

Multiconfigurational electronic structure calculations explain the role of ligands in g-tensor anisotropy for Ru^{III} complexes

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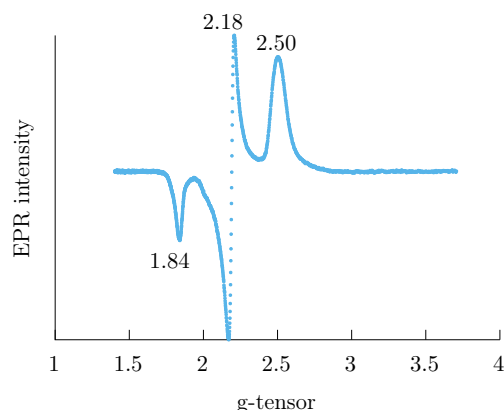


FIG. S1: EPR spectrum of $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH})]^{2+}$.

TABLE S1: Bond lengths (Å) in $[\text{Ru}^{\text{III}}(\text{bpy})(\text{EtO-tpy})\text{H}_2\text{O}]^{3+}$ and $[\text{Ru}^{\text{III}}(\text{EtO-tpy})(\text{pic})_2\text{H}_2\text{O}]^{3+}$.

$[\text{Ru}^{\text{III}}(\text{bpy})(\text{EtO-tpy})\text{H}_2\text{O}]^{3+}$	CASSCF	$[\text{Ru}^{\text{III}}(\text{EtO-tpy})(\text{pic})_2\text{H}_2\text{O}]^{3+}$	CASSCF
Ru–O1	2.227	Ru–O1	2.249
Ru–N1 (tpy)	2.128	Ru–N1 (tpy)	1.961
Ru–N2 (tpy)	2.034	Ru–N2 (tpy)	2.158
Ru–N3 (tpy)	2.131	Ru–N3 (tpy)	2.153
Ru–N4 (bpy)	2.084	Ru–N4 (pic)	2.160
Ru–N5 (bpy)	2.126	Ru–N5 (pic)	2.152

TABLE S2: Bond lengths (Å) in $[\text{Ru}^{\text{III}}(\text{tpy})(\text{Qc})\text{H}_2\text{O}]^{2+}$ and $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy-NO})]^{3+}$.

$[\text{Ru}^{\text{III}}(\text{tpy})(\text{Qc})\text{H}_2\text{O}]^{2+}$	CASSCF	$[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy-NO})]^{3+}$	CASSCF
Ru–O1 (Qc)	1.911	Ru–O1	1.998
Ru–O2 (H ₂ O)	2.214	Ru–N1 (bpy)	2.146
Ru–N1 (tpy)	2.020	Ru–N2 (bpy)	2.127
Ru–N2 (tpy)	2.138	Ru–N3 (Obpy)	2.185
Ru–N3 (tpy)	2.156	Ru–N4 (bpy)	2.101
Ru–N4 (Qc)	2.171	Ru–N5 (bpy)	2.128

TABLE S3: Bond lengths (Å) in hypothetical N-oxide intermediates $[\text{Ru}^{\text{III}}(\text{pic})_2(\text{dpp-NO})]^{3+}$ and $[\text{Ru}^{\text{III}}(\text{pic})_2(\text{dpp-NO,NO})]^{3+}$.

$[\text{Ru}^{\text{III}}(\text{pic})_2(\text{dpp-NO})]^{3+}$	CASSCF	$[\text{Ru}^{\text{III}}(\text{pic})_2(\text{dpp-NO,NO})]^{3+}$	CASSCF
Ru–O	2.029	Ru–O1	2.022
Ru–N1 (dpp)	2.083	Ru–O2	2.022
Ru–N2 (dpp)	2.033	Ru–N3 (dpp)	2.077
Ru–N3 (dpp)	2.213	Ru–N4 (dpp)	2.077
Ru–N4 (pic)	2.189	Ru–N5 (bpy)	2.157
Ru–N5 (pic)	2.154	Ru–N5 (bpy)	2.157

TABLE S4: Convergence of the g-matrix components evaluated for $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}$ at the SA-CASSCF structure with SA-CASSCF(9e,7o)/cc-pVTZ(C,N,O),cc-pVDZ(H),ANO-RCC-VTZP(Ru) with respect to the number of interacting states within only doublets (d) and doublets and quartets (d,q). The same orbitals are used in all calculations in the table.

	d				d+q		
2d	1.611	1.612	3.433				
3d	1.177	2.291	3.345				
4d	1.201	2.333	3.339				
5d	1.145	2.336	3.347				
6d	1.135	2.346	3.342				
7d	1.133	2.271	3.353				
8d	1.120	2.286	3.284				
9d	1.128	2.292	3.287				
10d	1.128	2.293	3.290				
11d	1.125	2.271	3.290	11d1q	1.137	2.323	3.249
12d	1.124	2.271	3.290	11d2q	1.098	2.283	3.301
13d	1.124	2.269	3.290	11d3q	1.065	2.257	3.337
14d	1.127	2.265	3.286	11d4q	1.081	2.266	3.324
15d	1.121	2.277	3.288	11d5q	1.073	2.275	3.321
16d	1.121	2.274	3.282	11d6q	1.082	2.275	3.317
17d	1.121	2.278	3.281	11d7q	1.083	2.276	3.317
18d	1.120	2.280	3.291	11d8q	1.083	2.275	3.318
19d	1.120	2.292	3.289				
20d	1.119	2.279	3.288				

TABLE S5: Convergence of the g-matrix components evaluated for $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}$ at the SA-CASSCF structure with SA-CASSCF(9e,7o)/cc-pVTZ(C,N,O),cc-pVDZ(H),ANO-RCC-VTZP(Ru) with NEVPT2 energies with respect to the number of interacting states within only doublets (d) and doublets and quartets (d,q). The same orbitals are used in all calculations in the table.

	d				d+q		
2d	1.702	1.702	3.271				
3d	1.381	2.292	3.229				
4d	1.402	2.336	3.224				
5d	1.349	2.338	3.234				
6d	1.336	2.345	3.226				
7d	1.335	2.274	3.238				
8d	1.321	2.287	3.172				
9d	1.328	2.293	3.174				
10d	1.328	2.294	3.176				
11d	1.327	2.274	3.177	11d1q	1.333	2.308	3.150
12d	1.326	2.274	3.174	11d2q	1.307	2.282	3.191
13d	1.327	2.271	3.174	11d3q	1.285	2.265	3.221
14d	1.329	2.266	3.170	11d4q	1.297	2.272	3.209
15d	1.323	2.279	3.172	11d5q	1.291	2.279	3.207
16d	1.322	2.276	3.165	11d6q	1.298	2.278	3.203
17d	1.322	2.280	3.164	11d7q	1.299	2.279	3.203
18d	1.321	2.281	3.176	11d8q	1.299	2.278	3.203
19d	1.321	2.294	3.174				
20d	1.319	2.281	3.172				

TABLE S6: Convergence of the g-tensor components evaluated for $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}$ at the SA-CASSCF structure with QD-NEVPT2/cc-pVTZ(C,N,O),cc-pVDZ(H),ANO-RCC-VTZP(Ru) with respect to the number of interacting states within only doublets (d) and doublets and quartets (d,q). The same orbitals are used in all calculations in the table.

