Supplementary Information for

Lanthanide Chloride Clusters, $Ln_xCl_{3x+1}^-$, x=1-6: an Ion Mobility and DFT Study of Isomeric Structures and Interconversion Timescales

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1. CCS-calculations, determination of Lennard-Jones parameters for chlorine and lanthanide atoms

In the trajectory calculations implemented in IMoS the ion-buffer gas interaction is modelled (atom-by-atom) with Lennard-Jones-type interactions with element specific parameters. The LJ-parameters ε and σ are explicitly calibrated against experimental CCS only of the light elements C, H, N, O, and F. For the other elements the (uncalibrated) default values are ε=2.6 meV and σ=3.5 Å. With these values we obtain for the lowest energy structures of $LaCl_4^-$, $La_3Cl_{10}^-$, $La_4Cl_{13}^-$ and $La_6Cl_{19}^-$ $^{theo}CCS_{N2}$ that are on average ca. 7% smaller than the experimental values ($^{TW}CCS_{N2}$), therefore a calibration process is needed. First, we keep for both Cl and Ln the parameter ε at its default value (2.6 meV), and adjust σ to match experiment and calculation. With σ_{Cl}=3.85 Å σ_{La}=3.0 Å (based on the fact that the radius of La^{3+} is ca. 0.8 Å smaller than Cl^-) we obtain a close match for $La_4Cl_{13}^-$ ($^{theo}CCS_{N2}$=194.9 Å^2, $^{TW}CCS_{N2}$= 196.6 Å^2), but for $LaCl_4^-$ we underestimate the experimental value by ca. 2.2% ($^{theo}CCS_{N2}$=114.3 Å^2, $^{TW}CCS_{N2}$= 116.8 Å^2), while we overestimate it for $La_6Cl_{19}^-$ by 2.3% ($^{theo}CCS_{N2}$=233.9 Å^2, $^{TW}CCS_{N2}$= 228.7 Å^2). As can be seen in **Figure S1**, the best-matching radius for chlorine decreases from σ_{Cl} = 3.95 Å for $LaCl_4^-$ to σ_{Cl}= 3.75 Å for $La_6Cl_{19}^-$. We decided to use 3.85 Å throughout since it minimizes the overall error. Test calculations show that ε and σ are correlated, i.e. several combinations thereof can be used to reproduce the experimental data (with the problem remaining that the CCS of the $LaCl_4^-$ is underestimated and $La_6Cl_{19}^-$ is overestimated). Furthermore, σ_{La} is ca. 10-fold less sensitive than σ_{Cl}, increasing it dramatically from 3 Å^2 to 3.5 Å^2 increases the $^{theo}CCS_{N2}$ by merely 1% (see also **Figure 6** in the main text). This reflects the smaller number of lanthanide atoms in the $Ln_xCl_{3x+1}^-$ cluster and the fact that the chlorine atoms are on average closer to the cluster surface, i.e. in closer contact to the collision gas (nitrogen) molecules. As consequence, we use same the Lennard-Jones parameter for all lanthanides (σ_{Ln} = 3.0 Å). Since partial charges localized on each atom are necessary to model the ion-induced dipole and ion-quadrupole interaction in IMoS, we also tested several charge-localization algorithms implemented in TURBOMOLE, specifically ESP-fit, Mulliken and natural bond analysis. While in some cases the charges assigned differ significantly, the calculated CCS show only a very weak dependence on the partial charge distribution. Since ESP-fit is known to show very weak basis set dependence, we use this algorithm. Since the experiments integrate over the isotope distributions, the calculations were performed with average atomic masses. Isotope effects are below 0.1%, i.e. not resolvable in our experiment.

