Computational treatment of the lanthanide(+III) hydration - ESI

S-1 Thermodynamic cycles

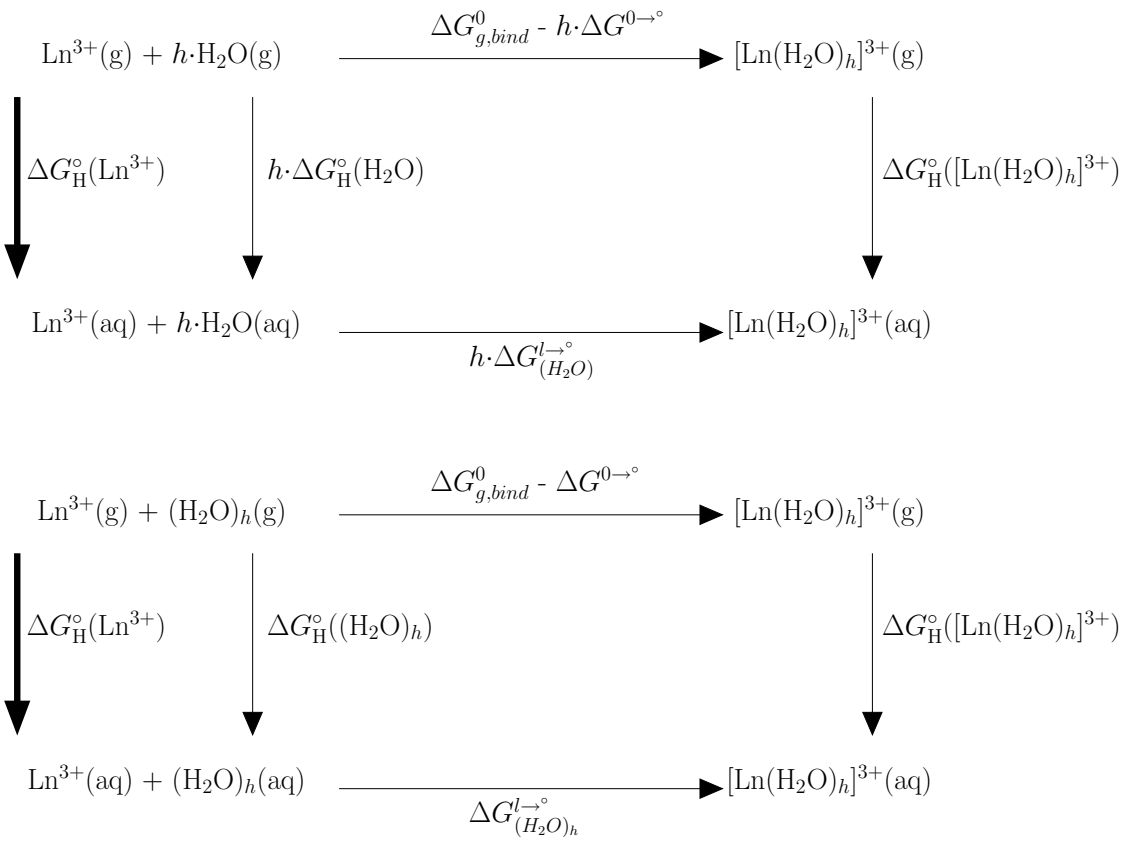

Fig. 1 Underlying thermodynamic cycles for the treatment of Ln^{III} hydration. At the top is the monomer cycle and at the bottom the cluster cycle.

S-2 $[Ln(H_2O)_7]^{3+}$

Table 1 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_7]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the DFT-BP86 level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	255.0	104.10	0.638	17.66	-32.22	-0.898	-2966.3	-2983.5
Ce	252.9	104.16	0.634	17.97	-32.75	-0.917	-3011.9	-3029.5
Pr	250.9	104.22	0.629	18.27	-33.09	-0.925	-3041.5	-3059.4
Nd	249.1	104.28	0.625	18.56	-33.40	-0.930	-3070.0	-3088.2
Pm	247.4	104.33	0.621	18.82	-33.69	-0.933	-3097.4	-3116.0
Sm	245.8	104.38	0.618	19.08	-33.97	-0.934	-3124.7	-3143.5
Eu	244.2	104.43	0.614	19.35	-34.27	-0.932	-3153.6	-3172.7
Gd	242.9	104.49	0.612	19.59	-34.53	-0.943	-3176.0	-3195.3
Tb	241.6	104.54	0.608	19.84	-34.82	-0.950	-3201.2	-3220.9
Dy	240.0	104.59	0.605	20.08	-35.09	-0.956	-3226.0	-3245.9
Ho	238.6	104.64	0.602	20.32	-35.36	-0.960	-3250.3	-3270.5
Er	237.3	104.69	0.599	20.55	-35.62	-0.964	-3274.4	-3294.9
Tm	236.1	104.73	0.596	20.76	-35.86	-0.964	-3297.5	-3318.2
Yb	234.9	104.78	0.593	20.99	-36.12	-0.963	-3322.8	-3343.8
Lu	234.1	104.84	0.591	21.16	-36.30	-0.947	-3345.1	-3366.3
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	255.0	104.10	0.638	15.97	-31.93	-0.055	-3077.3	-3070.2
Ce	252.9	104.16	0.634	16.29	-32.46	-0.074	-3122.9	-3116.3
Pr	250.9	104.22	0.629	16.59	-32.79	-0.082	-3152.5	-3146.2
Nd	249.1	104.28	0.625	16.87	-33.10	-0.087	-3181.0	-3175.0
Pm	247.4	104.33	0.621	17.14	-33.40	-0.090	-3208.4	-3202.7
Sm	245.8	104.38	0.618	17.40	-33.68	-0.091	-3235.7	-3230.3
Eu	244.2	104.43	0.614	17.66	-33.98	-0.089	-3264.6	-3259.5
Gd	242.9	104.49	0.612	17.90	-34.24	-0.100	-3286.9	-3282.1
Tb	241.6	104.54	0.608	18.15	-34.53	-0.107	-3312.2	-3307.6
Dy	240.0	104.59	0.605	18.39	-34.80	-0.113	-3337.0	-3332.7
Ho	238.6	104.64	0.602	18.63	-35.06	-0.117	-3361.3	-3357.3
Er	237.3	104.69	0.599	18.87	-35.32	-0.121	-3385.4	-3381.7
Tm	236.1	104.73	0.596	19.08	-35.56	-0.121	-3408.5	-3405.0
Yb	234.9	104.78	0.593	19.31	-35.82	-0.120	-3433.8	-3430.6
Lu	234.1	104.84	0.591	19.47	-36.01	-0.104	-3456.1	-3453.0