	d				d+q		
2d	1.702	1.702	3.271				
3d	1.385	2.294	3.218				
4d	1.408	2.348	3.212				
5d	1.354	2.348	3.232				
6d	1.335	2.355	3.227				
7d	1.334	2.284	3.237				
8d	1.321	2.259	3.172				
9d	1.315	1.525	2.793				
10d	1.328	2.307	3.167				
11d	1.323	2.285	3.199	11d1q	1.327	2.315	3.139
12d	1.305	2.280	3.162	11d2q	1.293	2.289	3.180
13d	1.324	2.276	3.154	11d3q	1.279	2.273	3.208
14d	1.326	2.272	3.146	11d4q	1.292	2.279	3.197
15d	1.336	2.275	3.139	11d5q	1.287	2.286	3.194
16d	1.332	2.266	3.129	11d6q	1.294	2.286	3.190
17d	1.341	2.264	3.125	11d7q	1.295	2.286	3.190
18d	1.344	2.265	3.125	11d8q	1.295	2.285	3.189
19d	1.344	2.265	3.123				
20d	1.342	2.264	3.123				

TABLE S7: Theoretical g-tensor components at different geometries compared with the experimental estimates. In all the cases, we used 20 doublet and 8 quartet states to evaluate components of the g-tensors from the effective Hamiltonians. Additional details and references are given in the main text.

	averaging over 3d2q			averaging over 3d			Exp
	CASSCF	CASSCF/ NEVPT2	NEVPT2	CASSCF	CASSCF/ NEVPT2	NEVPT2	
[Ru ^{III} (bpy)(tpy)Cl] ²⁺ , vac ^a	1.074	1.290	1.316	1.237	1.439	1.449	1.66
	2.286	2.287	2.271	2.193	2.202	2.214	2.25
	3.318	3.202	3.151	3.204	3.100	3.075	2.79
[Ru ^{III} (bpy)(tpy)Cl] ²⁺ , 2H ₂ O ^a	1.072	1.283	1.309	1.079	1.313	1.328	
	2.382	2.366	2.344	2.395	2.367	2.346	
	3.246	3.146	3.100	3.225	3.119	3.098	
[Ru ^{III} (bpy)(tpy)Cl] ²⁺ , 3H ₂ O ^a	1.067	1.282	1.307	1.056	1.298	1.315	
	2.411	2.405	2.382	2.421	2.404	2.382	
	3.226	3.116	3.073	3.218	3.102	3.076	
[Ru ^{III} (bpy)(tpy)Cl] ²⁺ , 2H ₂ O, DFT geom ^b	1.343	1.506	1.522	1.354	1.530	1.538	
	2.445	2.424	2.401	2.464	2.422	2.399	
	3.027	2.898	2.863	3.000	2.870	2.859	
[Ru ^{III} (bpy)(tpy)Cl] ²⁺ , DFT geom ^c	1.362	1.521	1.536	1.413	1.582	1.583	
	2.383	2.361	2.343	2.409	2.369	2.368	
	3.062	2.932	2.894	3.031	2.905	2.877	

^a SA-CASSCF(9e,7o) optimized geometries for the lowest doublet state without explicit water molecules. The explicit water molecules are optimized with r²SCAN with the frozen SA-CASSCF geometry of the complex.

^b B3LYP geometry with two explicit water molecules

^c Same B3LYP geometry of the complex as in ^c, but with removed explicit water

TABLE S8: Theoretical g-tensor components at different geometries and experimental estimates. We used 20 doublet and 8 quartet states to evaluate components of the g-tensors from the effective Hamiltonians in all cases unless explicitly specified.

	averaging over 3d2q			averaging over 3d			Exp
	CASSCF	CASSCF/ NEVPT2	NEVPT2	CASSCF	CASSCF/ NEVPT2	NEVPT2	
[Ru ^{III} (bpy)(tpy)OH] ²⁺ , vac ^a	1.718	1.826	1.827	1.769 ^b	1.881 ^b	1.878 ^b	1.84
	2.227	2.228	2.243	2.216	2.213	2.229	2.18
	2.798	2.575	2.528	2.727	2.496	2.492	2.50
[Ru ^{III} (bpy)(tpy)OH] ²⁺ , 2H ₂ O, DFT geom ^c	1.719	1.835	1.839	1.750	1.839	1.843	
	2.210	2.215	2.230	2.260	2.223	2.237	
	2.807	2.564	2.513	2.709	2.546	2.497	
[Ru ^{III} (bpy)(tpy)OH] ²⁺ , DFT geom ^d	1.734	1.838	1.839	1.723	1.852	1.855	
	2.236	2.231	2.245	2.267	2.240	2.252	
	2.741	2.524	2.481	2.779	2.532	2.490	
[Ru ^{III} (bpy)(tpy)H ₂ O] ³⁺ , vac ^a	1.007	1.025	1.051	1.241	1.264	1.154	1.66
	2.700	2.722	2.683	2.489	2.565	2.632	2.40
	3.037	3.002	2.968	2.973	2.896	2.974	2.60
[Ru ^{III} (bpy)(EtO- tpy)H ₂ O] ³⁺ , vac ^a	0.945	0.804	0.852	1.020	0.902	1.058	1.53
	2.413	2.336	2.362	2.262	2.223	2.413	2.33
	3.291	3.387	3.278	3.232	3.286	3.206	2.78

^a SA-CASSCF(9e,7o) optimized geometries for the lowest doublet state without explicit water molecules. The explicit water molecules are optimized with r²SCAN with the frozen SA-CASSCF geometry of the complex.

^b The QD-NEVPT2 effective Hamiltonian is reduced to 10 doublets and 2 quartets because of intruder state problems with larger effective Hamiltonians

^c B3LYP geometry with two explicit water molecules.

^d Same B3LYP geometry of the complex as in *c*, but with removed explicit water

TABLE S9: Theoretical g-tensor components at different geometries and experimental estimates. We used 20 doublet and 8 quartet states to evaluate components of the g-tensors from the effective Hamiltonians in all the cases. Additional details and references are given in the main text.

	averaging over 3d2q			averaging over 3d			
	CASSCF	CASSCF/ NEVPT2	NEVPT2	CASSCF	CASSCF/ NEVPT2	NEVPT2	Exp
trans- [Ru ^{III} (bpy) ₂ (H ₂ O) ₂] ³⁺ , vac ^a	1.537	1.655	1.667	1.555	1.700	1.703	1.88
	2.532	2.542	2.528	2.587	2.513	2.505	2.27
	2.877	2.672	2.638	2.832	2.652	2.646	2.38
trans- [Ru ^{III} (bpy) ₂ (H ₂ O) ₂] ³⁺ , vac, DFT geom ^b	1.530	1.650	1.662	1.555	1.700	1.703	
	2.549	2.533	2.548	2.587	2.513	2.505	
	2.847	2.675	2.609	2.832	2.652	2.646	
cis- [Ru ^{III} (bpy) ₂ (H ₂ O) ₂] ³⁺ , vac ^a	1.356	1.490	1.505	1.607	1.659	1.651	1.75
	2.539	2.522	2.503	2.434	2.429	2.425	2.40
	3.026	2.908	2.860	2.815	2.710	2.720	2.55
cis- [Ru ^{III} (bpy) ₂ (H ₂ O) ₂] ³⁺ , vac, DFT geom ^b	1.367	1.474	1.491	1.433	1.533	1.554	
	2.658	2.611	2.605	2.624	2.606	2.592	
	2.919	2.859	2.795	2.943	2.872	2.835	

^a SA-CASSCF(9e,7o) optimized geometries for the lowest doublet state without explicit water molecules.

^b M06-L geometry.

