Supporting Information

Stabilization of hydrated Ac^{III} cation: The existence of superatom states

Yang Gao,[a,b] Payal Grover,[b] Georg Schreckenbach,[b]*

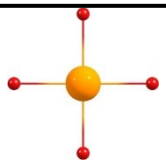
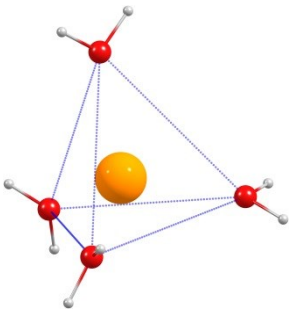
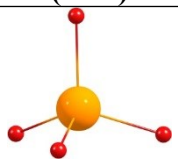
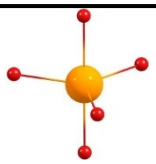
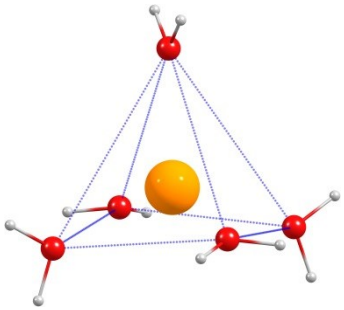
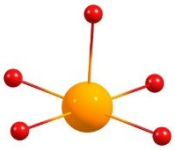
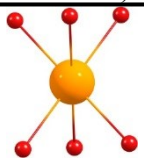
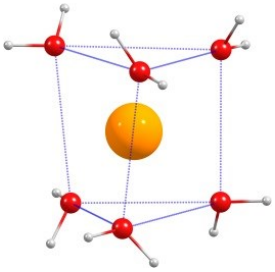
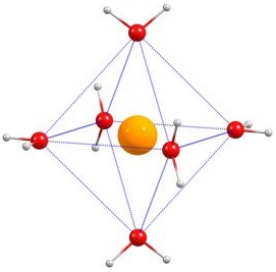
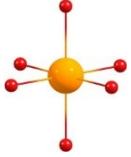
a. Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu, Sichuan, 610054, China

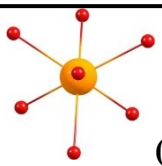
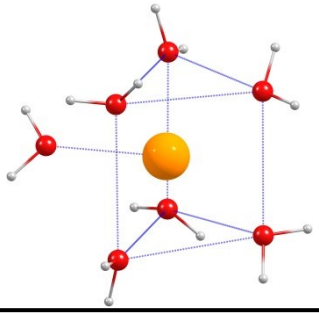
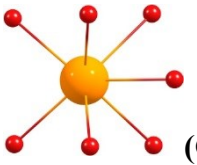
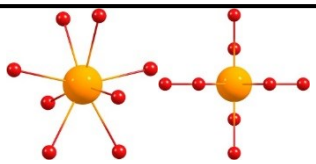
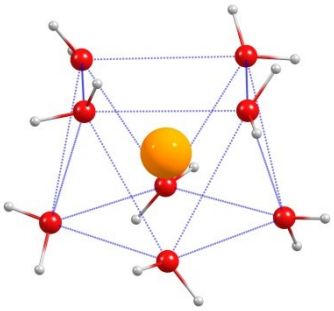
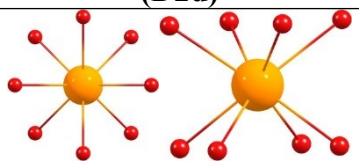
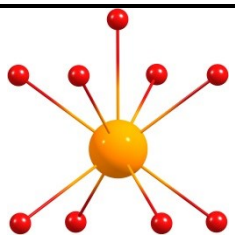
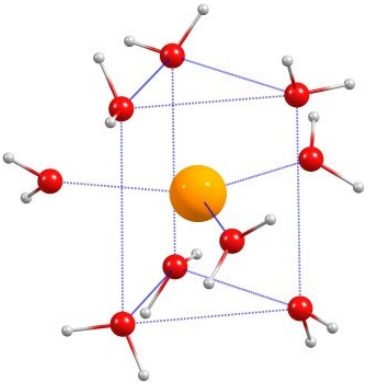
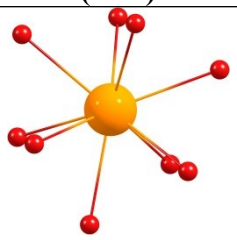
b. Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

