1241	78	C	-0.1372			
33	H	0.1313	79	H	0.1467			
34	H	0.1341	80	H	0.1175			
35	C	-0.4023	81	C	0.0787			
36	H	0.1379	82	C	-0.4077			
37	H	0.1367	83	H	0.1298			
38	H	0.1373	84	H	0.1319			
39	C	-0.1386	85	H	0.1349			
40	H	0.143	86	C	-0.4029			
41	H	0.1209	87	H	0.1377			
42	C	0.0935	88	H	0.1368			
43	H	0.1324	89	H	0.1366			
44	C	-0.095	90	C	-0.1378			
45	C	-0.1212	91	H	0.1178			
46	H	0.1487	92	H	0.1485			

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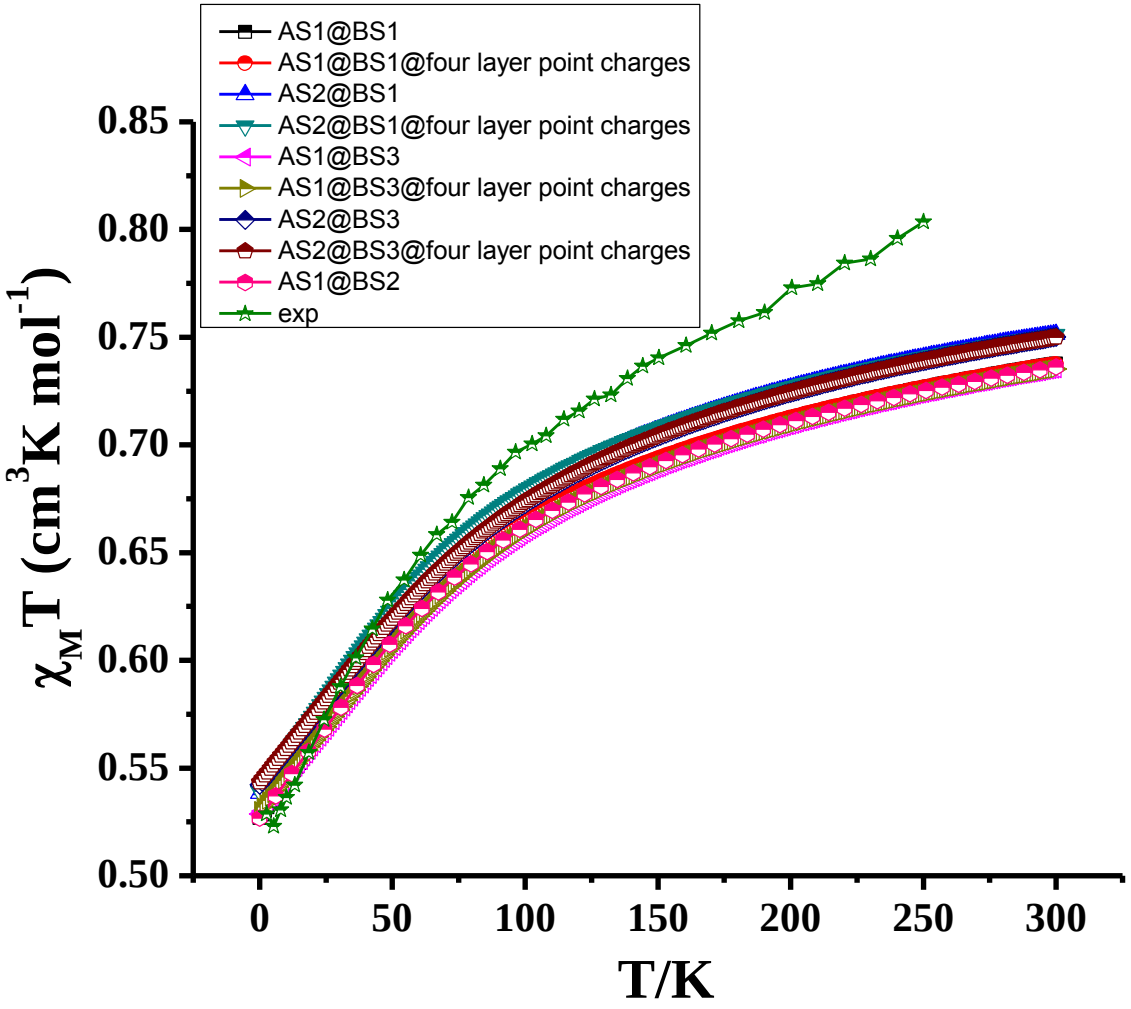

Figure S2. Experimental and *ab initio* computed molar magnetic susceptibility plots for complex **1**. Note the intermolecular interaction *zJ'* is taken as zero in these calculations.