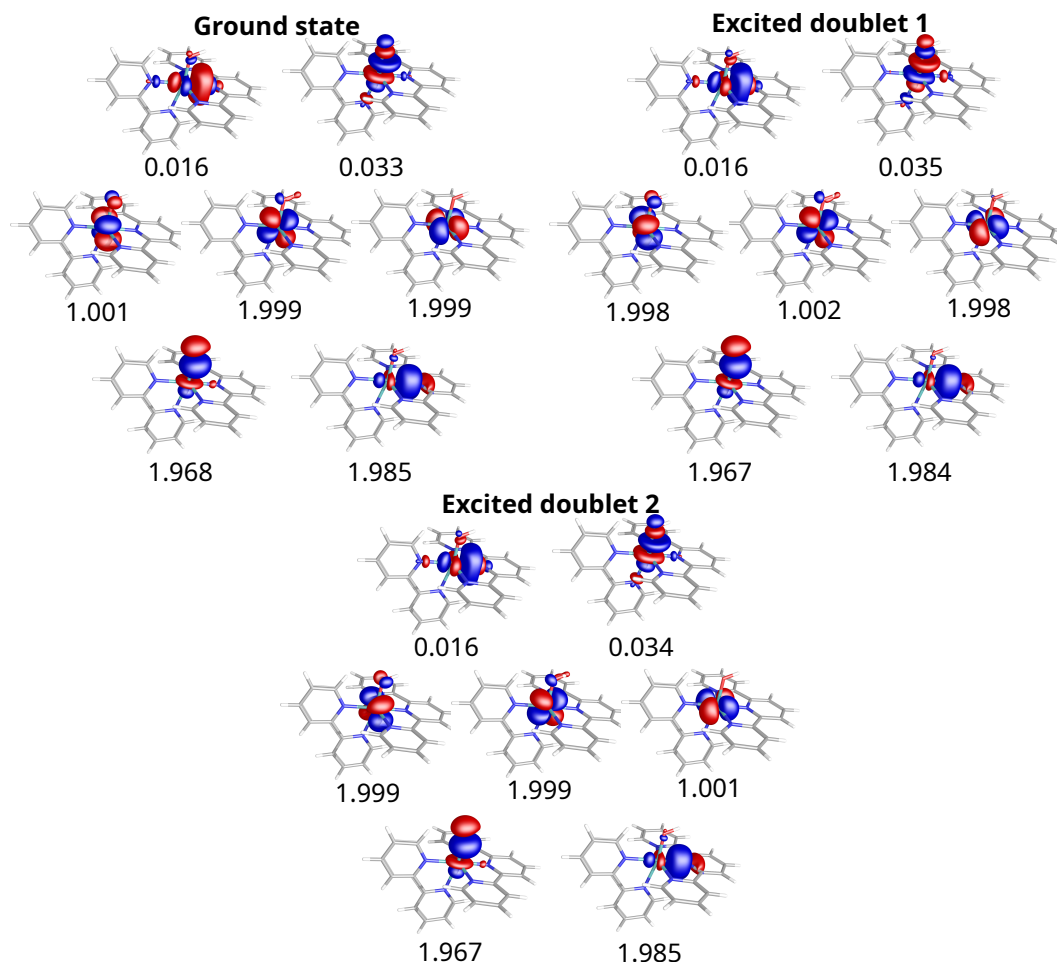


FIG. S2: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{OH}]^{2+}$. The occupations of every natural orbital are shown below the orbitals.

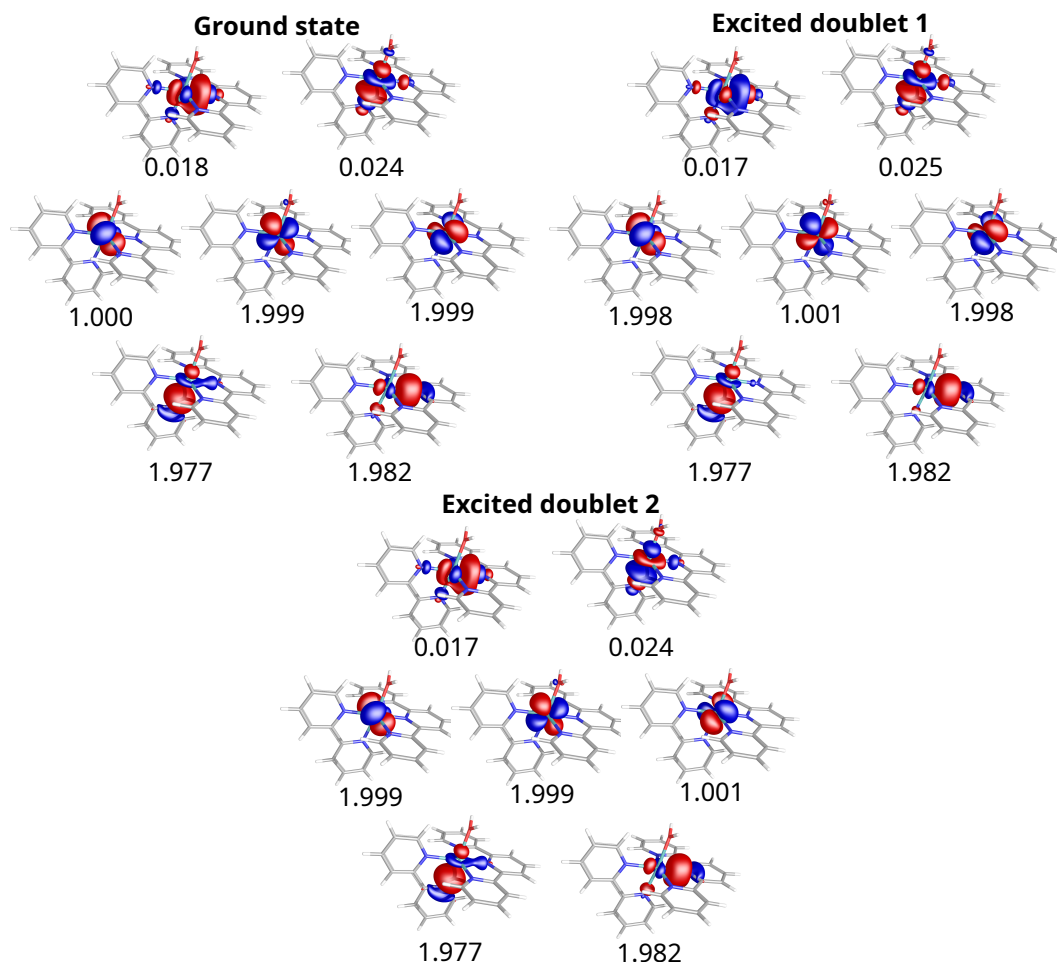


FIG. S3: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{bpy})(\text{tpy})\text{H}_2\text{O}]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