Table 2 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_7]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the DFT-B3LYP level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	255.9	104.42	0.635	17.69	-32.20	-0.899	-2964.3	-2982.1
Ce	253.8	104.48	0.631	18.01	-32.76	-0.918	-3012.5	-3030.6
Pr	251.8	104.54	0.626	18.32	-33.10	-0.927	-3042.6	-3061.2
Nd	250.0	104.59	0.622	18.62	-33.42	-0.932	-3071.5	-3090.3
Pm	248.2	104.64	0.618	18.89	-33.72	-0.935	-3099.9	-3119.1
Sm	246.6	104.69	0.614	19.16	-34.01	-0.936	-3128.0	-3147.5
Eu	245.0	104.74	0.611	19.43	-34.31	-0.934	-3157.3	-3177.1
Gd	243.6	104.79	0.608	19.67	-34.58	-0.945	-3180.0	-3200.0
Tb	242.0	104.84	0.604	19.93	-34.87	-0.953	-3205.8	-3226.0
Dy	240.6	104.88	0.601	20.18	-35.15	-0.958	-3230.9	-3251.5
Ho	239.2	104.93	0.598	20.43	-35.42	-0.962	-3256.0	-3276.9
Er	237.9	104.98	0.594	20.67	-35.69	-0.966	-3280.9	-3302.0
Tm	236.7	105.02	0.591	20.89	-35.94	-0.966	-3304.6	-3326.0
Yb	235.4	105.07	0.589	21.13	-36.20	-0.965	-3330.4	-3352.1
Lu	234.6	105.11	0.586	21.30	-36.40	-0.950	-3353.8	-3375.6
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	255.9	104.42	0.635	16.06	-32.01	-0.072	-3079.6	-3075.3
Ce	253.8	104.48	0.631	16.38	-32.57	-0.092	-3127.8	-3123.8
Pr	251.8	104.54	0.626	16.69	-32.91	-0.100	-3158.0	-3154.4
Nd	250.0	104.59	0.622	16.98	-33.22	-0.106	-3186.8	-3183.5
Pm	248.2	104.64	0.618	17.26	-33.52	-0.109	-3215.2	-3212.3
Sm	246.6	104.69	0.614	17.53	-33.82	-0.109	-3243.3	-3240.7
Eu	245.0	104.74	0.611	17.80	-34.12	-0.108	-3272.6	-3270.3
Gd	243.6	104.79	0.608	18.04	-34.39	-0.119	-3295.3	-3293.2
Tb	242.0	104.84	0.604	18.30	-34.68	-0.126	-3321.1	-3319.3
Dy	240.6	104.88	0.601	18.55	-34.95	-0.132	-3346.2	-3344.7
Ho	239.2	104.93	0.598	18.79	-35.23	-0.136	-3371.3	-3370.1
Er	237.9	104.98	0.594	19.04	-35.50	-0.140	-3396.2	-3395.2
Tm	236.7	105.02	0.591	19.26	-35.74	-0.140	-3419.9	-3419.2
Yb	235.4	105.07	0.589	19.49	-36.01	-0.139	-3445.7	-3445.3
Lu	234.6	105.11	0.586	19.67	-36.20	-0.124	-3469.1	-3468.8

Table 3 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_7]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the (SCS)-MP2 level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	253.5	103.84	0.571	17.32	-32.11	-0.963	-2935.6	-2965.7
Ce	251.3	103.91	0.560	17.63	-32.44	-0.989	-2960.4	-2990.9
Pr	249.3	103.98	0.553	17.94	-32.78	-1.000	-2989.5	-3020.3
Nd	247.5	104.04	0.548	18.22	-33.09	-1.006	-3017.6	-3048.7
Pm	245.8	104.09	0.543	18.50	-33.39	-1.010	-3045.4	-3076.7
Sm	244.1	104.15	0.539	18.81	-33.72	-1.011	-3077.3	-3108.9
Eu	242.5	104.20	0.535	19.03	-33.97	-1.010	-3101.9	-3133.7
Gd	241.1	104.26	0.532	19.27	-34.24	-1.021	-3124.4	-3156.4
Tb	239.7	104.31	0.529	19.53	-34.53	-1.028	-3150.0	-3182.4
Dy	238.2	104.37	0.526	19.78	-34.81	-1.033	-3175.4	-3208.0
Ho	236.9	104.43	0.523	20.02	-35.08	-1.037	-3200.5	-3233.3
Er	235.6	104.48	0.520	20.26	-35.35	-1.041	-3225.2	-3258.2
Tm	234.4	104.52	0.517	20.50	-35.60	-1.040	-3250.2	-3283.4
Yb	233.1	104.58	0.515	20.72	-35.85	-1.039	-3274.5	-3307.9
Lu	232.4	104.62	0.513	20.87	-36.02	-1.024	-3295.2	-3328.7
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	253.5	103.84	0.571	16.08	-32.34	-0.072	-3112.1	-3110.4
Ce	251.3	103.91	0.560	16.39	-32.68	-0.098	-3136.9	-3135.6
Pr	249.3	103.98	0.553	16.70	-33.01	-0.109	-3166.0	-3165.0
Nd	247.5	104.04	0.548	16.98	-33.32	-0.115	-3194.1	-3193.4
Pm	245.8	104.09	0.543	17.26	-33.62	-0.119	-3221.9	-3221.4
Sm	244.1	104.15	0.539	15.57	-33.96	-0.120	-3253.9	-3253.6
Eu	242.5	104.20	0.535	17.79	-34.21	-0.118	-3278.4	-3278.4
Gd	241.1	104.26	0.532	18.03	-34.48	-0.129	-3300.9	-3301.1
Tb	239.7	104.31	0.529	18.29	-34.77	-0.137	-3326.6	-3327.1
Dy	238.2	104.37	0.526	18.54	-35.04	-0.142	-3352.0	-3352.7
Ho	236.9	104.43	0.523	18.78	-35.32	-0.146	-3377.1	-3378.0
Er	235.6	104.48	0.520	19.03	-35.58	-0.149	-3401.8	-3402.9
Tm	234.4	104.52	0.517	19.26	-35.84	-0.149	-3426.7	-3428.1
Yb	233.1	104.58	0.515	19.48	-36.09	-0.148	-3451.0	-3452.6
Lu	232.4	104.62	0.513	19.63	-36.26	-0.133	-3471.8	-3473.5

S-3 $[Ln(H_2O)_8]^{3+}$

Table 4 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_8]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the DFT-BP86 level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	258.0	104.49	0.679	18.81	-32.63	-1.052	-2977.8	-2997.6
Ce	256.0	104.57	0.673	19.13	-32.99	-1.072	-3006.6	-3026.7
Pr	254.1	104.63	0.668	19.43	-33.34	-1.081	-3037.3	-3057.8
Nd	252.4	104.70	0.664	19.71	-33.66	-1.087	-3066.8	-3087.7
Pm	250.7	104.76	0.660	19.97	-33.96	-1.090	-3095.1	-3116.3
Sm	249.2	104.82	0.656	20.23	-34.26	-1.091	-3123.0	-3144.6
Eu	247.7	104.88	0.652	20.48	-34.55	-1.090	-3152.1	-3174.0
Gd	246.3	104.94	0.649	20.72	-34.82	-1.100	-3174.7	-3196.9
Tb	244.9	105.01	0.645	20.97	-35.11	-1.108	-3199.8	-3222.3
Dy	243.6	105.07	0.642	21.20	-35.37	-1.114	-3224.0	-3246.8
Ho	242.3	105.12	0.639	21.43	-35.64	-1.118	-3248.4	-3271.6
Er	241.1	105.18	0.636	21.66	-35.90	-1.121	-3272.5	-3295.9
Tm	240.0	105.22	0.633	21.86	-36.13	-1.122	-3295.1	-3318.8
Yb	238.8	105.28	0.630	22.08	-36.39	-1.121	-3319.7	-3343.7
Lu	238.1	105.33	0.628	22.24	-36.56	-1.105	-3341.2	-3365.4
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	258.0	104.49	0.679	16.62	-32.16	-0.026	-3108.2	-3096.8
Ce	256.0	104.57	0.673	16.93	-32.52	-0.047	-3136.9	-3126.0
Pr	254.1	104.63	0.668	17.23	-32.87	-0.055	-3167.6	-3157.1
Nd	252.4	104.70	0.664	17.52	-33.19	-0.061	-3197.1	-3186.9
Pm	250.7	104.76	0.660	17.78	-33.50	-0.064	-3225.4	-3215.6
Sm	249.2	104.82	0.656	18.03	-33.79	-0.065	-3253.3	-3243.8
Eu	247.7	104.88	0.652	18.29	-34.09	-0.064	-3282.4	-3273.3
Gd	246.3	104.94	0.649	18.53	-34.35	-0.075	-3305.1	-3296.2
Tb	244.9	105.01	0.645	18.77	-34.64	-0.082	-3330.1	-3321.5
Dy	243.6	105.07	0.642	19.01	-34.90	-0.088	-3354.3	-3346.1
Ho	242.3	105.12	0.639	19.24	-35.17	-0.092	-3378.7	-3370.8
Er	241.1	105.18	0.636	19.46	-35.43	-0.096	-3402.8	-3395.1
Tm	240.0	105.22	0.633	19.67	-35.67	-0.096	-3425.4	-3418.0
Yb	238.8	105.28	0.630	19.89	-35.92	-0.095	-3450.1	-3443.0
Lu	238.1	105.33	0.628	20.04	-36.09	-0.080	-3471.6	-3464.6