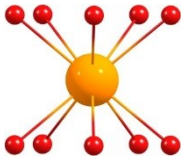
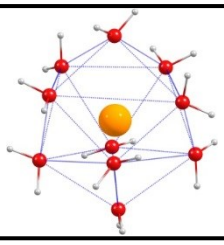
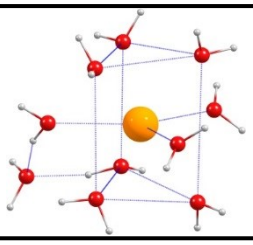
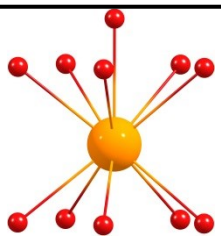
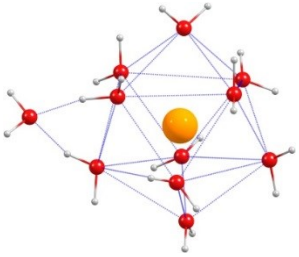
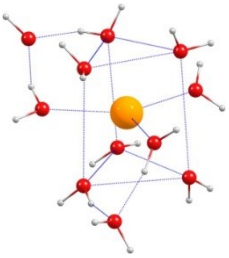
*E-mail: schreckecc.umanitoba.ca

Part 1. Different isomers of Ac^{III} aquo complexes.

Table S1. Different isomers used as initial structures of Ac^{III} aquo complexes for gas-phase aqueous solution optimizations at the PBE-D3/TZ2P level of theory.

	Initial Structures (symmetry: H atoms removed for clarity)	Optimized Structures
$[Ac^{III}(H_2O)_4]^{3+}$		
Isomer 1	 **(D4h)**	
Isomer 2	 **(Td)**	
$[Ac^{III}(H_2O)_5]^{3+}$		
Isomer 1	 **(D3h)**	
Isomer 2	 **(C4v)**	
$[Ac^{III}(H_2O)_6]^{3+}$	Initial Structures (symmetry: after removed H atoms)	Aqueous solution / Gas-phase
Isomer 1	 **(D3d)**	 
Isomer 2	 **(Oh)**	
$[Ac^{III}(H_2O)_7]^{3+}$	Initial	Optimized Structures

	Structures (symmetry: after removed H atoms)		
Isomer 1	 **(C3v)**		
Isomer 2	 **(C2v)**		
$[Ac^{III}(H_2O)_8]^{3+}$			
Isomer 1	 Sideview Topview **(D2d)**		
Isomer 2	 Sideview Topview **(D4d)**		
$[Ac^{III}(H_2O)_9]^{3+}$			
Isomer 1	 **(C4v)**		
Isomer 2	 **(D3h)**		
$[Ac^{III}(H_2O)_{10}]^{3+}$	Initial Structures (symmetry: after removed H atoms)	Aqueous solution	Gas-phase

Isomer 1	 **(D5h)**		
$[Ac^{III}(H_2O)_{11}]^{3+}$	Initial Structures (symmetry: after removed H atoms)	Aqueous solution	Gas-phase
Isomer 1	 **(C5v)**		

Part 2. Ac-O_{water} bond lengths of Ac^{III} aquo complexes

Table S2. Ac-O_{water} bond lengths (Å) of Ac^{III} aquo complexes in both gas phase and aqueous solution. Only the Ac-O_{water} bond lengths in the first hydration shell were included in the averages.

	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	Average
$[Ac^{III}(H_2O)_4]^{3+}$											
gas-SR-PBE-D3	2.523	2.525	2.525	2.523	/	/	/	/	/	/	2.524
gas-SOC-PBE-D3	2.522	2.524	2.524	2.522	/	/	/	/	/	/	2.523
aq-SR-PBE-D3	2.476	2.477	2.474	2.484	/	/	/	/	/	/	2.478
gas-SR-B3LYP-D3	2.544	2.546	2.546	2.544	/	/	/	/	/	/	2.545
gas-SOC-B3LYP-D3	2.542	2.544	2.544	2.542	/	/	/	/	/	/	2.543
aq-SR- B3LYP-D3	2.504	2.505	2.505	2.504	/	/	/	/	/	/	2.505
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	Average
$[Ac^{III}(H_2O)_5]^{3+}$											
gas-SR-PBE-D3	2.547	2.571	2.571	2.563	2.563	/	/	/	/	/	2.563
gas-SOC-PBE-D3	2.547	2.571	2.571	2.562	2.562	/	/	/	/	/	2.563
aq-SR-PBE-D3	2.516	2.516	2.516	2.520	2.520	/	/	/	/	/	2.518
gas-SR-B3LYP-D3	2.569	2.592	2.592	2.583	2.583	/	/	/	/	/	2.584
gas-SOC-B3LYP-D3	2.569	2.592	2.592	2.583	2.583	/	/	/	/	/	2.584
aq-SR- B3LYP-D3	2.541	2.540	2.540	2.543	2.543	/	/	/	/	/	2.541
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	Average
$[Ac^{III}(H_2O)_6]^{3+}$											
gas-SR-PBE-D3	2.599	2.598	2.599	2.599	2.598	2.599	/	/	/	/	2.599
gas-SOC-PBE-D3	2.599	2.599	2.599	2.599	2.599	2.599	/	/	/	/	2.599
aq-SR-PBE-D3	2.545	2.548	2.553	2.562	2.551	2.555	/	/	/	/	2.552
gas-SR-B3LYP-D3	2.620	2.619	2.620	2.620	2.619	2.620	/	/	/	/	2.620
gas-SOC-B3LYP-D3	2.618	2.618	2.618	2.618	2.618	2.618	/	/	/	/	2.618