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Table S6. Composition of wave functions of the ground J=5/2 of $Ce^{3+}$for complex **1** as derived from SINGLE_ANISO calculations with BS3 basis set and AS2 active space.

w.f.	m_J	c_i	
		real	*imag*
1	-2.5	-0.868821	-0.483320
	-1.5	-0.022973	0.024213
	-0.5	0.026279	-0.017753
	0.5	0.013990	0.019781
	1.5	0.091157	-0.022585
	2.5	-0.005071	0.000000
2	-2.5	-0.004431	-0.002465
	-1.5	-0.068681	-0.064052
	-0.5	0.021842	-0.010485
	0.5	-0.014335	-0.028289
	1.5	-0.008305	-0.032327
	2.5	0.994207	0.000000
3	-2.5	-0.012749	-0.075703
	-1.5	0.530245	0.403851
	-0.5	0.196256	0.191187
	0.5	0.095972	-0.070212
	1.5	-0.593688	-0.325953
	2.5	0.043937	-0.000000
4	-2.5	-0.007297	-0.043327
	-1.5	-0.420023	-0.531312
	-0.5	0.053299	-0.106300
	0.5	0.221125	0.161779
	1.5	-0.486303	-0.455813
	2.5	-0.076769	0.000000
5	-2.5	-0.000000	-0.000000
	-1.5	0.207479	0.086629
	-0.5	-0.429147	-0.102320
	0.5	0.445061	0.718667
	1.5	-0.041570	0.186599
	2.5	0.060849	0.000000
6	-2.5	-0.005100	-0.060635
	-1.5	0.182458	-0.057065
	-0.5	-0.753443	-0.383256
	0.5	-0.137931	-0.419061
	1.5	-0.103716	-0.199488
	2.5	-0.000000	0.000000

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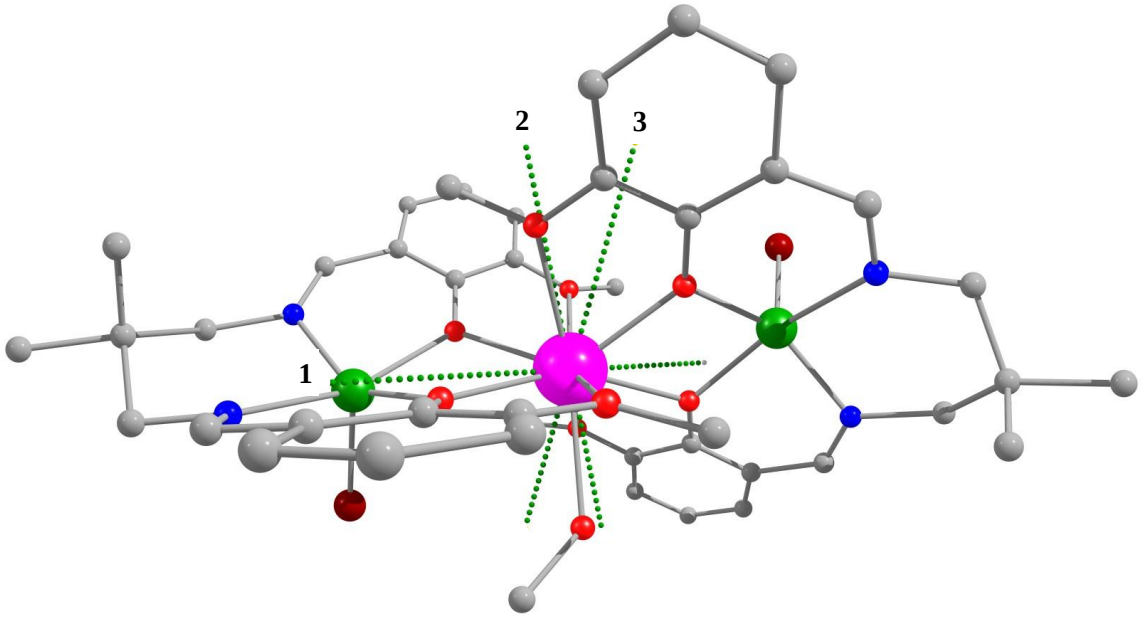