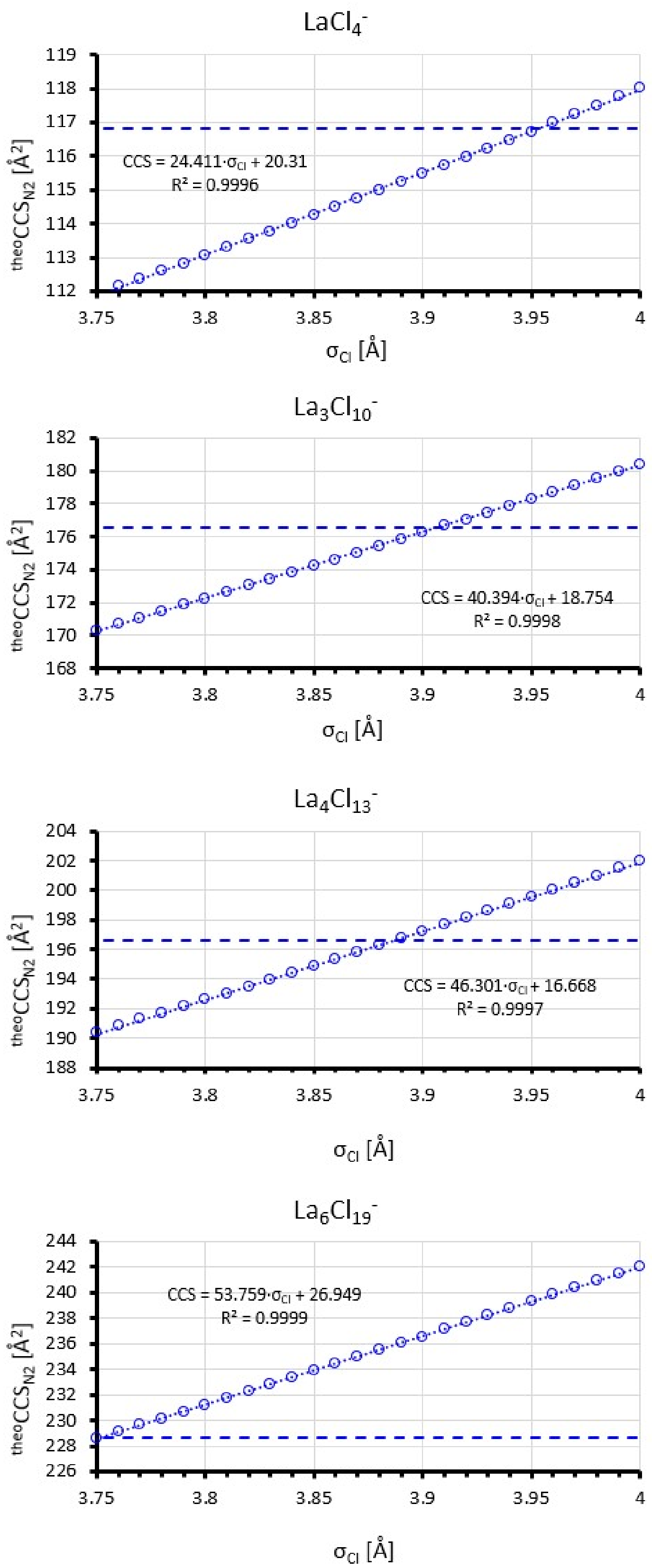


Figure S1: Variation of σ_{Cl} to match the experimental CCS for $LaCl_4^-$, $La_4Cl_{13}^-$ and $La_6Cl_{19}^-$. Other parameters are fixed, i.e. σ_{La}=3.00 Å, ε_{Cl}= ε_{La}=2.6 meV, partial charges by ESP-fit, ion-quadrupole interaction included.