Table 5 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_8]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the DFT-B3LYP level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	259.1	104.83	0.674	18.91	-32.67	-1.054	-2980.5	-3001.0
Ce	257.0	104.90	0.669	19.23	-33.04	-1.075	-3010.5	-3031.4
Pr	255.0	104.96	0.663	19.54	-33.40	-1.084	-3042.0	-3063.3
Nd	253.3	105.02	0.659	19.83	-33.73	-1.090	-3072.2	-3093.9
Pm	251.6	105.08	0.654	20.10	-34.04	-1.093	-3101.5	-3123.6
Sm	250.0	105.13	0.650	20.36	-34.34	-1.094	-3130.2	-3152.7
Eu	248.4	105.19	0.646	20.63	-34.65	-1.093	-3160.0	-3182.8
Gd	247.1	105.25	0.643	20.87	-34.92	-1.104	-3183.0	-3206.1
Tb	245.6	105.31	0.640	21.12	-35.22	-1.112	-3210.0	-3233.4
Dy	244.3	105.37	0.636	21.36	-35.50	-1.118	-3234.8	-3258.5
Ho	243.0	105.42	0.633	21.60	-35.77	-1.122	-3259.8	-3283.8
Er	241.8	105.47	0.629	21.83	-36.04	-1.126	-3284.4	-3308.7
Tm	240.6	105.51	0.627	22.04	-36.28	-1.126	-3307.7	-3332.4
Yb	239.5	105.57	0.624	22.27	-36.54	-1.125	-3332.9	-3357.8
Lu	238.7	105.61	0.622	22.43	-36.72	-1.110	-3355.2	-3380.3
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	259.1	104.83	0.674	16.81	-32.34	-0.050	-3117.6	-3109.5
Ce	257.0	104.90	0.669	17.13	-32.71	-0.071	-3147.5	-3139.9
Pr	255.0	104.96	0.663	17.44	-33.06	-0.080	-3179.0	-3171.8
Nd	253.3	105.02	0.659	17.73	-33.39	-0.086	-3209.2	-3202.4
Pm	251.6	105.08	0.654	18.00	-33.71	-0.089	-3238.5	-3232.1
Sm	250.0	105.13	0.650	18.26	-34.01	-0.090	-3267.3	-3261.2
Eu	248.4	105.19	0.646	18.53	-34.32	-0.089	-3297.1	-3291.3
Gd	247.1	105.25	0.643	18.77	-34.59	-0.100	-3320.0	-3314.6
Tb	245.6	105.31	0.640	19.02	-34.89	-0.108	-3347.1	-3341.9
Dy	244.3	105.37	0.636	19.26	-35.17	-0.114	-3371.9	-3367.0
Ho	243.0	105.42	0.633	19.50	-35.44	-0.118	-3396.8	-3392.3
Er	241.8	105.47	0.629	19.73	-35.70	-0.122	-3421.4	-3417.2
Tm	240.6	105.51	0.627	19.94	-35.95	-0.122	-3444.8	-3440.9
Yb	239.5	105.57	0.624	20.17	-36.21	-0.121	-3469.9	-3466.3
Lu	238.7	105.61	0.622	20.33	-36.39	-0.106	-3492.2	-3488.8

Table 6 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_8]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the (SCS)-MP2 level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	256,1	104,24	0,580	18,61	-32,44	-1,149	-2930,4	-2965,5
Ce	254,0	104,32	0,574	18,93	-32,81	-1,170	-2959,5	-2994,9
Pr	252,0	104,39	0,569	19,23	-33,15	-1,178	-2990,7	-3026,5
Nd	250,3	104,46	0,565	19,52	-33,48	-1,183	-3020,6	-3056,7
Pm	248,6	104,52	0,561	19,79	-33,79	-1,186	-3049,7	-3086,1
Sm	247,0	104,59	0,558	20,05	-34,09	-1,187	-3078,3	-3115,0
Eu	245,5	104,65	0,554	20,32	-34,39	-1,186	-3108,1	-3145,0
Gd	244,1	104,71	0,551	20,56	-34,67	-1,196	-3131,3	-3168,5
Tb	242,7	104,77	0,548	20,81	-34,96	-1,204	-3156,8	-3194,3
Dy	241,4	104,84	0,545	21,05	-35,23	-1,209	-3182,0	-3219,8
Ho	240,1	104,90	0,542	21,29	-35,50	-1,212	-3207,1	-3245,1
Er	238,9	104,96	0,539	21,52	-35,77	-1,216	-3231,8	-3270,1
Tm	237,8	105,01	0,537	21,75	-36,03	-1,215	-3256,8	-3295,3
Yb	236,6	105,06	0,535	21,96	-36,27	-1,214	-3280,8	-3319,5
Lu	235,9	105,11	0,533	22,10	-36,43	-1,199	-3300,7	-3339,6
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	256,1	104,24	0,580	16,94	-32,59	-0,089	-3130,3	-3127,5
Ce	254,0	104,32	0,574	17,26	-32,95	-0,110	-3159,4	-3157,0
Pr	252,0	104,39	0,569	17,56	-33,30	-0,118	-3190,5	-3188,5
Nd	250,3	104,46	0,565	17,85	-33,63	-0,123	-3220,5	-3218,8
Pm	248,6	104,52	0,561	18,12	-33,94	-0,126	-3249,5	-3248,2
Sm	247,0	104,59	0,558	18,38	-34,24	-0,127	-3278,1	-3277,1
Eu	245,5	104,65	0,554	18,65	-34,54	-0,126	-3307,9	-3307,1
Gd	244,1	104,71	0,551	18,89	-34,81	-0,136	-3331,1	-3330,6
Tb	242,7	104,77	0,548	19,14	-35,10	-0,144	-3356,7	-3356,4
Dy	241,4	104,84	0,545	19,38	-35,38	-0,149	-3381,8	-3381,8
Ho	240,1	104,90	0,542	19,62	-35,65	-0,152	-3406,9	-3407,2
Er	238,9	104,96	0,539	19,85	-35,92	-0,156	-3431,6	-3432,1
Tm	237,8	105,01	0,537	20,08	-36,17	-0,155	-3456,7	-3457,4
Yb	236,6	105,06	0,535	20,29	-36,42	-0,154	-3480,6	-3481,5
Lu	235,9	105,11	0,533	20,43	-36,58	-0,139	-3500,5	-3501,6