Figure S3. SINGLE_ANISO computed orientation of principal magnetization axes (g_{zz}) of all three low-lying KDs of complex **1**. Colour Code.: Pink, Ce; green, Zn; red, O; blue, N; brown, Br; grey; C. Hydrogens are omitted for clarity

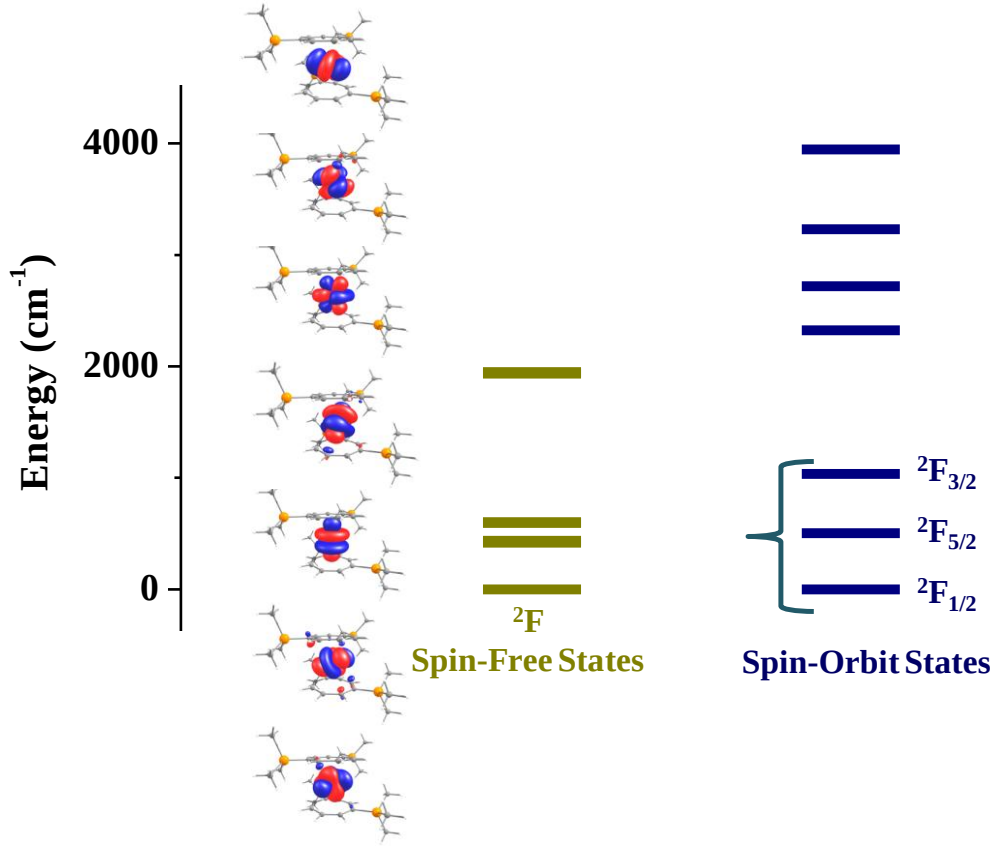

Figure S4. CASSCF+RASSI computed spin-free states and spin-orbit states of complex **2** along with CASSCF computed 4f orbitals.

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Table S7.CASSCF+RASSI computed energies of all low-lying KDs for complex **2** using BS2 and AS1 approach. SINGLE_ANISO computed g-tensors and relative energies of three low lying Kramers doublets for complex **2** along with the deviation from the principal magnetization axes of first KD.