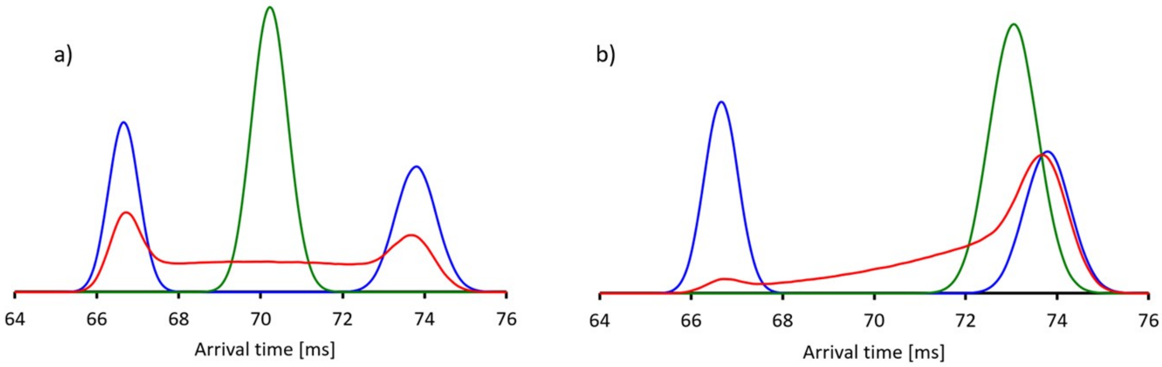


Figure S2: Calculated arrival time distributions for two interconverting isomers $A \rightleftharpoons B$ with interconversion rate constants k_{AB} and k_{BA} (based on the formalism developed in ref. 2, main text). The parameters are chosen to closely match the 10-cycle arrival time distributions of $Ln_2Cl_7^-$ (**Figure 2** in main text), i.e. average arrival time of species A is set to 66.5 ms, average arrival time of species B is 73.5 ms (10% difference, centered at 70 ms, which corresponds to the 5% CCS difference of the two isomers due to the square root CCS-arrival time dependence, **Figure 7** in main text). FWHM peak width without interconversion set to 1 ms. Initial intensities $A_0=B_0$.

a) Equal rate constants for interconversion, $k_{AB} = k_{BA}$. Blue: k_{AB}, $k_{BA} = 0$, i.e. no interconversion during the drift time, green: k_{AB}, $k_{BA} \rightarrow \infty$, i.e. many interconversions during the drift time, red: interconversion rate similar to the arrival time.

b) $k_{AB} = 10k_{BA}$. Blue: k_{AB} and k_{BA} small, i.e. no interconversion, green: k_{AB}, $k_{BA} \rightarrow \infty$, i.e. many interconversions during the drift time, red: interconversion rate similar to the arrival time.

For two species, in the limit of fast interconversions a sharp peak at the weighted average to the individual arrival times is observable, in line with our experimental observation.

2. Quantum chemical calculations

The general procedure of finding putatively all low-lying minima and relevant transition states is given in the main text. Here we first focus on the impact of different choices concerning functional, description of relativity and basis sets on the structure parameters of $LnCl_4^-$ as well as on the energy surface (minima and transition states) of $Ln_2Cl_7^-$ (**Figures S3-S4, Tables S1-S2**). Next, we list energies and Gibbs free energies, calculated within the harmonic oscillator rigid rotor model, at 0, 300 and 600 K of all relevant minimum structures of $Ln_xCl_{3x+1}^-$, Ln=La-Lu, x=2-6 (**Tables S3-S7**) with functionals PBE[1] and TPSS[2] employing newly designed and optimized lcecp-1-TZVP bases[3] and display them graphically (**Figures S5-S9**). The bases are listed in the supplementary file `bases.txt`, details of their development will be published elsewhere. The third part is dedicated to transformation pathways (**Figures S10-S13**) and transition state energies and enthalpies (**Tables S8-S9**).

Impact of different choices concerning functional, description of relativity and basis sets. DFT structure optimizations in this work were done employing f^{n-1} large-core effective core-potentials[4] and corresponding recently designed and optimized polarized bases (lcecp-1-XVP, X=SV, T, Q). For the estimation of the reliability concerning structure parameters, different quantum-chemical methods were tested at $LnCl_4^-$. The results are shown in Fig. S3. The impact of the way to describe relativity was investigated for the PBE0 functional[5] by comparing the all-electron relativistic X2C[6] method (x2c-QZVPall bases, in the following termed X2C/QZVPall)[7] and the lcecp-1-QZVP method, thus very close to the DFT basis-set limit. The errors of lcecp-1-TZVP with respect to lcecp-1-QZVP were estimated with the same functional, differences due to the use of different functionals (PBE, TPSS, PBE0) for lcecp-1-TZVP. As evident from Fig. S3, the changes/errors are very similar for all lanthanides and may be summarized as follows: d(TZVP)=d(QZVP)-0.3pm, d(PBE)=d(PBE0)+0.8pm=d(TPSS)-0.8pm, d(ECP)=d(X2C)+2.1pm.