S-4 $[Ln(H_2O)_9]^{3+}$

Table 7 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_9]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the DFT-BP86 level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	261.8	104.84	0.732	19.64	-32.71	-1.194	-2960.9	-2982.1
Ce	259.8	104.92	0.727	19.95	-33.06	-1.214	-2988.9	-3010.6
Pr	258.1	104.99	0.723	20.23	-33.40	-1.222	-3018.9	-3040.9
Nd	256.4	105.06	0.719	20.50	-33.71	-1.227	-3047.4	-3069.7
Pm	254.9	105.11	0.715	20.75	-34.00	-1.229	-3074.5	-3097.6
Sm	253.5	105.17	0.712	20.99	-34.28	-1.230	-3101.2	-3124.1
Eu	252.1	105.23	0.708	21.23	-34.56	-1.228	-3128.8	-3152.0
Gd	250.8	105.30	0.706	21.45	-34.81	-1.239	-3150.1	-3173.6
Tb	249.5	105.36	0.703	21.68	-35.07	-1.246	-3173.5	-3197.3
Dy	248.4	105.42	0.700	21.90	-35.32	-1.251	-3196.1	-3220.1
Ho	247.2	105.47	0.697	22.11	-35.57	-1.255	-3218.8	-3243.1
Er	246.1	105.52	0.694	22.32	-35.82	-1.258	-3242.1	-3266.7
Tm	245.1	105.57	0.692	22.51	-36.04	-1.257	-3263.1	-3287.9
Yb	244.1	105.61	0.690	22.71	-36.27	-1.256	-3286.1	-3311.1
Lu	243.5	105.65	0.690	22.85	-36.43	-1.239	-3306.5	-3331.6
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	261.8	104.84	0.732	17.14	-32.11	-0.030	-3101.2	-3088.2
Ce	259.8	104.92	0.727	17.45	-32.46	-0.050	-3129.2	-3116.6
Pr	258.1	104.99	0.723	17.73	-32.79	-0.058	-3159.2	-3147.0
Nd	256.4	105.06	0.719	18.00	-33.10	-0.063	-3187.7	-3175.8
Pm	254.9	105.11	0.715	18.25	-33.39	-0.066	-3214.8	-3203.2
Sm	253.5	105.17	0.712	18.49	-33.67	-0.067	-3241.4	-3230.2
Eu	252.1	105.23	0.708	18.73	-33.95	-0.065	-3269.0	-3258.1
Gd	250.8	105.30	0.706	18.95	-34.21	-0.075	-3290.3	-3279.6
Tb	249.5	105.36	0.703	19.18	-34.47	-0.083	-3313.8	-3303.4
Dy	248.4	105.42	0.700	19.40	-34.72	-0.087	-3336.3	-3326.2
Ho	247.2	105.47	0.697	19.61	-34.97	-0.091	-3359.0	-3349.1
Er	246.1	105.52	0.694	19.82	-35.22	-0.095	-3382.4	-3372.8
Tm	245.1	105.57	0.692	20.01	-35.44	-0.094	-3403.4	-3394.0
Yb	244.1	105.61	0.690	20.21	-35.67	-0.092	-3426.4	-3417.2
Lu	243.5	105.65	0.690	20.35	-35.83	-0.076	-3446.8	-3437.7

Table 8 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_9]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the DFT-B3LYP level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	262.6	105.18	0.721	19.80	-32.79	-1.203	-2965.8	-3099.0
Ce	260.6	105.25	0.715	20.11	-33.16	-1.223	-2996.0	-3129.6
Pr	258.7	105.32	0.711	20.40	-33.51	-1.231	-3026.6	-3160.6
Nd	257.0	105.38	0.706	20.68	-33.82	-1.237	-3055.6	-3190.0
Pm	255.4	105.43	0.703	20.93	-34.12	-1.240	-3083.6	-3218.3
Sm	253.9	105.49	0.699	21.18	-34.41	-1.241	-3110.9	-3245.9
Eu	252.3	105.54	0.696	21.43	-34.70	-1.239	-3139.1	-3274.5
Gd	251.0	105.60	0.693	21.65	-34.95	-1.250	-3160.6	-3296.2
Tb	249.6	105.66	0.690	21.89	-35.22	-1.257	-3184.5	-3320.4
Dy	248.3	105.71	0.687	22.11	-35.48	-1.262	-3207.5	-3343.8
Ho	247.0	105.76	0.683	22.33	-35.73	-1.266	-3230.7	-3367.3
Er	245.8	105.81	0.681	22.54	-35.98	-1.269	-3253.6	-3390.4
Tm	244.7	105.85	0.679	22.74	-36.20	-1.269	-3275.2	-3412.2
Yb	243.5	105.90	0.677	22.94	-36.43	-1.267	-3298.5	-3435.8
Lu	242.7	105.93	0.676	23.09	-36.60	-1.251	-3319.5	-3456.9
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	262.6	105.18	0.721	17.30	-32.35	-0.065	-3113.9	-3105.2
Ce	260.6	105.25	0.715	17.61	-32.72	-0.086	-3144.1	-3135.8
Pr	258.7	105.32	0.711	17.90	-33.06	-0.094	-3174.7	-3166.8
Nd	257.0	105.38	0.706	18.18	-33.38	-0.099	-3203.8	-3196.2
Pm	255.4	105.43	0.703	18.44	-33.68	-0.102	-3231.7	-3224.5
Sm	253.9	105.49	0.699	18.68	-33.97	-0.103	-3259.0	-3252.1
Eu	252.3	105.54	0.696	18.93	-34.25	-0.101	-3287.2	-3280.7
Gd	251.0	105.60	0.693	19.15	-34.51	-0.112	-3308.7	-3302.4
Tb	249.6	105.66	0.690	19.39	-34.78	-0.119	-3332.6	-3326.6
Dy	248.3	105.71	0.687	19.61	-35.04	-0.125	-3355.7	-3350.0
Ho	247.0	105.76	0.683	19.83	-35.29	-0.128	-3378.9	-3373.5
Er	245.8	105.81	0.681	20.04	-35.53	-0.132	-3401.7	-3396.6
Tm	244.7	105.85	0.679	20.24	-35.76	-0.131	-3423.3	-3418.4
Yb	243.5	105.90	0.677	20.44	-35.99	-0.130	-3446.7	-3442.0
Lu	242.7	105.93	0.676	20.59	-36.16	-0.113	-3467.7	-3463.1

Table 9 Mean Ln^{3+}–O distances d_{LnO} in pm, average HOH angle ϕ_{HOH} in deg., gas phase binding and hydrations energies D_0 and ΔE_H in eV, absolute entropies of $[Ln(H_2O)_9]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} and Gibbs free energies of hydration $\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$ and ΔG°_H in kJ mol^{-1} calculated at the (SCS)-MP2 level of theory.