aq-SR- B3LYP-D3	2.566	2.568	2.564	2.577	2.567	2.587	/	/	/	/	2.572
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	Average
$[Ac^{III}(H_2O)_7]^{3+}$											
gas-SR-PBE-D3	2.619	2.630	2.636	2.635	2.638	2.631	2.617	/	/	/	2.629
gas-SOC-PBE-D3	2.616	2.636	2.639	2.637	2.640	2.637	2.614	/	/	/	2.631
aq-SR-PBE-D3	2.574	2.581	2.582	2.580	2.579	2.591	2.573	/	/	/	2.580
gas-SR-B3LYP-D3	2.636	2.650	2.656	2.653	2.657	2.651	2.634	/	/	/	2.648
gas-SOC-B3LYP-D3	2.635	2.649	2.655	2.652	2.656	2.650	2.632	/	/	/	2.647
aq-SR- B3LYP-D3	2.594	2.602	2.602	2.600	2.599	2.609	2.593	/	/	/	2.600
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	Average
$[Ac^{III}(H_2O)_8]^{3+}$											
gas-SR-PBE-D3	2.657	2.653	2.654	2.658	2.661	2.662	2.653	2.659	/	/	2.657
gas-SOC-PBE-D3	2.663	2.659	2.661	2.663	2.662	2.664	2.660	2.661	/	/	2.662
aq-SR-PBE-D3	2.610	2.611	2.611	2.611	2.609	2.610	2.609	2.609	/	/	2.610
gas-SR-B3LYP-D3	2.679	2.676	2.677	2.679	2.679	2.680	2.677	2.678	/	/	2.678
gas-SOC-B3LYP-D3	2.677	2.674	2.675	2.677	2.677	2.678	2.675	2.676	/	/	2.676
aq-SR- B3LYP-D3	2.631	2.630	2.631	2.631	2.629	2.630	2.629	2.629	/	/	2.630
	$O_{1(cap)}$	$O_{2(cap)}$	$O_{3(cap)}$	$O_{4(prism)}$	$O_{5(cap)}$	$O_{6(prism)}$	$O_{7(cap)}$	$O_{8(cap)}$	$O_{9(prism)}$	O_{10}	Average
$[Ac^{III}(H_2O)_9]^{3+}$											
gas-SR-PBE-D3	2.687	2.690	2.689	2.692	2.689	2.693	2.690	2.692	2.693	/	2.690
gas-SOC-PBE-D3	2.691	2.693	2.692	**2.697**	2.695	**2.697**	2.695	2.697	**2.696**	/	2.695
aq-SR-PBE-D3	2.643	2.643	2.643	**2.640**	2.644	**2.640**	2.642	2.644	**2.639**	/	2.642
gas-SR-B3LYP-D3	2.703	2.705	2.704	2.708	2.706	2.708	2.706	2.709	2.707	/	2.706
gas-SOC-B3LYP-D3	2.704	2.703	2.705	**2.706**	2.708	**2.707**	2.706	2.708	**2.705**	/	2.706
aq-SR- B3LYP-D3	2.663	2.664	2.663	**2.660**	2.665	**2.661**	2.664	2.664	**2.659**	/	2.663
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	Average
$[Ac^{III}(H_2O)_9(H_2O)_1]^{3+}$											
gas-SR-PBE-D3	2.710	2.703	2.716	2.714	2.705	2.691	2.648	2.625	2.681	/	2.688
gas-SOC-PBE-D3	2.675	2.690	2.709	2.725	2.714	2.716	2.632	2.655	2.703	/	2.691
gas-SR-B3LYP-D3	2.731	2.718	2.731	2.730	2.717	2.708	2.664	2.646	2.695	/	2.704
gas-SOC-B3LYP-D3	2.729	2.717	2.728	2.728	2.715	2.706	2.661	2.643	2.693	/	2.702