Energies(cm^{-1})	g_{xx}	g_{yy}	g_{zz}	θ
0.000	2.4327	2.4327	1.0332	~
503.045	0.0023	0.0114	4.1160	0.982
1036.663	0.0328	0.0402	3.2097	1.322
2324.597				
2720.540				
3230.534				
3947.578				

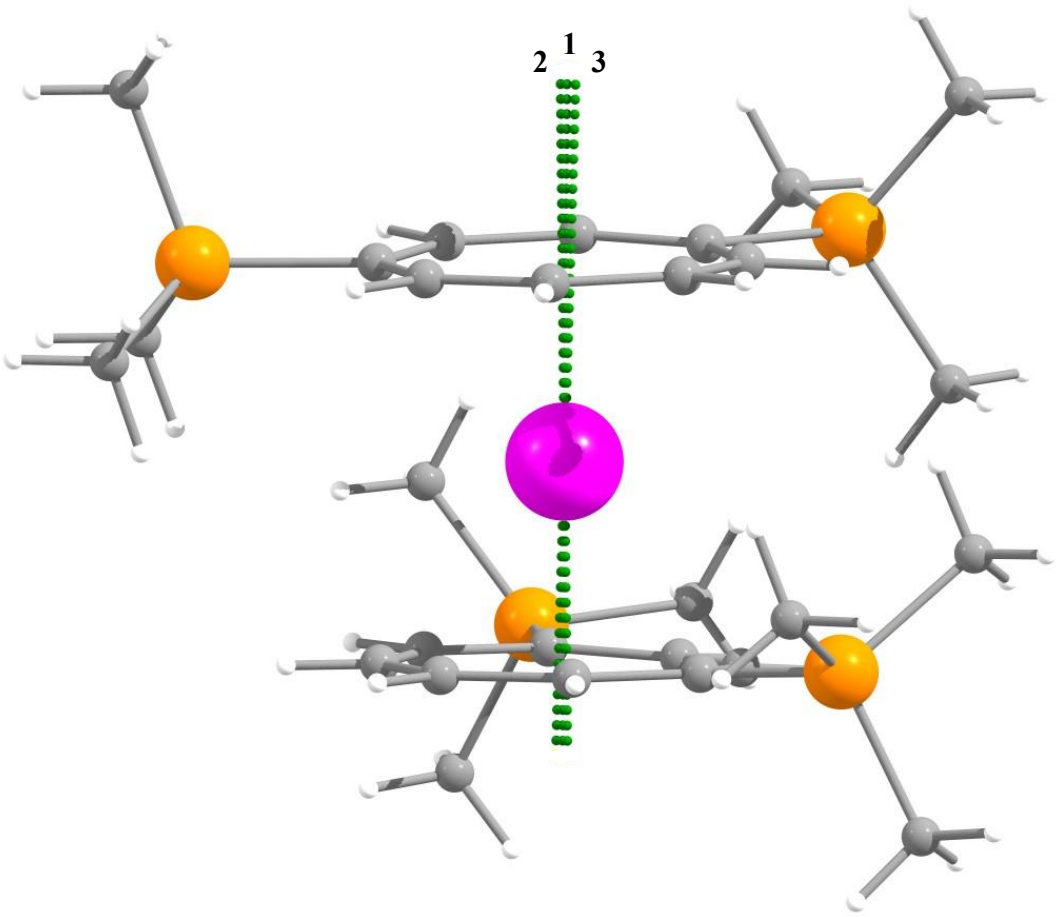

Figure S5. SINGLE_ANISO computed orientation of principal magnetization axes (g_{zz}) of all three low-lying KDs of complex **2**. Color Code: Pink, Ce; orange, Si; grey. C; white, H.