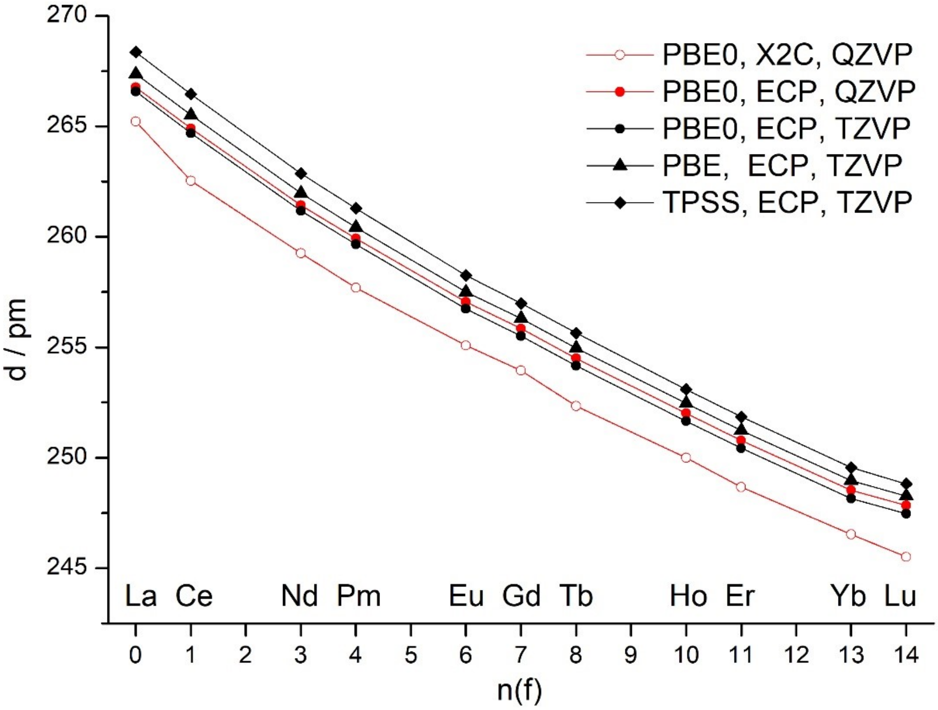


Figure S3. Distances obtained for $LnCl_4^-$ with various methods for all lanthanides that show either fully, half, or not occupied irreducible representations of the f shell in T_d symmetry.

The consistency of relative energies of different isomers was assessed at $Ln_2Cl_7^-$ for the same set of methods, **Table S1**, and additionally for PBE/lcecp-1-SVP. For this compound, the two most stable isomers A and B, see **Figure S4**, are of similar energy, and the transition state T between them can be guessed easily. For La, the preference of A over B, Δ_{AB}, amounts to 6…12 kJ/mol for all methods (14 kJ/mol for PBE/lcecp-1-SVP and slightly decreases towards Lu, where it amounts to −2…+5 kJ/mol. Functionals TPSS and PBE0 yield very similar values for Δ_{AB} throughout, PBE is ca. 5kJ/mol lower. TZVP and QZVP bases yield almost the same data (differences 0.1…0.4 kJ/mol), errors for the very compact SVP basis are still reasonably small, 2…4 kJ/mol. For ECPs, the decrease of Δ_{AB} from La to Lu is strictly monotonic, for all-electron treatments one rather observes steps at the half and at the fully filled f shell: similar numbers clearly above 10 kJ/mol from La to Eu, similar numbers for Gd to Yb around 5 kJ/mol, and 0 kJ/mol for Lu. It is noted that the all-electron relativistic calculation for partially filled f shells does not necessarily lead to more reliable relative energies: depending on details of the f occupation in the initial guess for the wave function, slightly different converged energies and wavefunctions can be obtained, even if Fermi smearing is used; for instance, the energy of B may change by up to ~5 kJ/mol when using the MOs of isomer A instead of Hückel MOs as initial guess. The numbers in **Table S1** are obtained for the first variant of initial MOs throughout. Further, the usage of pure DFT functionals in case of partially filled f shells is sometimes problematic, as they tend to be too high in energy with such functionals, leading sometimes even to incorrect f occupation numbers. This being said, the most reasonable way for economically investigating the energy surface is a pre-scan with a genetic algorithm based on PBE/lcecp-1-SVP level followed by both PBE/lcecp-1-TZVP and TPSS/lcecp-1-TZVP. Finally, it has to be noted that the proven functionals PBE0, PBE or TPSS chosen by us do not span the full range of obtainable values for Δ_{AB}: For $La_2Cl_7^-$ (ECP/TZVP) ~20 kJ/mol are obtained with the wB[8] series and also with MP2[9], and even more than 30 kJ/mol with M06[10] or LHJ14.[11]