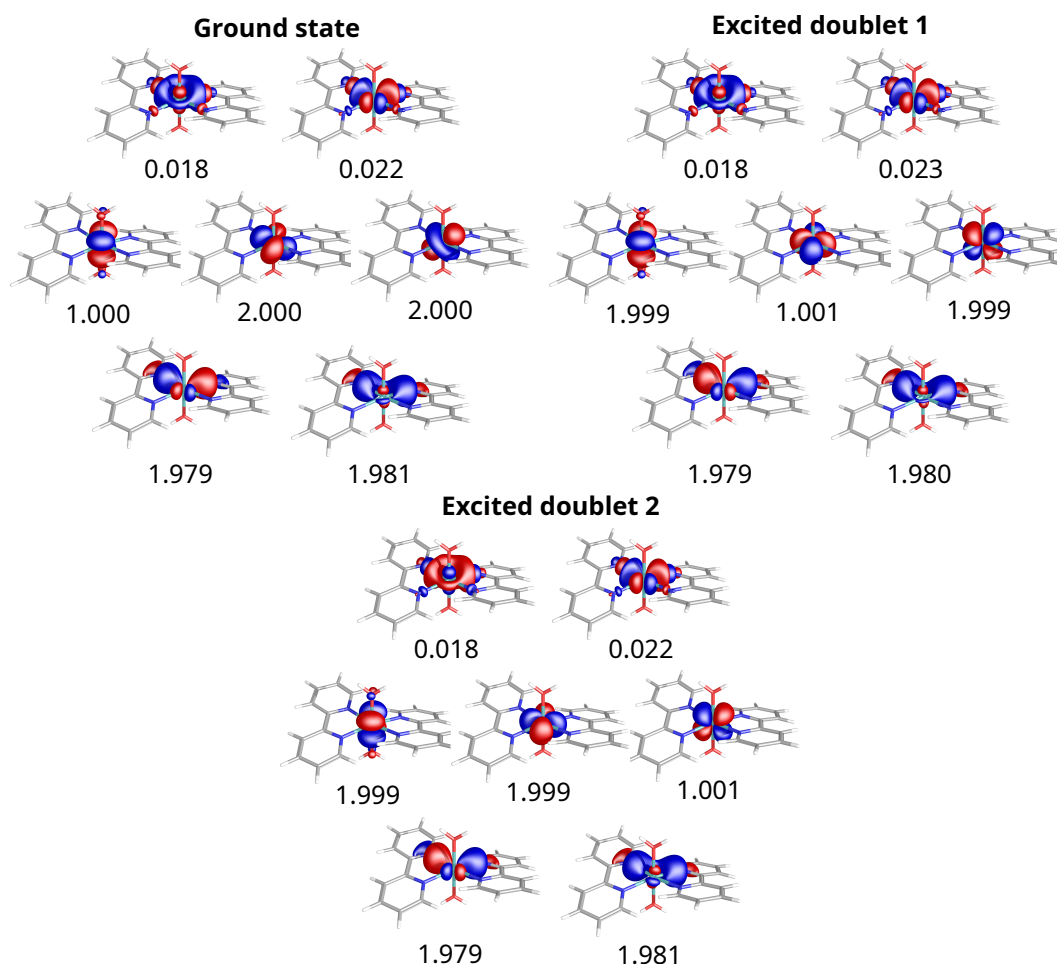


FIG. S4: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $trans\text{-}[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

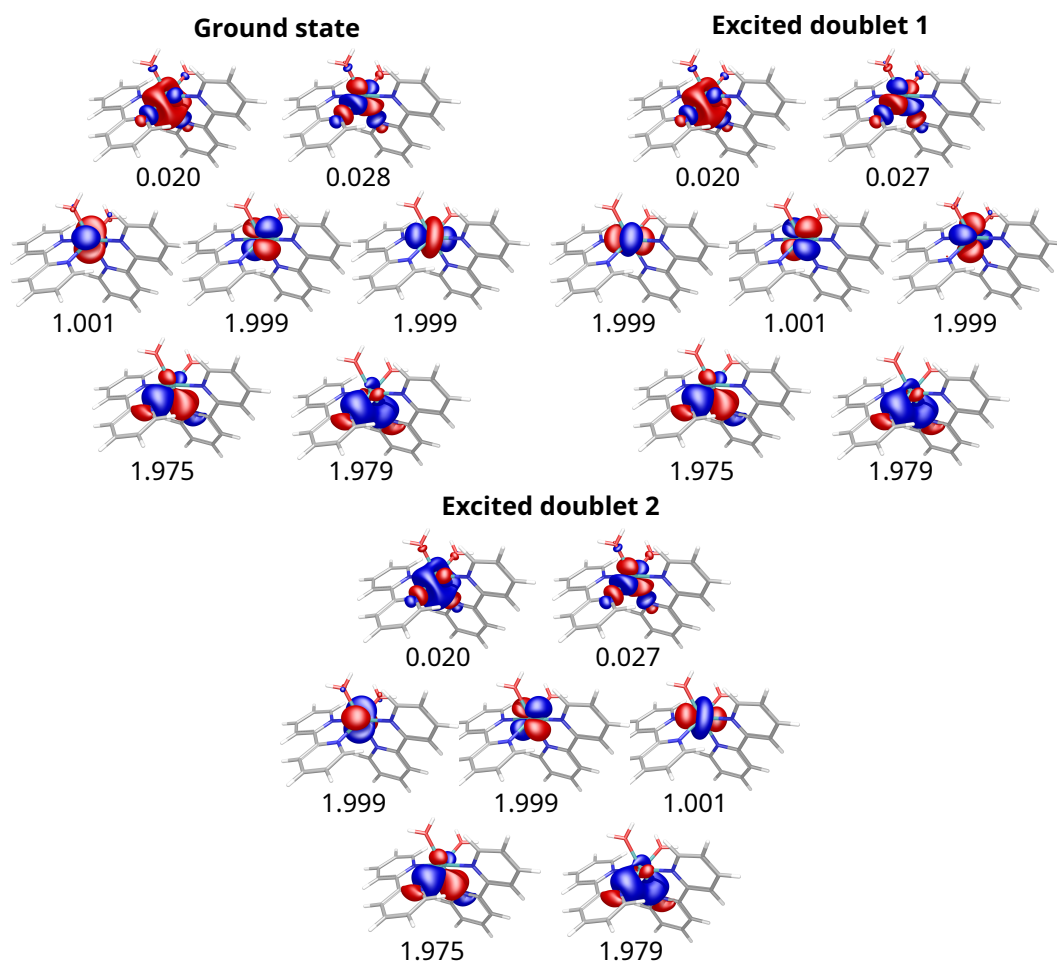


FIG. S5: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $cis\text{-}[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{H}_2\text{O})_2]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

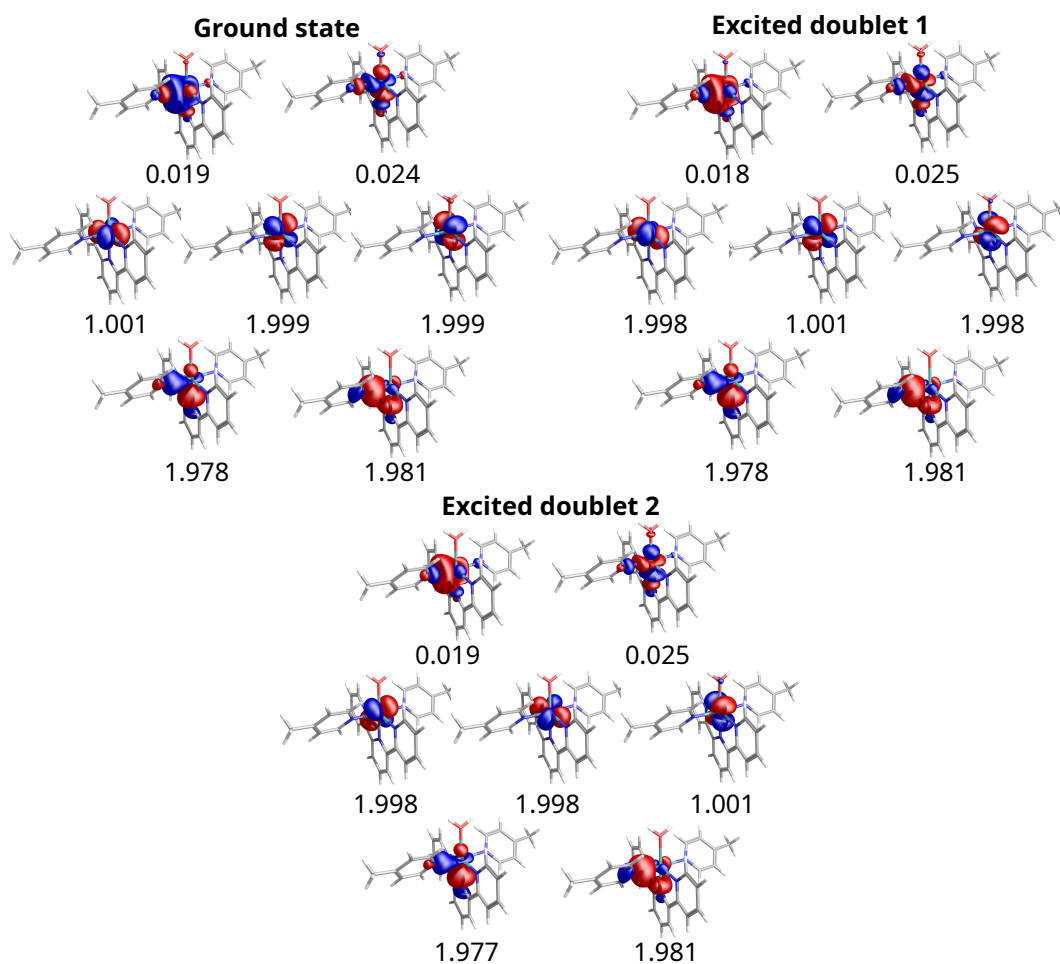


FIG. S6: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{tpy})(\text{pic})_2(\text{H}_2\text{O})]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