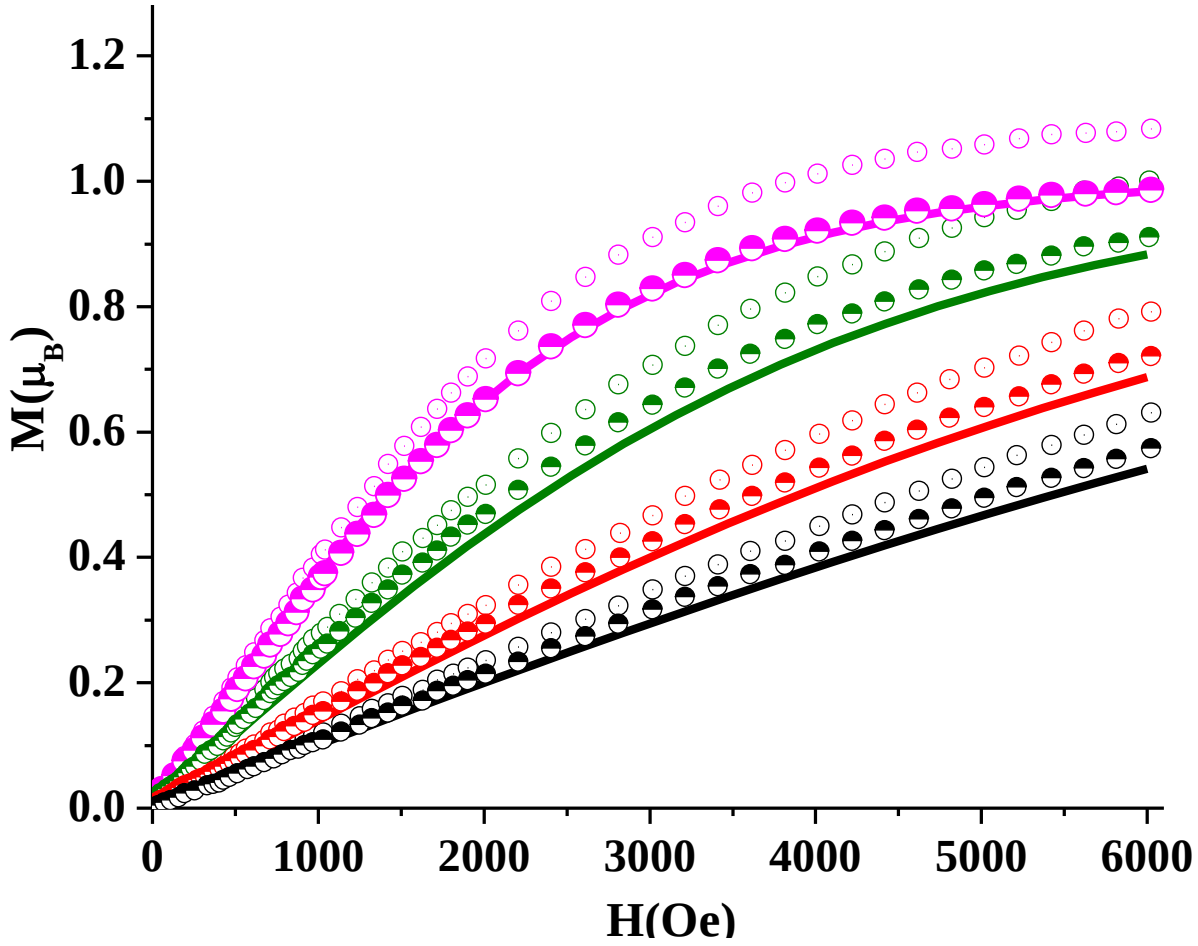

Figure S6. SINGLE_ANISO computed molar magnetization data for complex **2**. The circles here represents the experimental points, solid lines are the computed molar magnetization data, while half filled circles are the experimental points scaled by a factor of 0.91. The color code comprises: Pink for data at 1.8K, green for 3.0K, red for 5.0K and black for 7.0K.

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Table S8. Composition of wave functions of the ground J=5/2 of $Ce^{3+}$for complex **2** as derived from SINGLE_ANISO calculations using BS2 basis set and AS1 active space.

w.f.	m_J	c_i	
		real	*imag*
1	-2.5	0.000000	0.000000
	-1.5	0.000520	-0.004457
	-0.5	0.748804	-0.066139
	0.5	0.349675	-0.559044
	1.5	0.007414	-0.002684
	2.5	0.005757	0.000000
2	-2.5	0.004068	-0.004073
	-1.5	-0.007139	0.003349
	-0.5	0.642648	0.147670
	0.5	-0.575969	0.483054
	1.5	0.002786	0.003518
	2.5	0.000000	0.000000
3	-2.5	-0.305431	0.951920
	-1.5	0.006750	-0.021892
	-0.5	0.003697	-0.001023
	0.5	-0.001744	0.004163
	1.5	0.000796	-0.000316
	2.5	0.000000	0.000000
4	-2.5	0.000000	0.000000
	-1.5	-0.000544	0.000661
	-0.5	-0.004497	0.000389
	0.5	-0.002104	0.003208
	1.5	0.022908	0.000261
	2.5	0.999720	0.000000
5	-2.5	0.000000	0.000000
	-1.5	0.023816	-0.027648
	-0.5	0.008032	-0.000355
	0.5	0.003935	0.000498
	1.5	-0.998973	-0.010685
	2.5	0.022968	0.000000
6	-2.5	0.000989	0.022946
	-1.5	0.053684	0.997586
	-0.5	0.000667	0.003910
	0.5	0.000008	-0.008040
	1.5	-0.026597	0.024985
	2.5	0.000000	0.000000