Table S1. Energies of isomer B in kJ/mol relative to isomer A of $Ln_2Cl_7^-$ for selected lanthanides at different levels of calculation.

	Relativity	Functional	Basis	La	Ce	Nd	Pm	Eu	Gd	Tb	Ho	Yb	Lu
1	ECP	PBE0	QZVP	9.9	9.4	7.9	7.6	6.9	6.6	6.2	5.4	3.7	3.1
2	ECP	PBE0	TZVP	10.3	9.7	8.3	8.0	7.0	6.7	6.4	5.6	3.9	3.3
3	ECP	PBE	TZVP	5.5	4.8	3.3	2.9	1.9	1.6	1.3	0.6	-0.8	-1.5
4	ECP	TPSS	TZVP	9.8	9.3	8.3	8.0	7.3	7.1	6.9	6.5	5.2	4.6
5	As 4, but for the ECP/PBE/TZVP structure			9.7	9.2	8.0	7.7	7.0	6.8	6.6	6.2	4.9	4.3
6	ECP	PBE	SV(P)	14.1	13.4	12.6	11.3	9.1	8.0	7.7	8.4	7.1	5.3
7	X2C	PBE0	QZVP	12.4	15.7	12.4	12.5	15.5	5.6	5.4	2.4	6.1	0.0
8	As 7, but for the ECP/PBE/TZVP structure			11.1	13.5	10.3	10.5	13.2	4.8	4.3	1.7	5.2	-0.5
9	Average of 2,3,4,7			9.5	9.9	8.1	7.9	7.9	5.3	5.0	3.8	3.6	1.6

For a maybe more realistic simulation of the experimental conditions one might also compare the Gibbs free energies, G, of minima and transition states. This is done in **Table S2** for the energy/Gibbs free energy of isomer B and for the transition state (relative to isomer A). For T=0, G is the sum of the electronic energy and the zero-point energy, for finite temperatures further the logarithm of the product of translational, rotational and vibrational sums of states (multiplied by RT) are added. The latter sensitively depends on the vibrational frequencies, which requires tight settings for convergence criteria. Here and in the following, for the structure optimization we chose 10^{-8} E_h for the energy and 10^{-5} for the norm of the gradient, the SCF procedure was done with fine grids (gridsize 5)[12] and weight derivatives, and an SCF energy convergence threshold of 10^{-9} E_h.

Table S2. Electronic energies E of isomer B and the transition state T between isomer A and isomer B of $Ln_2Cl_7^-$ relative to isomer A with PBE/lcecp-1-TZVP and TPSS/lcecp-1-TZVP as well as Gibbs free energies G at 0, 300 and 600 K (data for isomer B are also listed in **Table S3**).