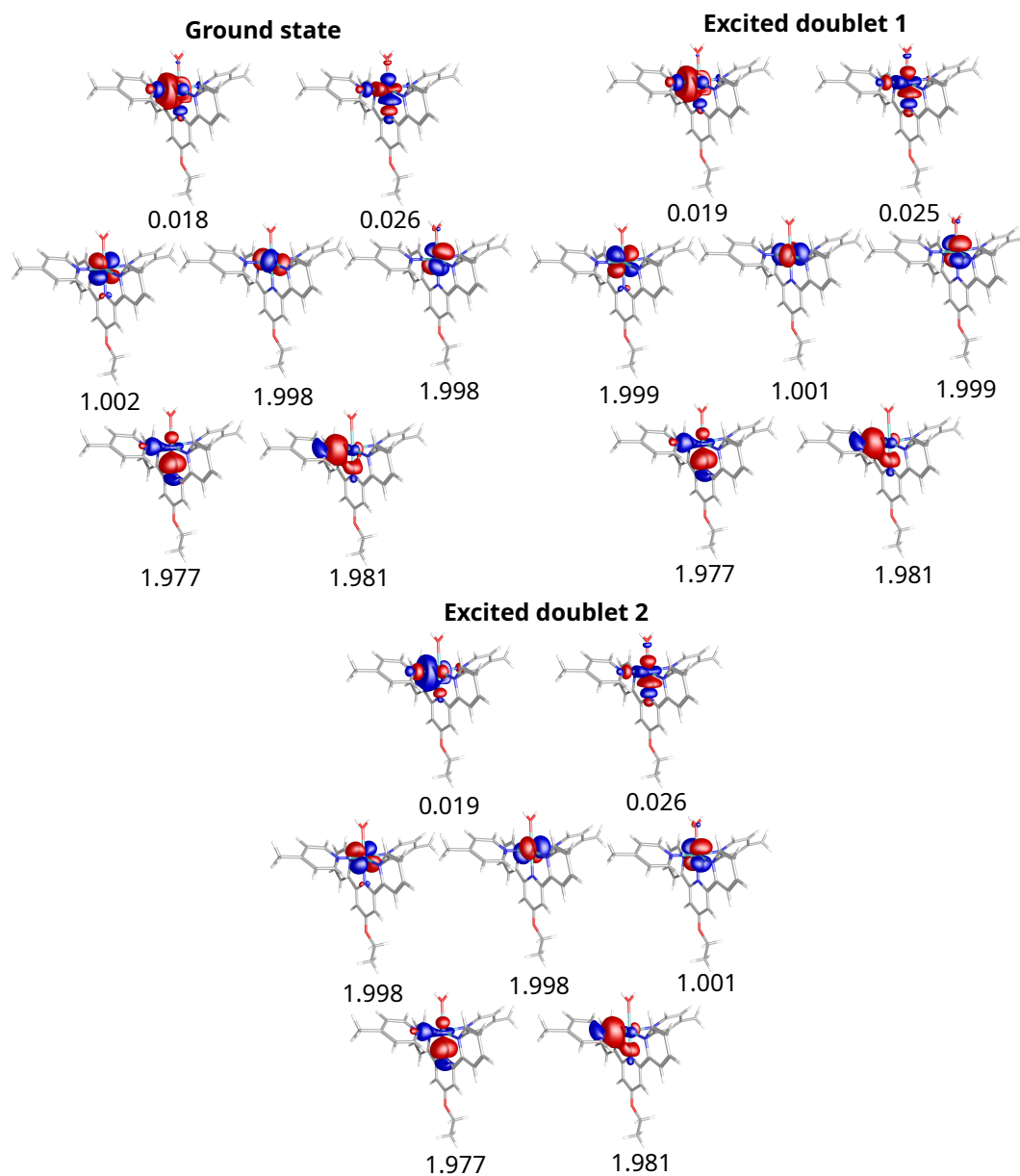


FIG. S7: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{EtO-tpy})(\text{pic})_2(\text{H}_2\text{O})]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

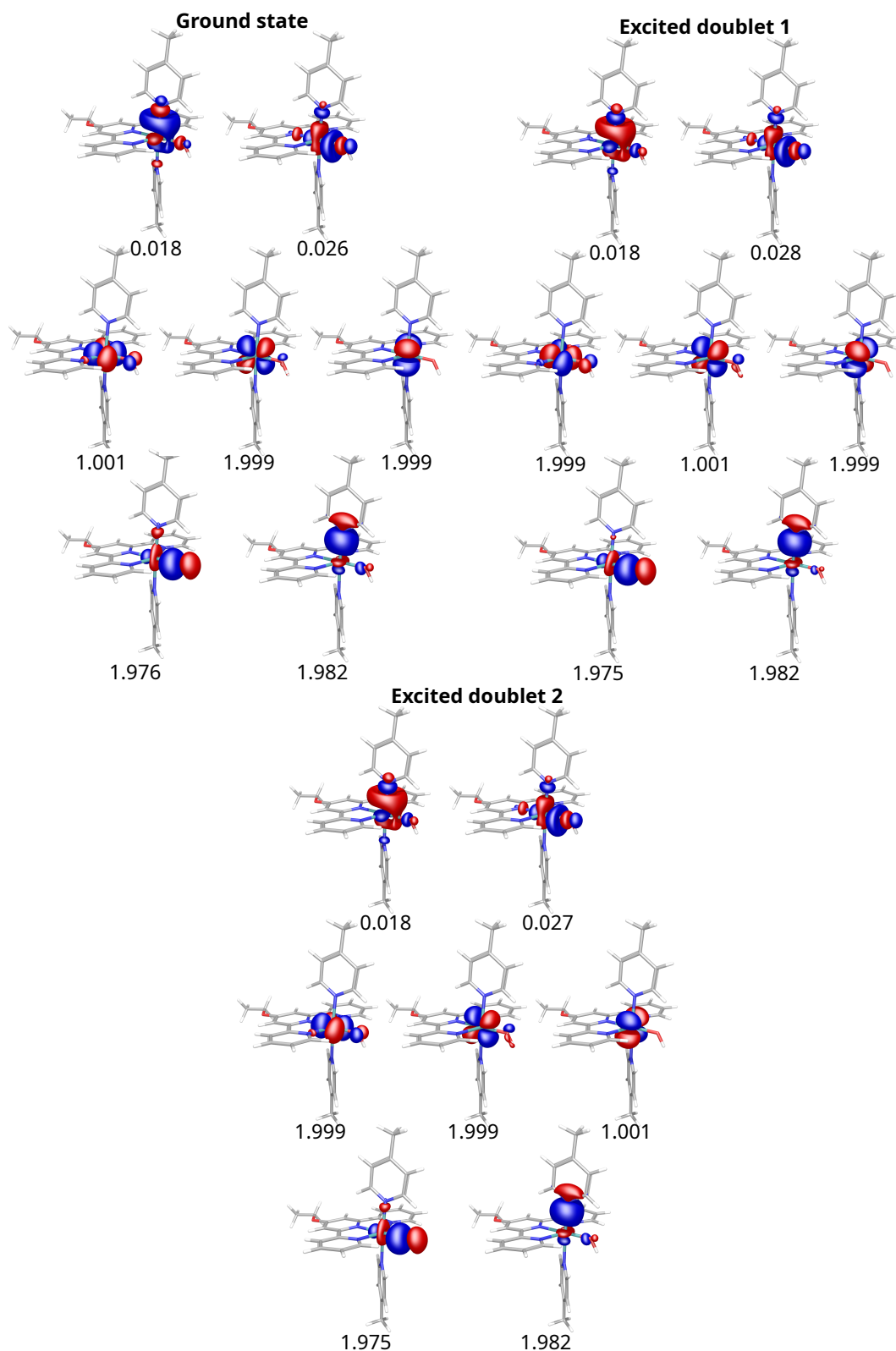


FIG. S8: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{EtO-tpy})(\text{pic})_2\text{OH}]^{2+}$. The occupations of every natural orbital are shown below the orbitals.