$[Ac^{III}(H_2O)_{10}]^{3+}$											
aq-SR-PBE-D3	2.662	2.702	2.675	2.722	2.693	2.652	2.707	2.686	2.718	2.678	2.690
aq-SR- B3LYP-D3	2.687	2.720	2.701	2.736	2.713	2.679	2.726	2.709	2.737	2.705	2.711
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	$O_{10/11}$	Average
$[Ac^{III}(H_2O)_9(H_2O)_2]^{3+}$											
gas-SR-PBE-D3	2.705	2.674	2.652	2.696	2.733	2.655	2.664	2.699	2.731	/	2.690
gas-SOC-PBE-D3	2.703	2.672	2.649	2.693	2.730	2.653	2.661	2.695	2.728	/	2.687
gas-SR-B3LYP-D3	2.715	2.686	2.665	2.707	2.742	2.669	2.675	2.711	2.739	/	2.701
gas-SOC-B3LYP-D3	2.714	2.685	2.664	2.705	2.740	2.668	2.674	2.710	2.737	/	2.700
$[Ac^{III}(H_2O)_{10}(H_2O)_1]^{3+}$											
aq-SR-PBE-D3	2.718	2.651	2.688	2.700	2.757	2.665	2.643	2.696	2.723	2.689	2.693
aq-SR- B3LYP-D3	2.724	2.663	2.697	2.711	2.756	2.676	2.657	2.704	2.728	2.695	2.701
	O_1	O_2	O_3	O_4	O_5	O_6	O_7	O_8	O_9	O_{10}	Average
$[Ac^{III}(H_2O)_8(H_2O)_{16}]^{3+}$											
aq-SR-PBE-D3	2.640	2.640	2.639	2.640	2.641	2.640	2.640	2.640	/	/	2.640
	$O_{1(prism)}$	$O_{2(prism)}$	$O_{3(prism)}$	$O_{4(cap)}$	$O_{5(cap)}$	$O_{6(prism)}$	$O_{7(prism)}$	$O_{8(cap)}$	$O_{9(prism)}$	O_{10}	Average
$[Ac^{III}(H_2O)_9(H_2O)_{18}]^{3+}$											
aq-SR-PBE-D3	2.684	2.645	2.645	2.617	2.616	2.665	2.659	2.617	2.684	/	2.648

Part 3. Detailed composition of superatom MOs of $Ac^{III}(H_2O)_9]^{3+}$ complexes.

Table S3. Detailed composition of superatom MOs of the $[Ac^{III}(H_2O)_9]^{3+}$, complexes.

Superatom Orbitals	Ac^{III} cation				$(H_2O)_9$ Ligand		
	6d	7s	7p	5f	1s (H)	2s (O)	2p (O)
1D	2.33%				2.12%	5.73%	71.17%
1D	1.44%				3.22%	6.13%	68.69%
1D	2.17%				2.89%	6.18%	71.48%
1D	5.79%				5.01%	6.51%	70.33%
1D	5.50%				3.24%	8.32%	70.12%
1P			4.90%			8.68%	71.85%
1P			2.79%			5.88%	73.30%
1P			4.41%			8.66%	73.72%
1S		6.50%					74.06%

Part 4. Molecular orbitals of $[Ac^{III}(H_2O)_9]^{3+}$ and $[Ac@Au_{14}]^-$ based on the Jellium model