	PBE					TPSS				
	B				T	B				T
	E	G_0	G_{300}	G_{600}	E	E	G_0	G_{300}	G_{600}	E
La	5.5	5.2	1.8	-2.1	10.88	9.7	9.4	7.1	4.4	14.56
Ce	4.7	4.4	0.9	-2.9	10.17	9.1	8.7	7.1	5.1	13.94
Pr	3.9	3.6	0.1	-3.9	9.45	8.5	8.1	7.4	6.3	13.29
Nd	3.2	2.9	-0.7	-4.7	8.89	8.1	7.8	6.3	4.5	12.93
Pm	2.8	2.5	-1.1	-5.2	8.56	7.8	7.4	4.2	0.5	12.75
Sm	2.2	1.9	-1.8	-5.8	8.14	7.4	7.0	3.6	-0.2	12.41
Eu	1.7	1.3	-2.4	-6.6	7.74	7.1	6.6	2.9	-1.5	12.09
Gd	1.3	0.9	-2.8	-7.0	7.43	6.9	6.4	1.8	-3.3	11.91
Tb	0.8	0.5	-3.3	-7.6	7.07	6.6	6.1	1.7	-3.2	11.58
Dy	0.5	0.2	-3.7	-8.0	6.78	6.4	5.9	1.4	-3.7	11.36
Ho	0.1	-0.3	-4.2	-8.5	6.44	6.1	5.6	1.0	-4.2	11.06
Er	-0.5	-0.9	-4.7	-9.0	6.03	5.7	5.2	0.5	-4.8	10.69
Tm	-0.8	-1.1	-5.0	-9.4	5.79	5.5	5.0	0.2	-5.2	10.47
Yb	-1.5	-1.9	-5.8	-10.1	5.29	4.8	4.3	-0.4	-5.7	9.94
Lu	-2.2	-2.6	-6.4	-10.7	4.96	4.2	3.7	-1.0	-6.3	9.56

The zero-point energy (G(T=0K)-E) is almost negligible, amounting to 0.6 kJ/mol at most. In contrast, G(T=300K) differs from the bare electronic energies by a few kJ/mol. The favouring of A over B becomes smaller by typically 3…5 kJ/mol (which actually means a disfavouring of A for the heavier lanthanides), and the energy difference of the transition state T to A increases by about the same amount, which is also similar to the difference between PBE and TPSS. At 600K these effects are about three times larger. The results are graphically displayed in **Figure S3**; they suggest that by the calculation of the Gibbs free energy at 300 K with PBE/ECP/TZVP or TPSS/ECP/TZVP the energetic situation in the experiment is reproduced with an accuracy of approx. 10 kJ/mol, whereby the greatest uncertainty arises from the choice of the functional; thus, in the following data for both functionals are calculated and listed.