monomer cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	259.1	104.59	0.609	19.57	-32.62	-1.314	-2916.5	-2956.3
Ce	257.1	104.67	0.605	19.88	-32.98	-1.334	-2944.9	-2985.1
Pr	255.1	104.74	0.600	20.17	-33.32	-1.342	-2975.5	-3016.0
Nd	253.5	104.80	0.596	20.44	-33.63	-1.347	-3004.1	-3045.0
Pm	251.8	104.86	0.593	20.70	-33.93	-1.349	-3032.0	-3073.2
Sm	250.3	104.92	0.590	20.94	-34.21	-1.350	-3059.3	-3100.7
Eu	248.8	104.98	0.587	21.19	-34.50	-1.348	-3087.7	-3129.4
Gd	247.5	105.04	0.584	21.41	-34.76	-1.358	-3109.4	-3151.3
Tb	246.2	105.09	0.581	21.65	-35.03	-1.365	-3133.2	-3175.4
Dy	244.9	105.15	0.579	21.87	-35.28	-1.370	-3156.5	-3199.0
Ho	243.6	105.21	0.576	22.08	-35.54	-1.373	-3180.6	-3223.3
Er	242.4	105.26	0.574	22.30	-35.79	-1.376	-3203.3	-3246.2
Tm	241.3	105.31	0.572	22.49	-36.01	-1.376	-3225.1	-3268.2
Yb	240.2	105.36	0.570	22.69	-36.24	-1.374	-3248.2	-3291.5
Lu	239.5	105.39	0.569	22.82	-36.39	-1.358	-3266.9	-3310.3
cluster cycle								
Ln^{3+}	d_{LnO}	ϕ_{HOH}	S°	D_0	ΔE_H	ΔS°_H	$\Delta G^\circ_H(\Delta E_H \sim \Delta H^\circ_H)$	ΔG°_H
La	259.1	104.59	0.609	17.68	-32.74	-0.110	-3138.1	-3136.2
Ce	257.1	104.67	0.605	17.98	-33.09	-0.130	-3166.6	-3165.0
Pr	255.1	104.74	0.600	18.28	-33.43	-0.138	-3197.1	-3196.0
Nd	253.5	104.80	0.596	18.55	-33.74	-0.143	-3225.7	-3224.9
Pm	251.8	104.86	0.593	18.80	-34.04	-0.145	-3253.7	-3253.1
Sm	250.3	104.92	0.590	19.05	-34.33	-0.146	-3280.9	-3280.7
Eu	248.8	104.98	0.587	19.30	-34.61	-0.144	-3309.3	-3309.3
Gd	247.5	105.04	0.584	19.52	-34.87	-0.154	-3331.0	-3331.2
Tb	246.2	105.09	0.581	19.75	-35.14	-0.161	-3354.9	-3355.3
Dy	244.9	105.15	0.579	19.97	-35.40	-0.166	-3378.2	-3378.9
Ho	243.6	105.21	0.576	20.19	-35.66	-0.169	-3402.2	-3403.2
Er	242.4	105.26	0.574	20.40	-35.90	-0.172	-3424.9	-3426.1
Tm	241.3	105.31	0.572	20.60	-36.12	-0.172	-3446.7	-3448.1
Yb	240.2	105.36	0.570	20.80	-36.36	-0.170	-3469.8	-3471.4
Lu	239.5	105.39	0.569	20.93	-36.50	-0.154	-3488.5	-3490.2

S-5 $[Ln(H_2O)_7 \cdot H_2O]^{3+}$

Table 10 Mean Ln^{3+}–O distances for 1st and 2nd hydration shell $d_{LnO(1)}$ and $d_{LnO(2)}$ in pm, average HOH angle in 1st and 2nd hydration shell $\phi_{HOH(1)}$ and $\phi_{HOH(2)}$ in deg., gas phase binding and hydration energies D_0 and ΔE_H in eV, entropies of $[Ln(H_2O)_7 \cdot H_2O]^{3+}$ and hydration entropies S° and ΔS_H° in kJ mol^{-1} K^{-1} at the DFT-BP86 level of theory.

monomer cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	254.4	104.67	432.9	104.37	0.680	18.95	-32.54	-1.051
Ce	252.4	104.74	431.2	104.38	0.675	19.27	-32.90	-1.071
Pr	250.4	104.80	429.6	104.39	0.671	19.58	-33.22	-1.079
Nd	248.6	104.86	428.2	104.40	0.667	19.87	-33.57	-1.084
Pm	246.9	104.92	426.9	104.39	0.664	20.15	-33.88	-1.086
Sm	245.3	104.97	425.7	104.40	0.660	20.41	-34.17	-1.087
Eu	243.8	105.03	424.5	104.41	0.657	20.69	-34.47	-1.085
Gd	242.4	105.09	423.5	104.40	0.655	20.93	-34.75	-1.095
Tb	240.9	105.15	422.4	104.41	0.651	21.19	-35.03	-1.103
Dy	239.5	105.20	421.4	104.42	0.648	21.44	-35.30	-1.108
Ho	238.2	105.25	420.4	104.42	0.645	21.68	-35.58	-1.112
Er	236.9	105.30	419.4	104.42	0.642	21.93	-35.85	-1.116
Tm	235.7	105.36	418.6	104.42	0.639	22.15	-36.09	-1.115
Yb	234.5	105.41	417.7	104.42	0.637	22.38	-36.36	-1.114
Lu	233.7	105.45	417.0	104.42	0.634	22.55	-36.54	-1.099
cluster cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	254.4	104.67	432.9	104.37	0.680	16.75	-32.07	-0.025
Ce	252.4	104.74	431.2	104.38	0.675	17.08	-32.43	-0.045
Pr	250.4	104.80	429.6	104.39	0.671	17.39	-32.75	-0.053
Nd	248.6	104.86	428.2	104.40	0.667	17.68	-33.10	-0.058
Pm	246.9	104.92	426.9	104.39	0.664	17.96	-33.41	-0.060
Sm	245.3	104.97	425.7	104.40	0.660	18.22	-33.70	-0.061
Eu	243.8	105.03	424.5	104.41	0.657	18.49	-34.01	-0.059
Gd	242.4	105.09	423.5	104.40	0.655	18.74	-34.28	-0.069
Tb	240.9	105.15	422.4	104.41	0.651	19.00	-34.56	-0.077
Dy	239.5	105.20	421.4	104.42	0.648	19.25	-34.83	-0.082
Ho	238.2	105.25	420.4	104.42	0.645	19.49	-35.11	-0.086
Er	236.9	105.30	419.4	104.42	0.642	19.73	-35.38	-0.090
Tm	235.7	105.36	418.6	104.42	0.639	19.95	-35.63	-0.090
Yb	234.5	105.41	417.7	104.42	0.637	20.19	-35.89	-0.088
Lu	233.7	105.45	417.0	104.42	0.634	20.36	-36.08	-0.073

Table 11 Mean Ln^{3+}–O distances for 1st and 2nd hydration shell $d_{\mathrm{LnO(1)}}$ and $d_{\mathrm{LnO(2)}}$ in pm, average HOH angle in 1st and 2nd hydration shell $\phi_{\mathrm{HOH(1)}}$ and $\phi_{\mathrm{HOH(2)}}$ in deg., gas phase binding and hydration energies D_0 and ΔE_H in eV, entropies of $[Ln(H_2O)_7 \cdot H_2O]^{3+}$ and hydration entropies S° and ΔS_H° in kJ mol^{-1} K^{-1} at the DFT-B3LYP level of theory.