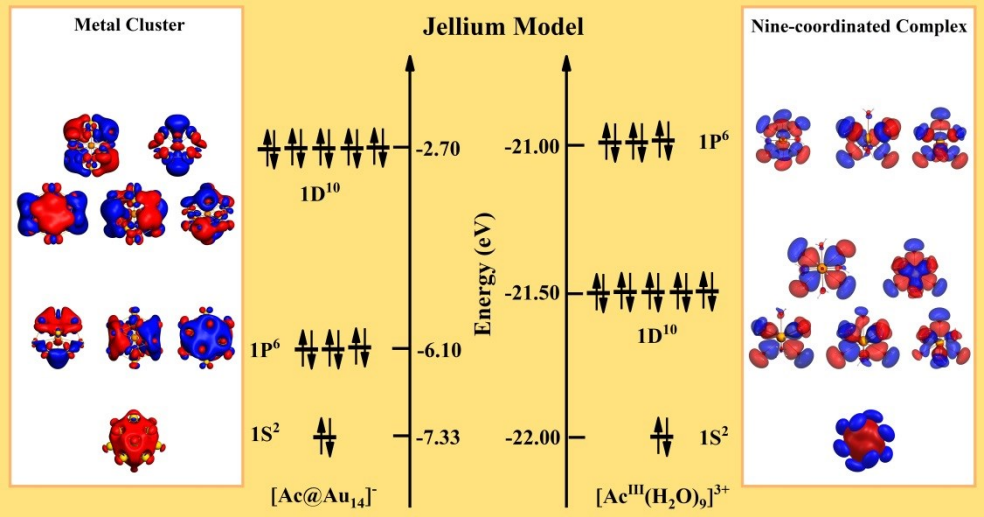


Figure S1. Molecular orbitals listed on the basis of the Jellium model. Left: molecular orbitals of the singlet metal cluster $[Ac@Au_{14}]^-$. Right: molecular orbitals of the singlet nine-coordinated complex $[Ac^{III}(H_2O)_9]^{3+}$.

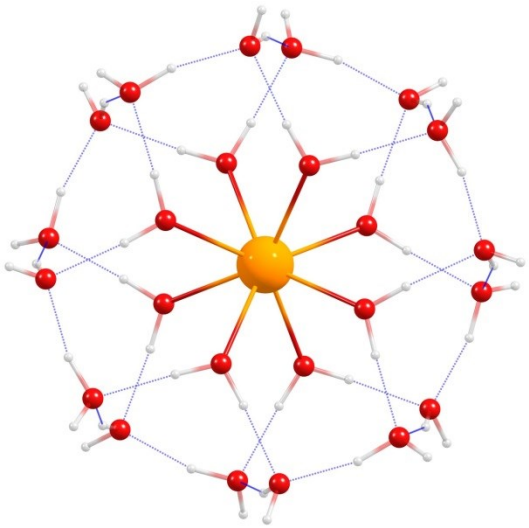
Part 5. EDA-NOCV results with and without the explicit second water shell

Table S4. EDA-NOCV results (kcal/mol) for the $[Ac^{III}(H_2O)_8]^{3+}$, $[Ac^{III}(H_2O)_9]^{3+}$, $[Ac^{III}(H_2O)_8(H_2O)_{16}]^{3+}$, $[Ac^{III}(H_2O)_9(H_2O)_{18}]^{3+}$ complexes in gas-phase at the PBE-D3/TZ2P level of theory.

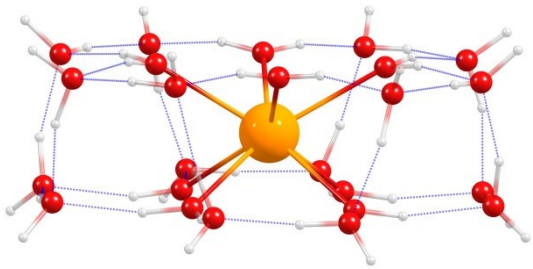
	Ac^{III} vs $(H_2O)_8$	Ac^{III} vs $(H_2O)_9$	Ac^{III} vs $(H_2O)_8(H_2O)_{16}$	Ac^{III} vs $(H_2O)_9(H_2O)_{18}$
ΔE_{int}	-444.69	-474.98	-686.86	-719.27
ΔE_{pauli}	141.32	136.70	160.30	163.79
ΔE_{dis}	-1.13 (0.19%)	-1.35 (0.22%)	-4.04 (0.48%)	-4.47 (0.51%)
ΔE_{elstat}	-335.06 (57.18%)	-350.14 (57.24%)	-534.24 (63.06%)	-550.88 (62.85%)
ΔE_{orb}	-249.81 (42.63%)	-260.19 (42.54%)	-308.89 (36.46%)	-327.71 (36.64□%)