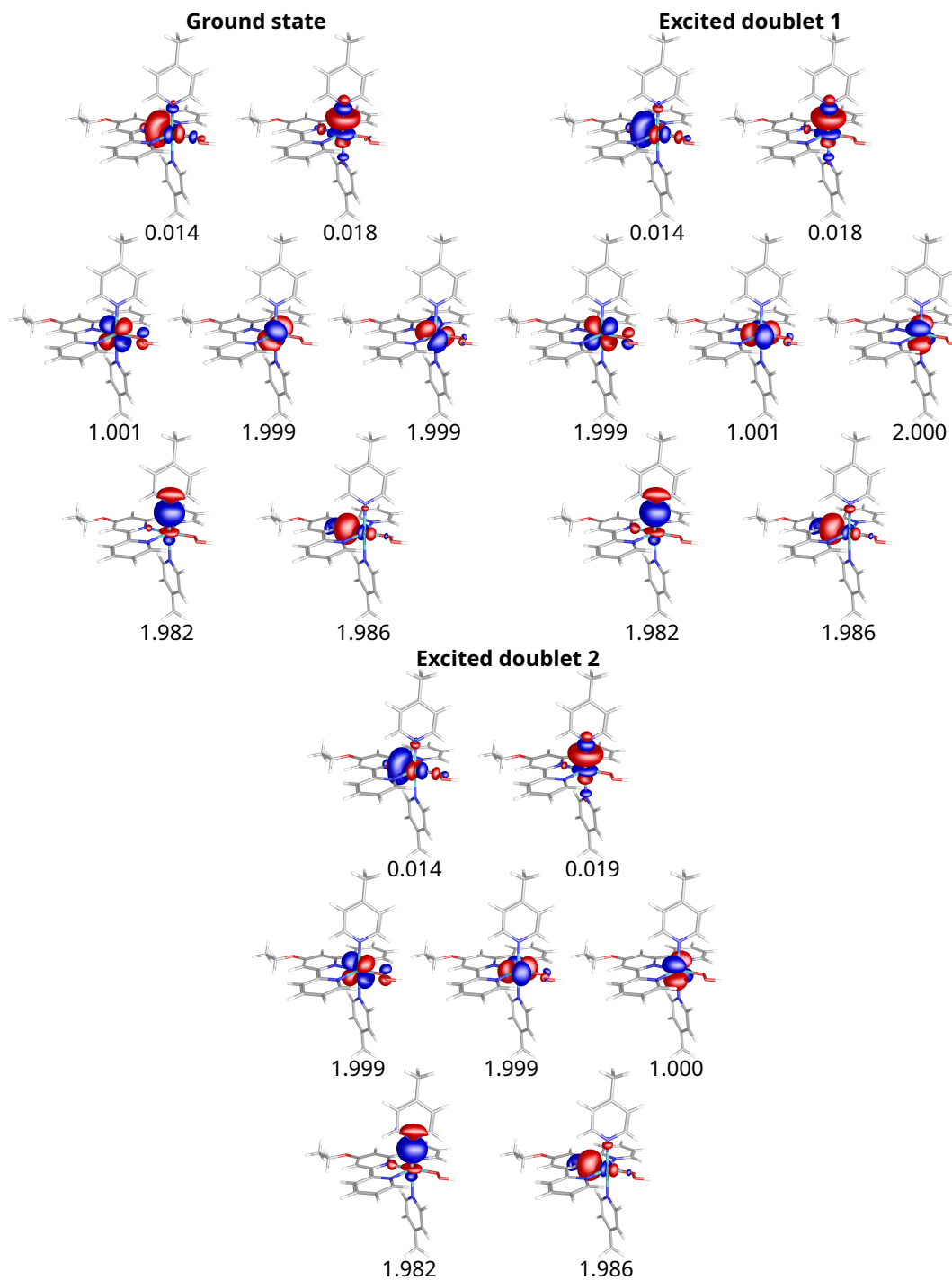


FIG. S9: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{EtO-tpy})(\text{pic})_2\text{OOH}]^{2+}$. The occupations of every natural orbital are shown below the orbitals.

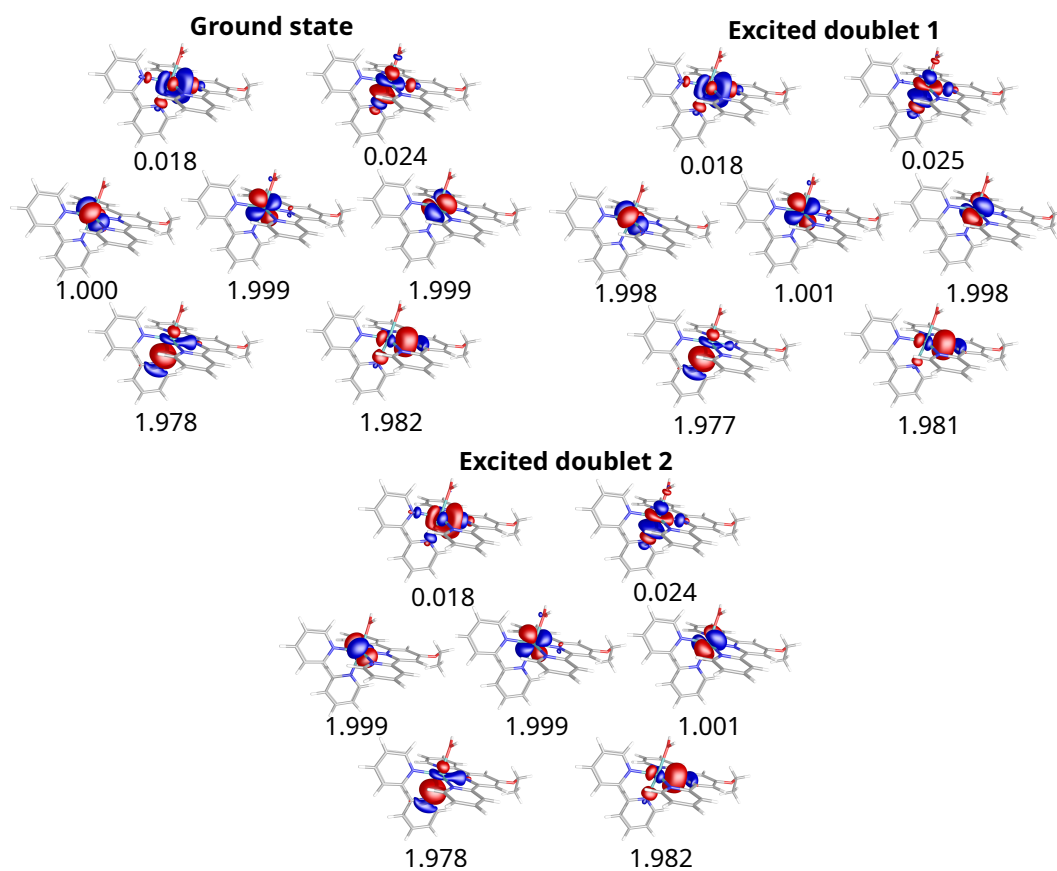


FIG. S10: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{bpy})(\text{EtO-tpy})(\text{H}_2\text{O})]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