monomer cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	255,4	104,96	435,7	104,52	0,675	18,94	-32,51	-1,053
Ce	253,3	105,02	434,1	104,52	0,670	19,27	-32,88	-1,073
Pr	251,3	105,07	432,5	104,53	0,666	19,59	-33,23	-1,081
Nd	249,5	105,13	431,1	104,54	0,662	19,89	-33,56	-1,087
Pm	247,7	105,18	429,8	104,54	0,658	20,18	-33,87	-1,089
Sm	246,1	105,23	428,6	104,54	0,655	20,45	-34,17	-1,090
Eu	244,5	105,28	427,4	104,54	0,652	20,73	-34,48	-1,088
Gd	243,1	105,34	426,4	104,54	0,649	20,98	-34,76	-1,098
Tb	241,6	105,39	425,3	104,54	0,646	21,25	-35,06	-1,106
Dy	240,2	105,44	424,3	104,54	0,643	21,50	-35,34	-1,110
Ho	238,8	105,49	423,3	104,54	0,640	21,75	-35,61	-1,114
Er	237,5	105,54	422,4	104,54	0,638	22,00	-35,89	-1,117
Tm	236,3	105,59	421,5	104,54	0,635	22,23	-36,14	-1,118
Yb	235,1	105,64	420,6	104,54	0,632	22,47	-36,41	-1,116
Lu	234,3	105,68	420,0	104,54	0,630	22,65	-36,60	-1,101
cluster cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	255.4	104.96	435.7	104.52	0.675	16.84	-32.18	-0.049
Ce	253.3	105.02	434.1	104.52	0.670	17.17	-32.55	-0.069
Pr	251.3	105.07	432.5	104.53	0.666	17.49	-32.90	-0.077
Nd	249.5	105.13	431.1	104.54	0.662	17.79	-33.23	-0.083
Pm	247.7	105.18	429.8	104.54	0.658	18.08	-33.54	-0.085
Sm	246.1	105.23	428.6	104.54	0.655	18.35	-33.84	-0.086
Eu	244.5	105.28	427.4	104.54	0.652	18.63	-34.15	-0.084
Gd	243.1	105.34	426.4	104.54	0.649	18.88	-34.43	-0.094
Tb	241.6	105.39	425.3	104.54	0.646	19.15	-34.73	-0.102
Dy	240.2	105.44	424.3	104.54	0.643	19.40	-35.01	-0.106
Ho	238.8	105.49	423.3	104.54	0.640	19.65	-35.28	-0.110
Er	237.5	105.54	422.4	104.54	0.638	19.90	-35.55	-0.113
Tm	236.3	105.59	421.5	104.54	0.635	20.13	-35.81	-0.114
Yb	235.1	105.64	420.6	104.54	0.632	20.37	-36.08	-0.112
Lu	234.3	105.68	420.0	104.54	0.630	20.55	-36.27	-0.097

Table 12 Mean Ln^{3+}–O distances for 1st and 2nd hydration shell $d_{\mathrm{LnO(1)}}$ and $d_{\mathrm{LnO(2)}}$ in pm, average HOH angle in 1st and 2nd hydration shell $\phi_{\mathrm{HOH(1)}}$ and $\phi_{\mathrm{HOH(2)}}$ in deg., gas phase binding and hydration energies D_0 and ΔE_H in eV, entropies of $[Ln(H_2O)_7 \cdot H_2O]^{3+}$ and hydration entropies S° and ΔS_H° in kJ mol^{-1} K^{-1} at the (SCS)-MP2 level of theory.

monomer cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	253.0	104.39	433.5	103.76	0.600	18.50	-32.10	-1.128
Ce	250.9	104.42	431.9	103.77	0.594	18.82	-32.43	-1.150
Pr	248.9	104.53	430.3	103.77	0.589	19.13	-32.80	-1.158
Nd	247.1	104.59	428.9	103.78	0.585	19.43	-33.13	-1.164
Pm	245.3	104.65	427.6	103.78	0.581	19.71	-33.44	-1.167
Sm	243.7	104.71	426.5	103.78	0.577	20.03	-33.79	-1.168
Eu	242.1	104.77	425.2	103.78	0.573	20.25	-34.05	-1.167
Gd	240.7	104.82	424.3	103.79	0.570	20.51	-34.31	-1.178
Tb	239.2	104.88	423.1	103.78	0.567	20.77	-34.61	-1.185
Dy	237.8	104.93	422.1	103.79	0.564	21.02	-34.89	-1.190
Ho	236.5	104.99	421.2	103.80	0.560	21.27	-35.17	-1.194
Er	235.1	105.05	420.3	103.79	0.558	21.52	-35.45	-1.198
Tm	234.0	105.10	419.5	103.80	0.555	21.76	-35.71	-1.197
Yb	232.8	105.15	418.6	103.80	0.553	21.99	-35.97	-1.196
Lu	232.0	105.19	418.0	103.80	0.551	22.14	-36.14	-1.181
cluster cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	253.0	104.39	433.5	103.76	0.600	16.83	-32.25	-0.069
Ce	250.9	104.42	431.9	103.77	0.594	17.15	-32.57	-0.090
Pr	248.9	104.53	430.3	103.77	0.589	17.46	-32.95	-0.098
Nd	247.1	104.59	428.9	103.78	0.585	17.76	-33.27	-0.104
Pm	245.3	104.65	427.6	103.78	0.581	18.04	-33.58	-0.107
Sm	243.7	104.71	426.5	103.78	0.577	18.35	-33.93	-0.107
Eu	242.1	104.77	425.2	103.78	0.573	18.58	-34.19	-0.107
Gd	240.7	104.82	424.3	103.79	0.570	18.83	-34.46	-0.118
Tb	239.2	104.88	423.1	103.78	0.567	19.10	-34.75	-0.125
Dy	237.8	104.93	422.1	103.79	0.564	19.35	-35.04	-0.130
Ho	236.5	104.99	421.2	103.80	0.560	19.60	-35.32	-0.134
Er	235.1	105.05	420.3	103.79	0.558	19.85	-35.59	-0.138
Tm	234.0	105.10	419.5	103.80	0.555	20.09	-35.86	-0.137
Yb	232.8	105.15	418.6	103.80	0.553	20.32	-36.12	-0.136
Lu	232.0	105.19	418.0	103.80	0.551	20.47	-36.29	-0.121

S-6 $[Ln(H_2O)_8 \cdot H_2O]^{3+}$

Table 13 Mean Ln^{3+}–O distances for 1st and 2nd hydration shell $d_{LnO(1)}$ and $d_{LnO(2)}$ in pm, average HOH angle in 1st and 2nd hydration shell $\phi_{HOH(1)}$ and $\phi_{HOH(2)}$ in deg., gas phase binding and hydration energies D_0 and ΔE_H in eV, entropies of $[Ln(H_2O)_8 \cdot H_2O]^{3+}$ and hydration entropies S° and ΔS°_H in kJ mol^{-1} K^{-1} at the DFT-BP86 level of theory.

monomer cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS°_H
La	257.9	104.95	437.8	104.24	0.723	19.97	-32.80	-1.203
Ce	255.8	105.03	436.0	104.25	0.718	20.29	-33.17	-1.223
Pr	253.9	105.09	434.4	104.24	0.713	20.59	-33.52	-1.231
Nd	252.2	105.15	432.9	104.24	0.709	20.88	-33.85	-1.236
Pm	250.5	105.21	431.5	104.24	0.705	21.15	-34.15	-1.239
Sm	249.0	105.27	430.2	104.24	0.702	21.41	-34.45	-1.240
Eu	247.5	105.32	428.9	104.24	0.698	21.67	-34.75	-1.238
Gd	246.2	105.38	427.8	104.24	0.696	21.91	-35.02	-1.249
Tb	244.8	105.45	426.6	104.24	0.692	22.17	-35.30	-1.257
Dy	243.4	105.50	425.5	104.25	0.689	22.40	-35.57	-1.262
Ho	242.2	105.55	424.5	104.24	0.686	22.64	-35.84	-1.266
Er	240.9	105.61	423.4	104.24	0.683	22.87	-36.10	-1.269
Tm	239.9	105.65	422.5	104.24	0.680	23.08	-36.34	-1.269
Yb	238.7	105.70	421.5	104.24	0.678	23.30	-36.59	-1.268
Lu	238.0	105.75	420.9	104.23	0.676	23.46	-36.77	-1.253
cluster cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS°_H
La	257.9	104.95	437.8	104.24	0.723	17.47	-32.20	-0.040
Ce	255.8	105.03	436.0	104.25	0.718	17.79	-32.57	-0.059
Pr	253.9	105.09	434.4	104.24	0.713	18.10	-32.92	-0.068
Nd	252.2	105.15	432.9	104.24	0.709	18.38	-33.24	-0.073
Pm	250.5	105.21	431.5	104.24	0.705	18.65	-33.55	-0.076
Sm	249.0	105.27	430.2	104.24	0.702	18.91	-33.84	-0.076
Eu	247.5	105.32	428.9	104.24	0.698	19.18	-34.14	-0.075
Gd	246.2	105.38	427.8	104.24	0.696	19.41	-34.41	-0.085
Tb	244.8	105.45	426.6	104.24	0.692	19.67	-34.70	-0.093
Dy	243.4	105.50	425.5	104.25	0.689	19.90	-34.97	-0.098
Ho	242.2	105.55	424.5	104.24	0.686	20.14	-35.23	-0.102
Er	240.9	105.61	423.4	104.24	0.683	20.37	-35.50	-0.106
Tm	239.9	105.65	422.5	104.24	0.680	20.58	-35.73	-0.106
Yb	238.7	105.70	421.5	104.24	0.678	20.80	-35.99	-0.105
Lu	238.0	105.75	420.9	104.23	0.676	20.96	-36.16	-0.089