Ac^{III} vs $(H_2O)_8(H_2O)_{16}$

Top View



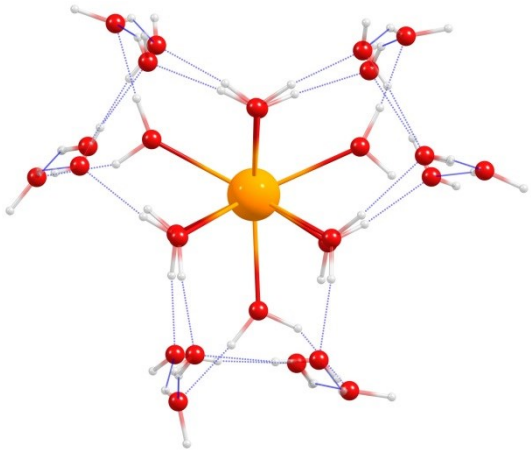
Side View

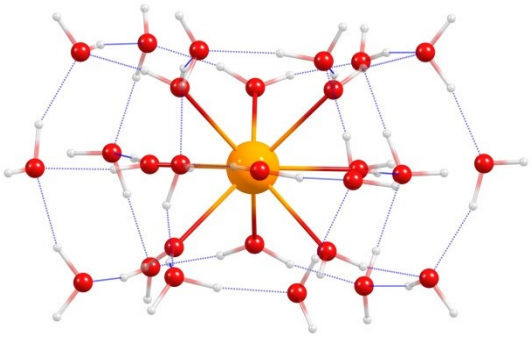


Ac^{III} vs $(H_2O)_9(H_2O)_{18}$

Top View

Side View





Part 6. Electronic structure of $[Ac^{III}(NH_3)_9]^{3+}$ and $[Ac^{III}(PH_3)_9]^{3+}$ complexes

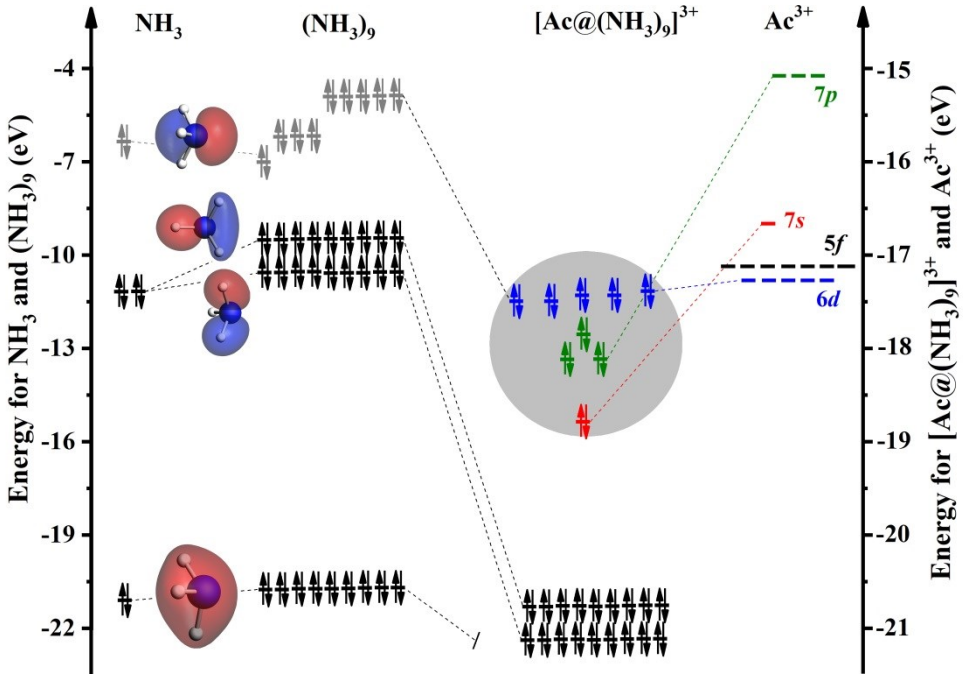


Figure S2. Electronic structure diagram of the $[Ac^{III}(NH_3)_9]^{3+}$ complex in gas-phase at the PBE-D3/TZ2P level of theory. The MO energies of the NH_3 molecule and $(NH_3)_9$ fragment correspond to the left Y axis, and the MO energies of the Ac^{3+} cation and $[Ac^{III}(NH_3)_9]^{3+}$ complex are shown on the right Y axis.