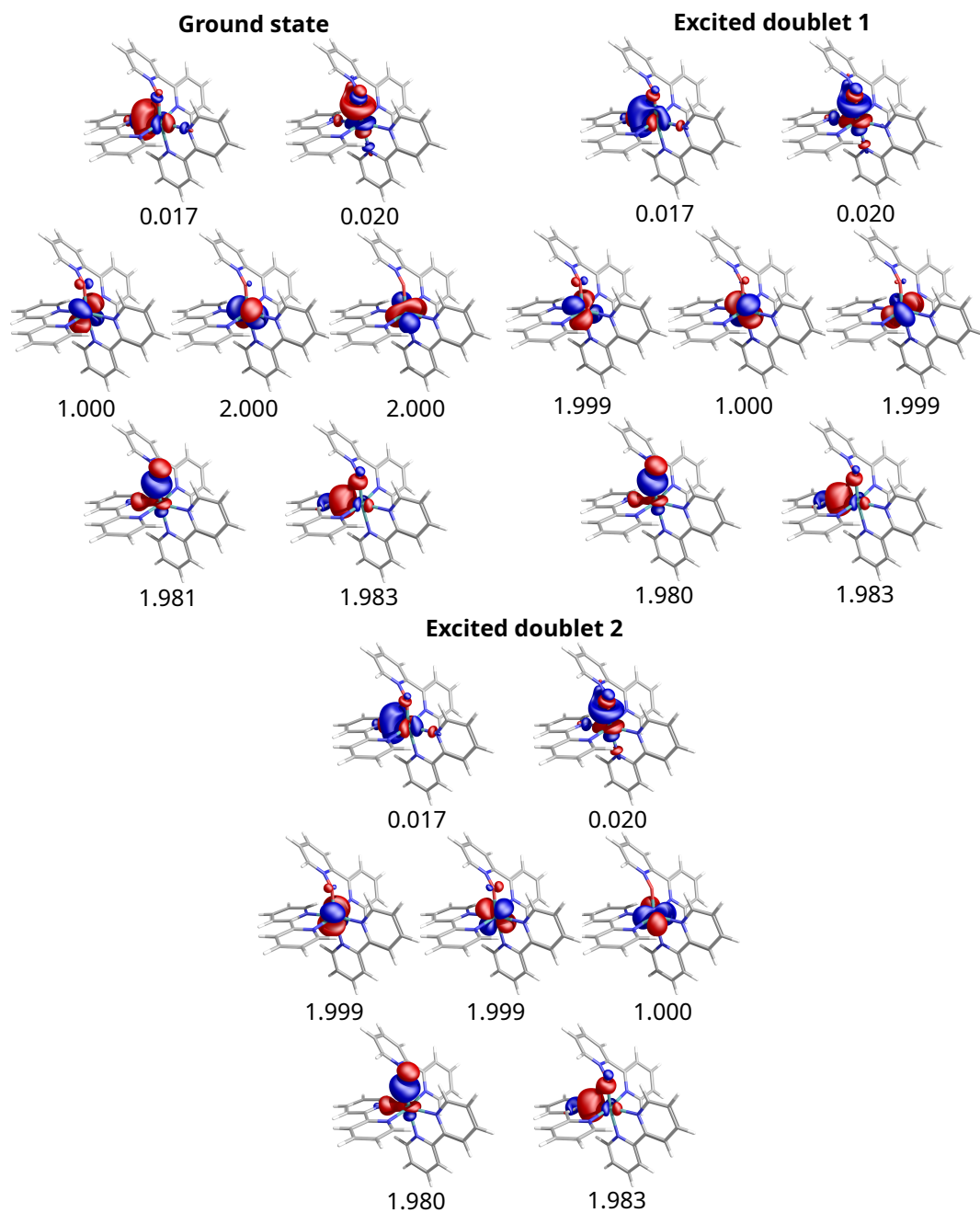


FIG. S11: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy-NO})]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

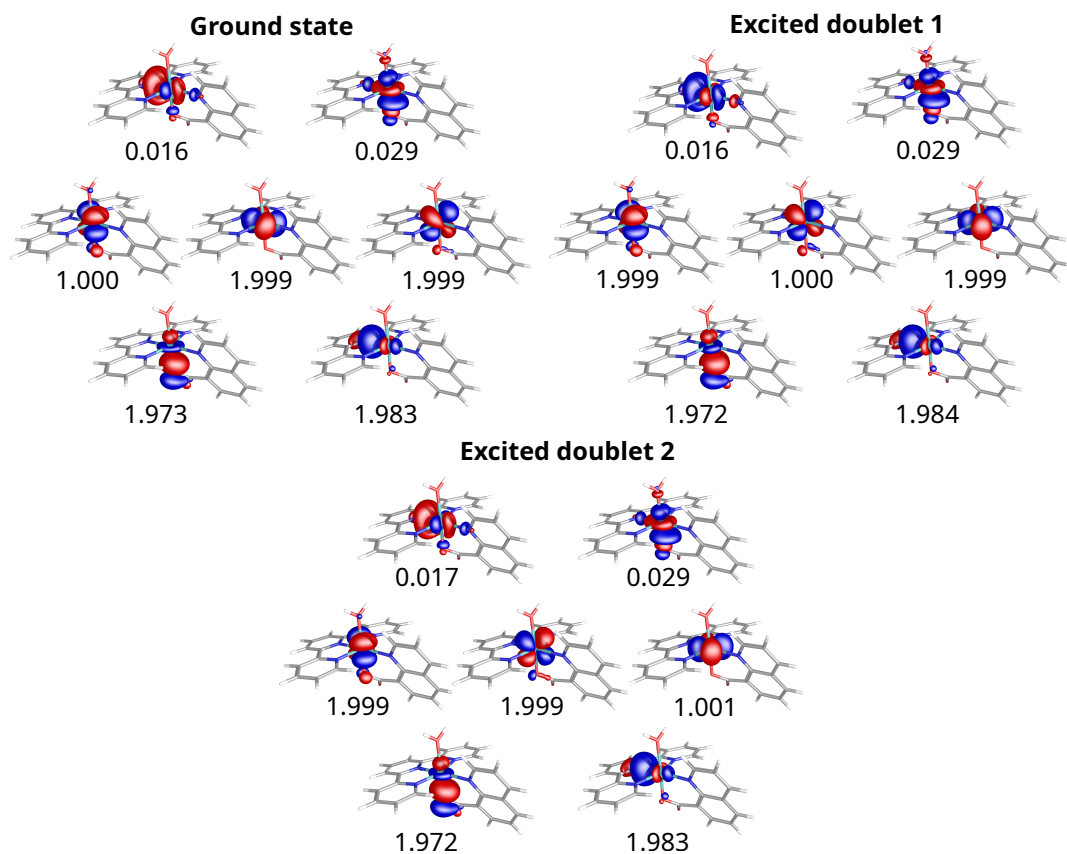


FIG. S12: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{tpy})(\text{Qc})\text{H}_2\text{O}]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