Table 14 Mean Ln^{3+}–O distances for 1st and 2nd hydration shell $d_{\mathrm{LnO(1)}}$ and $d_{\mathrm{LnO(2)}}$ in pm, average HOH angle in 1st and 2nd hydration shell $\phi_{\mathrm{HOH(1)}}$ and $\phi_{\mathrm{HOH(2)}}$ in deg., gas phase binding and hydration energies D_0 and ΔE_H in eV, entropies of $[Ln(H_2O)_8 \cdot H_2O]^{3+}$ and hydration entropies S° and ΔS_H° in kJ mol^{-1} K^{-1} at the DFT-B3LYP level of theory.

monomer cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	258.8	105.27	440.8	104.42	0.719	20.03	-32.80	-1.205
Ce	256.7	105.34	439.1	104.42	0.714	20.36	-33.18	-1.225
Pr	254.8	105.39	437.4	104.42	0.709	20.67	-33.54	-1.233
Nd	253.1	105.45	435.9	104.41	0.705	20.97	-33.88	-1.238
Pm	251.4	105.50	434.5	104.42	0.701	21.25	-34.19	-1.241
Sm	249.8	105.55	433.2	104.42	0.697	21.52	-34.50	-1.242
Eu	248.3	105.61	431.9	104.41	0.693	21.79	-34.80	-1.241
Gd	246.9	105.67	430.8	104.41	0.691	22.03	-35.08	-1.252
Tb	245.5	105.72	429.6	104.41	0.687	22.29	-35.38	-1.260
Dy	244.2	105.77	428.5	104.41	0.684	22.53	-35.65	-1.265
Ho	242.9	105.82	427.4	104.41	0.680	22.77	-35.92	-1.269
Er	241.6	105.89	426.4	104.41	0.677	23.01	-36.19	-1.272
Tm	240.5	105.91	425.5	104.40	0.675	23.22	-36.44	-1.272
Yb	239.4	105.96	424.5	104.30	0.672	23.45	-36.69	-1.271
Lu	238.6	106.00	423.9	104.40	0.670	23.62	-36.88	-1.256
cluster cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	258.8	105.27	440.8	104.42	0.719	17.63	-32.36	-0.067
Ce	256.7	105.34	439.1	104.42	0.714	17.96	-32.74	-0.087
Pr	254.8	105.39	437.4	104.42	0.709	18.28	-33.10	-0.096
Nd	253.1	105.45	435.9	104.41	0.705	18.57	-33.43	-0.101
Pm	251.4	105.50	434.5	104.42	0.701	18.85	-33.75	-0.104
Sm	249.8	105.55	433.2	104.42	0.697	19.12	-34.06	-0.105
Eu	248.3	105.61	431.9	104.41	0.693	19.39	-34.36	-0.103
Gd	246.9	105.67	430.8	104.41	0.691	19.63	-34.64	-0.114
Tb	245.5	105.72	429.6	104.41	0.687	19.89	-34.93	-0.122
Dy	244.2	105.77	428.5	104.41	0.684	20.13	-35.21	-0.127
Ho	242.9	105.82	427.4	104.41	0.680	20.37	-35.48	-0.131
Er	241.6	105.89	426.4	104.41	0.677	20.61	-35.75	-0.135
Tm	240.5	105.91	425.5	104.40	0.675	20.83	-35.99	-0.135
Yb	239.4	105.96	424.5	104.30	0.672	21.06	-36.25	-0.134
Lu	238.6	106.00	423.9	104.40	0.670	21.22	-36.44	-0.119

Table 15 Mean Ln^{3+}–O distances for 1st and 2nd hydration shell $d_{\mathrm{LnO(1)}}$ and $d_{\mathrm{LnO(2)}}$ in pm, average HOH angle in 1st and 2nd hydration shell $\phi_{\mathrm{HOH(1)}}$ and $\phi_{\mathrm{HOH(2)}}$ in deg., gas phase binding and hydration energies D_0 and ΔE_H in eV, entropies of $[Ln(H_2O)_8 \cdot H_2O]^{3+}$ and hydration entropies S° and ΔS_H° in kJ mol^{-1} K^{-1} at the (SCS)-MP2 level of theory.

monomer cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	255.8	104.67	437.7	103.62	0.619	19.67	-32.50	-1.304
Ce	253.7	104.74	435.9	103.63	0.614	19.99	-32.87	-1.324
Pr	251.7	104.81	434.3	103.62	0.609	20.30	-33.23	-1.333
Nd	250.0	104.87	432.8	103.62	0.605	20.59	-33.56	-1.338
Pm	248.3	104.93	431.4	103.62	0.602	20.87	-33.87	-1.341
Sm	246.8	104.99	430.2	103.62	0.598	21.14	-34.17	-1.342
Eu	245.2	105.05	428.9	103.62	0.595	21.41	-34.48	-1.340
Gd	243.9	105.10	427.8	103.62	0.592	21.65	-34.75	-1.351
Tb	242.5	105.16	426.7	103.61	0.589	21.91	-35.04	-1.358
Dy	241.2	105.23	425.7	103.61	0.586	22.15	-35.32	-1.363
Ho	240.0	105.28	424.6	103.61	0.583	22.40	-35.59	-1.366
Er	238.7	105.33	423.6	103.61	0.580	22.63	-35.86	-1.370
Tm	237.4	105.36	422.7	103.61	0.578	22.88	-36.11	-1.369
Yb	236.4	105.43	421.9	103.60	0.576	23.07	-36.36	-1.368
Lu	235.8	105.47	421.3	103.60	0.574	23.22	-36.52	-1.352
cluster cycle								
Ln^{3+}	$d_{LnO(1)}$	$\phi_{HOH(1)}$	$d_{LnO(2)}$	$\phi_{HOH(2)}$	S°	D_0	ΔE_H	ΔS_H°
La	255.8	104.67	437.7	103.62	0.619	17.77	-32.62	-0.100
Ce	253.7	104.74	435.9	103.63	0.614	18.10	-32.99	-0.120
Pr	251.7	104.81	434.3	103.62	0.609	18.41	-33.34	-0.129
Nd	250.0	104.87	432.8	103.62	0.605	18.70	-33.67	-0.134
Pm	248.3	104.93	431.4	103.62	0.602	18.98	-33.98	-0.137
Sm	246.8	104.99	430.2	103.62	0.598	19.24	-34.29	-0.138
Eu	245.2	105.05	428.9	103.62	0.595	19.51	-34.59	-0.136
Gd	243.9	105.10	427.8	103.62	0.592	19.76	-34.87	-0.147
Tb	242.5	105.16	426.7	103.61	0.589	20.01	-35.16	-0.154
Dy	241.2	105.23	425.7	103.61	0.586	20.26	-35.43	-0.159
Ho	240.0	105.28	424.6	103.61	0.583	20.55	-35.71	-0.162
Er	238.7	105.33	423.6	103.61	0.580	20.74	-35.98	-0.166
Tm	237.4	105.36	422.7	103.61	0.578	20.96	-36.19	-0.165
Yb	236.4	105.43	421.9	103.60	0.576	21.18	-36.48	-0.164
Lu	235.8	105.47	421.3	103.60	0.574	21.32	-36.64	-0.148

S-7 Experimental Gibbs free energies of hydration

Table 16 Experimental Gibbs free energies of hydration for the trivalent lanthanide ions in kJ mol^{-1} taken from the work of David, Vokhmin and Ionova(1) and of Marcus(2).