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Table S9. SINGLE_ANISO computed crystal field parameters of Complex **2** using BS2 basis set and AS1 active space.

k	q	B_k^q
2	-2	-0.234504E+00
	-1	-0.822842E-01
	0	**0.176172E+02**
	1	0.478948E+01
	2	-0.136369E+01
4	-4	0.121472E-01
	-3	0.197318E-01
	-2	-0.310444E-01
	-1	0.453246E-02
	0	**-0.310164E+01**
	1	0.115914E+00
	2	0.117634E+00
	3	0.117634E+00
	4	0.109341E-01

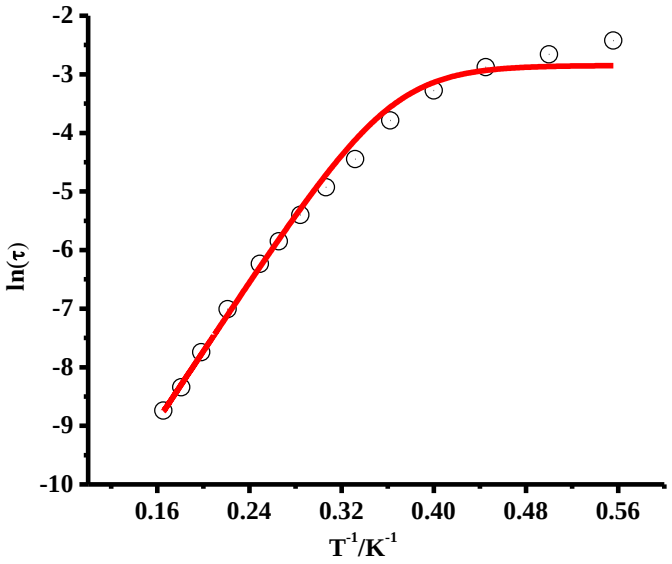

Figure S7. Fitting the relaxation time of the magnetization ln(τ) vs. T^{-1} for complex **2**. (Nonlinear Arrhenius plot using ac data) under 400 Oe applied field. The black hollow circles here are the extracted data from experimental plot. The solid lines here correspond to Arrhenius non-linear fit.

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Table S10. SINGLE_ANISO computed g-tensors and relative energies of three low lying Kramers doublets along with the deviation from the principal magnetization axes of first KD for all the model complexes ranging from C.N. 1 to C.N. 12.