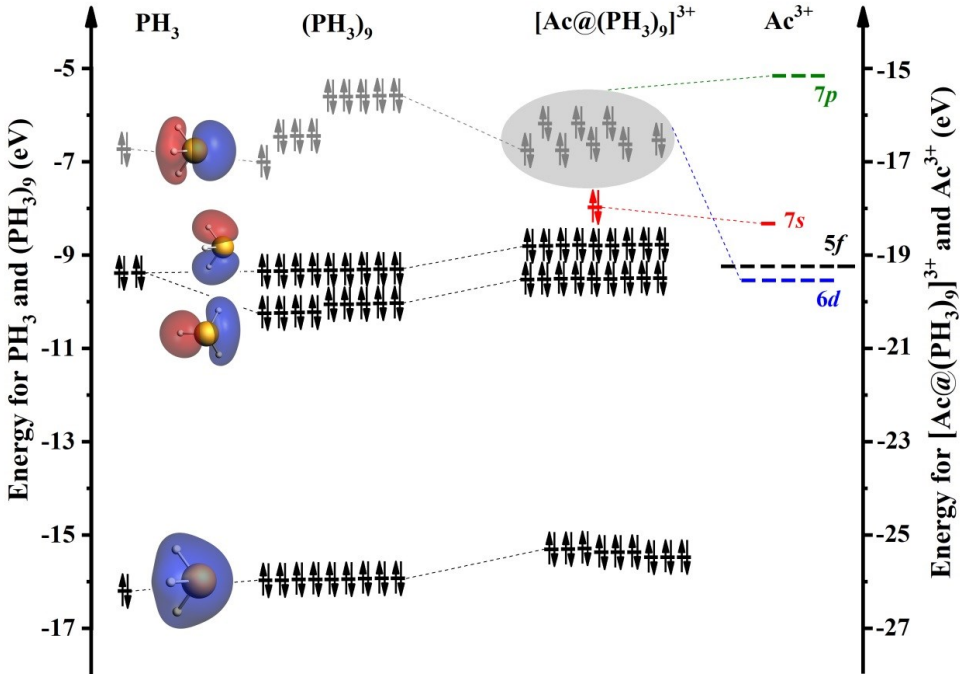


Figure S3. Electronic structure diagram of the $[Ac^{III}(PH_3)_9]^{3+}$ complex in gas-phase at the PBE-D3/TZ2P level of theory. The MO energies of the PH_3 molecule and $(PH_3)_9$ fragment correspond to the left Y axis, and the MO energies of the Ac^{3+} cation and $[Ac^{III}(PH_3)_9]^{3+}$ complex are shown on the right Y axis.

Table S5. Detailed composition of superatom MOs of the $[Ac^{III}(NH_3)_9]^{3+}$ and $[Ac^{III}(PH_3)_9]^{3+}$ complexes.

Superatom Orbitals	Ac^{III} cation				$(NH_3)_9$ Ligand		
	6d	7s	7p	5f	1s (H)	2s (N)	2p (N)
1D	5.76%			2.06%		6.89%	67.57%
1D	7.26%					7.16%	61.96%
1D	8.60%			1.14%		6.98%	65.03%
1D	10.37%					7.68%	65.19%
1D	10.41%			1.22%		9.91%	67.06%
1P			4.37%			6.65%	71.07%
1P			4.68%			9.99%	73.49%
1P			5.49%			10.17%	73.69%
1S		13.24%					71.09%
	Ac^{III} cation				$(PH_3)_9$ Ligand		
	6d	7s	7p	5f	1s (H)	3s (P)	3p (P)
1D and 1P	7.34%		1.17%	1.71%	6.60%	9.65%	53.59%
	9.87%			1.75%	15.59%	12.34%	52.17%
	6.25%		3.15%		12.71%	11.64%	54.74%
	4.40%		4.84%		11.95%	11.50%	55.50%
	7.15%		3.01%		12.22%	11.09%	54.99%
	5.35%		2.86%		12.75%	10.26%	53.40%
	2.50%		5.00%		13.43%	10.66%	53.02%
	13.92%				13.16%	10.57%	50.97%
1S		21.17%					63.32%

Part 7. Electronic structure diagrams for the of Ac cation with coordination numbers from 7 to 10