Ln^{3+}	$\Delta G_H^\circ(1)$	$\Delta G_H^\circ(2)$
La	-3061	-3145
Ce	-3112	-3200
Pr	-3156	-3245
Nd	-3183	-3280
Pm	-3210	-3250
Sm	-3228	-3325
Eu	-3279	-3360
Gd	-3292	-3375
Tb	-3331	-3400
Dy	-3337	-3425
Ho	-3382	-3470
Er	-3404	-3495
Tm	-3431	-3515
Yb	-3473	-3570
Lu	-3488	-3515

(1): F. David, V. Vokhmin and G. Ionova, J. Mol. Liq., 2001, **90**, 40-62.
(2): Y. Marcus, J. Chem. Soc. Faraday Trans., 1991, **87**, 2995-2999.

S-8 Plots for results obtained at the DFT-B3LYP level of theory

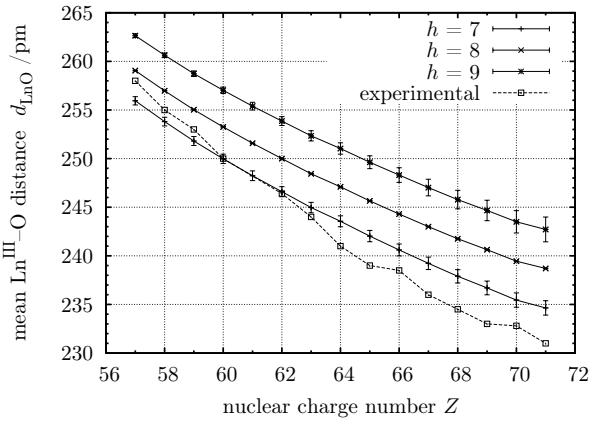

Fig. 2 Mean Ln^{III}–O distances d_{LnO} for $[Ln^{III}(H_2O)_h]^{3+}$ systems at the DFT-B3LYP level of theory; increasing d_{LnO} rms are caused by non-symmetry equivalent Ln^{III}–O distances that deviate from the total average value; Experimental values from EXAFS and X-ray spectroscopy are taken from David and Fourest*.

* F. H. David and B. Fourest, New J. Chem., 1997, **21**, 167-176.

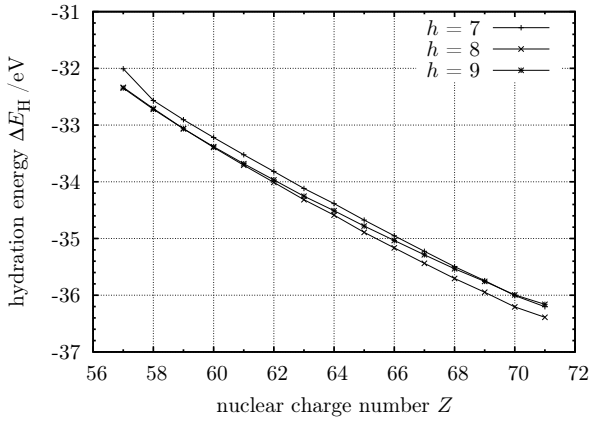

Fig. 3 Hydration energies of Ln^{III} for $[Ln^{III}(H_2O)_h]^{3+}$ and hydration number h = 7, 8, 9 at the DFT-B3LYP level of theory.

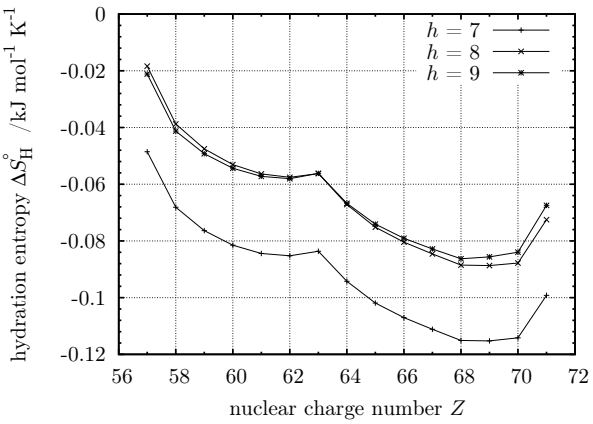

Fig. 4 Hydration entropies of Ln^{III}) for hydration numbers h = 7, 8 and 9 calculated at the DFT-B3LYP level of theory.

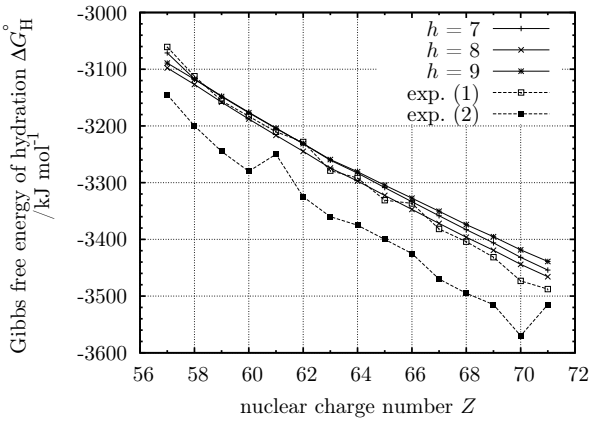

Fig. 5 Ln^{III} Gibbs free energies of hydration for primary hydration numbers h = 7, 8, 9 at the DFT-B3LYP level of theory. Experimental results were taken from the work of David, Vokhmin and Ionova (1) and of Marcus (2).

(1): F. David, V. Vokhmin and G. Ionova, J. Mol. Liq., 2001, **90**, 40-62.
(2): Y. Marcus, J. Chem. Soc. Faraday Trans., 1991, **87**, 2995-2999.

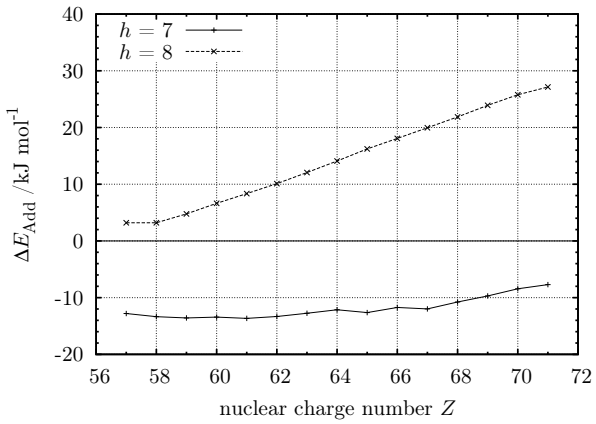

Fig. 6 Reaction energy ΔE_{trans} for h = 8, 9 at the DFT-B3LYP level of theory.