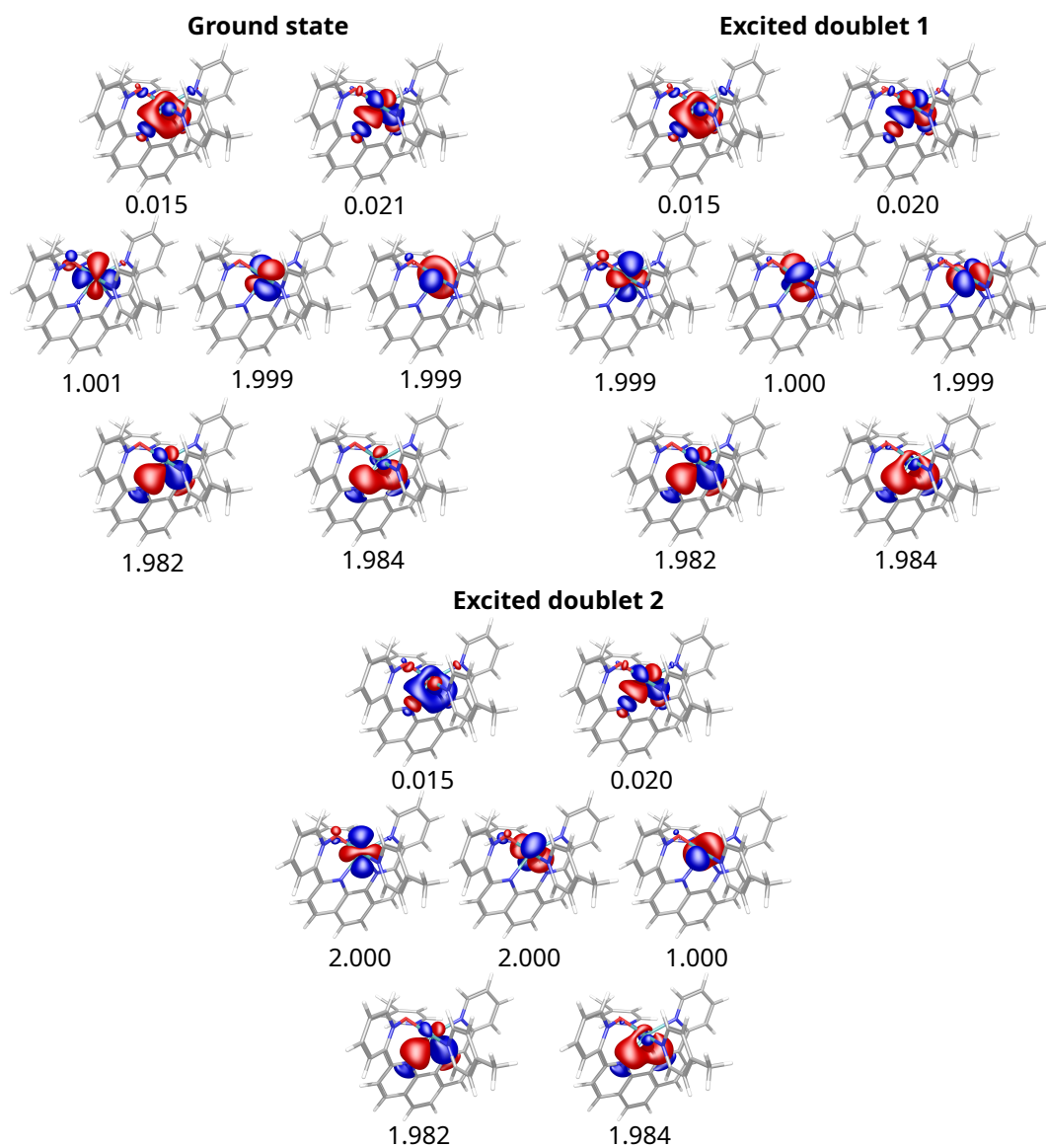


FIG. S13: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{pic})_2(\text{dpp-NO})]^{3+}$. The occupations of every natural orbital are shown below the orbitals.

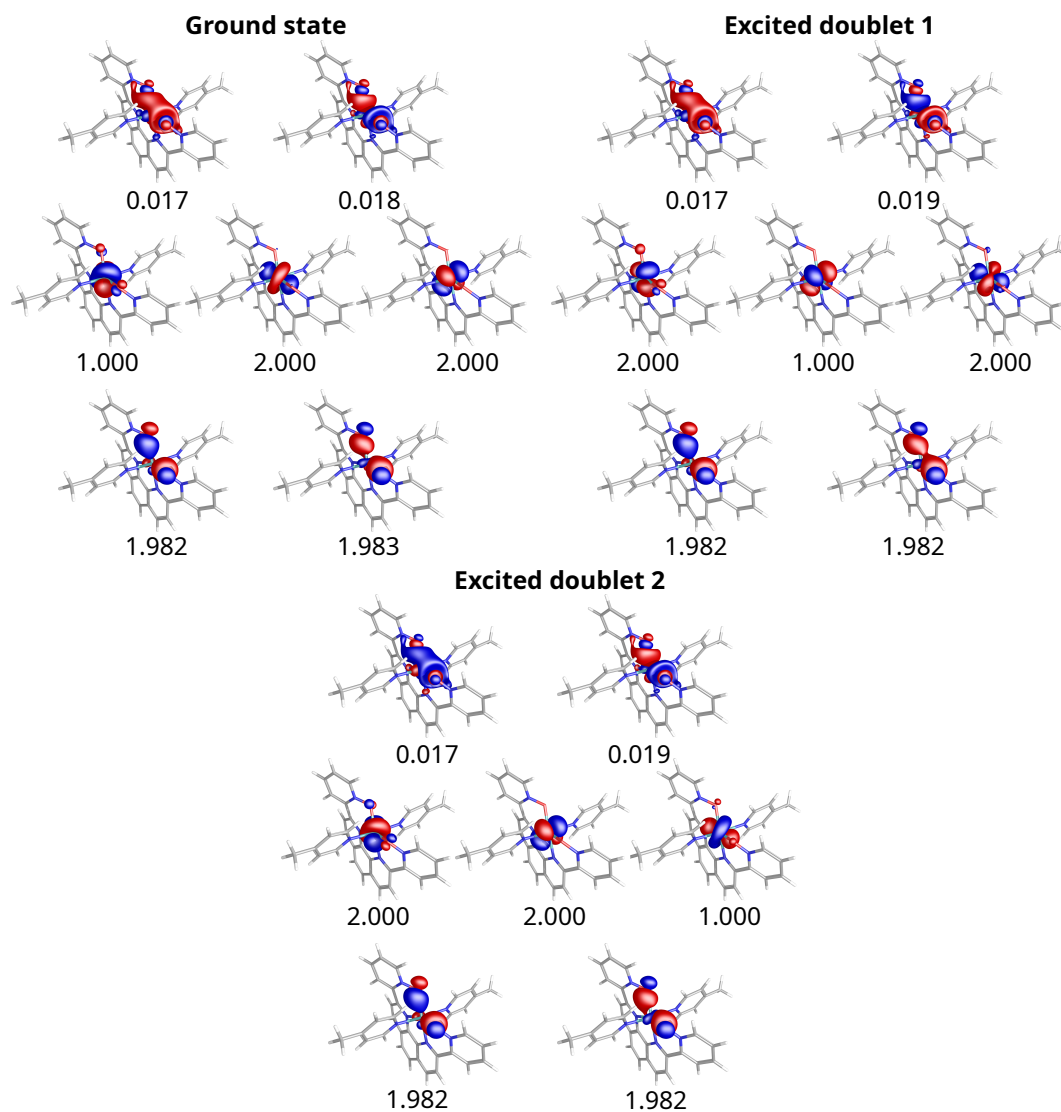


FIG. S14: Spin-averaged natural orbitals of individual states found with SA-CASSCF(9e,7o) shown for $[\text{Ru}^{\text{III}}(\text{pic})_2(\text{dpp-NO,NO})]^{3+}$. The occupations of every natural orbital are shown below the orbitals.