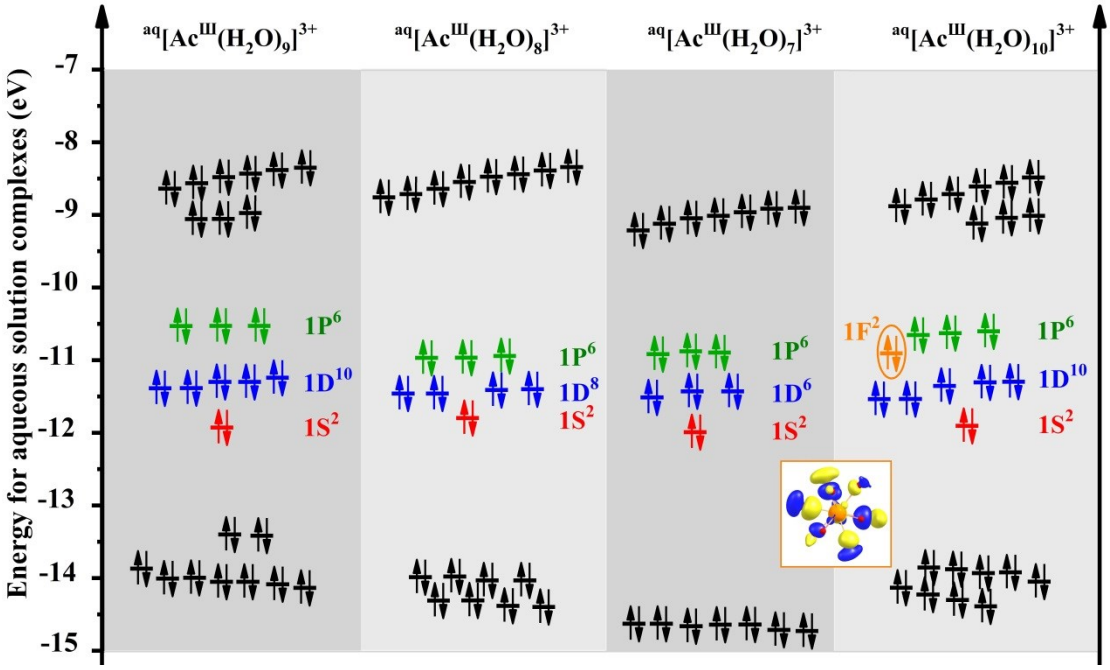


Figure S4. Electronic structure diagrams of $^{aq}[Ac^{III}(H2O)_9]^{3+}$, $^{aq}[Ac^{III}(H2O)_8]^{3+}$, $^{aq}[Ac^{III}(H2O)_7]^{3+}$, $^{aq}[Ac^{III}(H2O)_{10}]^{3+}$ complexes at the PBE-D3/TZ2P level of theory. The uppercase letters represent superatomic molecular orbitals.

Part 8. Optimized geometry of the $^{aq}[Ac^{III}(H_2O)_{10}(H_2O)_{35}]^{3+}$ complex

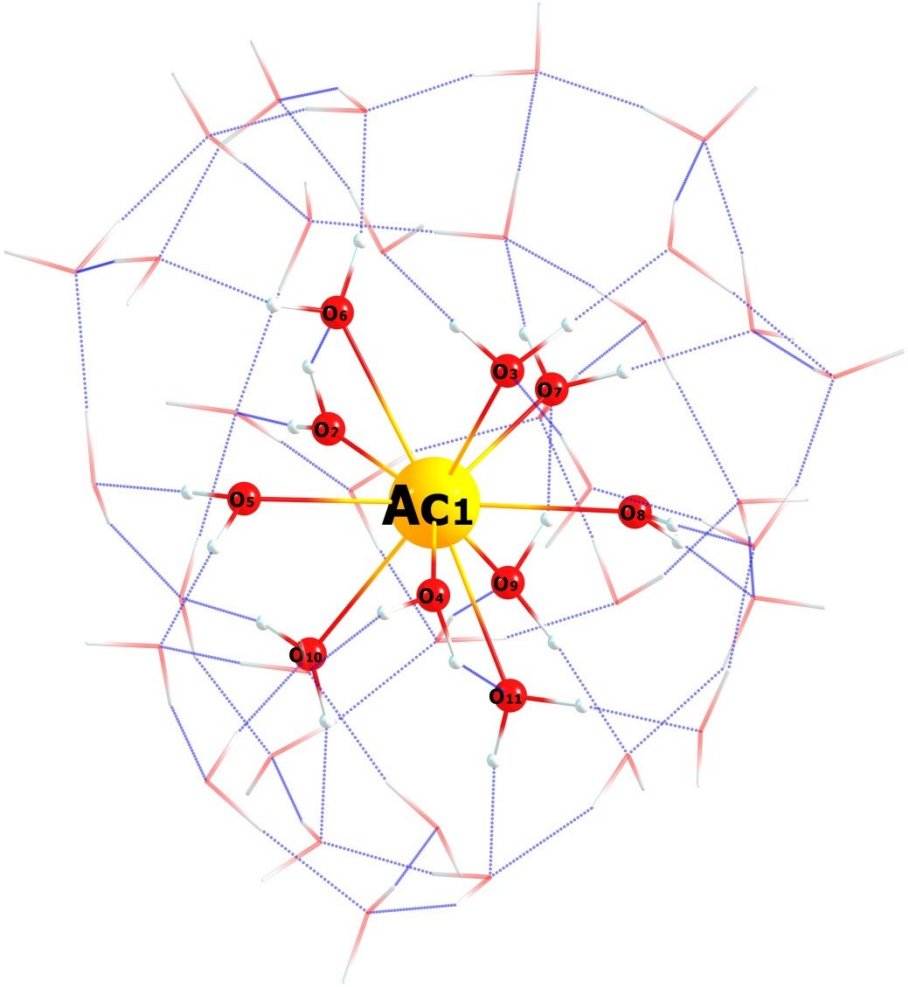


Figure S5. Optimized geometry of the $^{aq}[Ac^{III}(H_2O)_{10}(H_2O)_{35}]^{3+}$ complex in aqueous solution at the PBE-D3/TZ2P level of theory.