C.N.1 $C_{\infty v}$ $[Ce(OH)]^{2+}$					**C.N.7** D_{5h} $[Ce(OH)_7]^{4-}$				
KDs	g_{xx}	g_{yy}	g_{zz}	*Angle*					
0	0.441	0.643	3.96	0	0	0.0263	0.0340	2.4297	0
472.377	2.029	1.772	1.283	88.283	440.206	2.5733	2.5091	0.6978	0
1257.853	0.361	0.589	4.282	90.035	648.392	0.0095	0.0116	4.5085	0
C.N.2 $D_{\infty h}$ $[Ce(OH)_2]^{+}$					**C.N.8** D_{4d} $[Ce(OH)_8]^{5-}$				
0	0.0004	0.0013	4.1268	0	0	2.409	2.3794	0.9586	0
472.377	0.0001	0.0003	2.2151	0	327.947	0.0005	0.0030	4.1343	0.759
2247.455	0.0001	0.0001	8.0023	0	485.205	0.0091	0.0235	2.7335	1.178
C.N.3 D_{3h} $[Ce(OH)_3]$					**C.N.9** D_{3h} $[Ce(OH)_9]^{6-}$				
0	2.5266	2.5239	0.8935	0	0	2.0022	2.0022	2.0023	0
310.553	0.0002	0.0031	2.6837	0	3457.997	0.3067	0.3633	1.0629	92.853
1488.150	0.0026	0.0043	4.7815	0	3843.521	0.7380	1.2637	3.2449	141.342
C.N.4 D_{4h} $[Ce(OH)_4]^{-}$					**C.N.10** D_{3h} $[Ce(OH)_{10}]^{7-}$				
0	2.4966	2.4898	0.8771	0	0	1.1442	1.2190	1.4758	0
347.320	0.8305	0.8384	2.1477	0	158.902	1.4728	1.4740	2.4968	86.179
2080.849	0.4953	0.4958	4.4101	0	1305.981	1.0824	1.4461	1.9901	89.392
C.N.5 C_{4v} $[Ce(OH)_5]^{2-}$					**C.N.11** D_{3h} $[Ce(OH)_{11}]^{8-}$				
0	2.5897	2.3694	0.8457	0	0	0.5553	0.9662	3.2700	0
28.989	0.7698	0.9912	1.8508	0.343	359.838	1.0501	1.2501	2.3359	79.624
1345.344	0.6225	0.6233	3.9071	0.232	1065.301	0.2971	0.4857	3.8701	98.629
C.N.5 D_{3h} $[Ce(OH)_5]^{2-}$					**C.N.12** D_{3h} $[Ce(OH)_{12}]^{9-}$				
0	0.0063	0.0143	2.3309	0	0	2.0023	2.0023	2.0032	0
57.513	0.0501	0.0684	4.2647	0	4432.760	2.0021	2.0022	2.0026	72.732
864.338	2.5358	2.5283	0.6010	0	9621.859	2.0012	2.0008	1.9877	89.593
C.N.6O_h: $[Ce(OH)_6]^{3-}$									
0	0.6683	1.1425	1.7011	0					
576.842	1.3702	1.5112	2.6374	97.201					
1548.189	0.0493	0.0901	0.5229	69.813					

Supplementary Information

Table S11.CASSCF+RASSI vs. CASPT2+RASSI computed energies of all low-lying KDs for complex **2-red** using BS2 and AS1 approach.

		CASSCF+RASSI	*CASPT2+RASSI*
		(cm^{-1})	*(cm^{-1})*
		0.000	0.000
		0.000	0.000
		597.830	596.825
		597.830	596.825
		1081.282	1141.371
		1081.282	1141.371
		2323.596	2321.834
		2323.596	2321.834
		2814.977	2800.397
		2814.977	2800.397
		3295.838	3434.010
		3295.838	3434.010
		4047.246	4256.490
		4047.246	4256.490
		Main values of the *g* tensor	
KD1	g_X	2.432	2.447
	g_Y	2.339	2.370
	g_Z	1.042	1.022
KD2	g_X	0.002	0.000
	g_Y	0.006	0.007
	g_Z	4.116	4.101
KD3	g_X	0.045	0.036
	g_Y	0.048	0.037
	g_Z	3.249	3.349

The structure of the **2-red** compound is obtained from **2** by replacing all $Si(CH_3)_3$ groups by H at 1.0 Angstrom C-H distance. **2-red** corresponds to the $[Ce(COT)_2]^-$ anion. No artificial symmetrization to higher point group symmetry of the **2-red** was enforced. No optimization of the geometry was done as well.

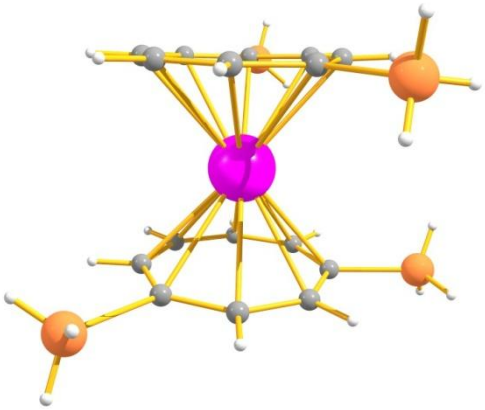

Figure S8.Pictorial representation of complex **2-red**.