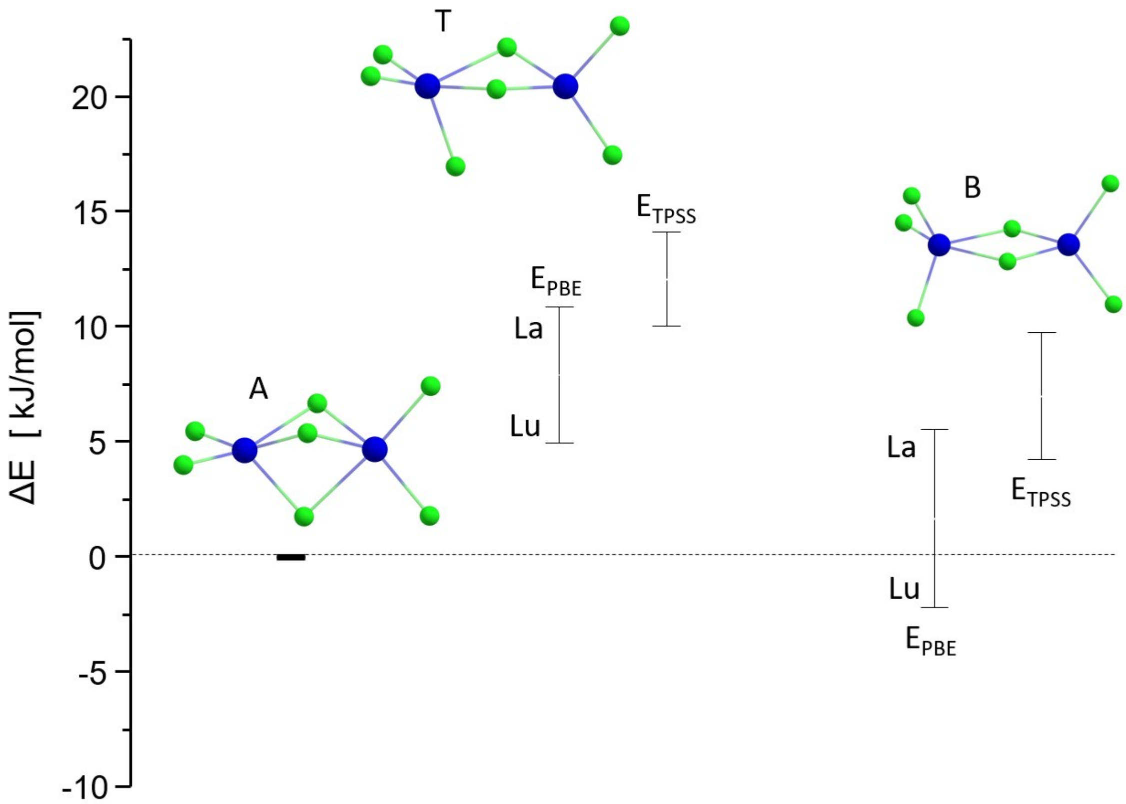


Figure S4. Energies E of isomer B and transition state T relative to isomer A for La-Lu at levels PBE/ECP/TZVP and TPSS/ECP/TZVP.

Relative energies and Gibbs free energies of minima (relative to the minimum with lowest energy for Ln=La). In the following we list the energies and Gibbs free energies of the most stable isomers of $Ln_xCl_{3x+1}^-$, Ln=La-Lu, separately for x=2-6 and graphically display the PBE data for E and G(300K).

Table S3. Isomers of of $Ln_2Cl_7^-$, Ln=La-Lu. Energies E and Gibbs free energies, G, for T=0, 300, 600 K of isomers B and C relative to isomer A, in kJ/mol at levels PBE/ECP/TZVP and TPSS/ECP/TZVP (data for isomer B are also listed in **Table S2**).

	PBE								TPSS							
	B				C				B				C			
	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}
La	5.5	5.2	1.8	-2.1	32.2	31.7	33.3	34.4	9.7	9.4	7.1	4.4	38.0	37.5	40.7	43.3
Ce	4.7	4.4	0.9	-2.9	31.4	31.0	32.7	33.8	9.1	8.7	7.1	5.1	37.2	36.7	40.7	44.1
Pr	3.9	3.6	0.1	-3.9	30.6	30.2	31.8	33.0	8.5	8.1	7.4	6.3	36.3	35.9	40.9	45.4
Nd	3.2	2.9	-0.7	-4.7	29.8	29.4	31.2	32.5	8.1	7.8	6.3	4.5	35.6	35.3	39.9	44.1
Pm	2.8	2.5	-1.1	-5.2	29.4	29.0	30.8	32.1	7.8	7.4	4.2	0.5	35.3	35.0	38.1	40.8
Sm	2.2	1.9	-1.8	-5.8	28.9	28.5	30.2	31.5	7.4	7.0	3.6	-0.2	34.8	34.5	37.7	40.6
Eu	1.7	1.3	-2.4	-6.6	28.5	28.0	29.7	31.0	7.1	6.6	2.9	-1.5	34.4	34.0	37.0	39.6
Gd	1.3	0.9	-2.8	-7.0	28.1	27.7	29.4	30.7	6.9	6.4	1.8	-3.3	34.1	33.6	36.0	37.8
Tb	0.8	0.5	-3.3	-7.6	27.7	27.3	29.2	30.5	6.6	6.1	1.7	-3.2	33.7	33.3	35.9	38.1
Dy	0.5	0.2	-3.7	-8.0	27.5	27.1	29.0	30.5	6.4	5.9	1.4	-3.7	33.4	33.0	35.7	37.9
Ho	0.1	-0.3	-4.2	-8.5	27.2	26.8	28.8	30.3	6.1	5.6	1.0	-4.2	33.0	32.6	35.5	37.9
Er	-0.5	-0.9	-4.7	-9.0	26.8	26.4	28.4	29.9	5.7	5.2	0.5	-4.8	32.6	32.3	35.4	38.0
Tm	-0.8	-1.1	-5.0	-9.4	26.6	26.2	28.1	29.6	5.5	5.0	0.2	-5.2	32.4	32.0	35.2	38.0
Yb	-1.5	-1.9	-5.8	-10.1	26.0	25.6	27.5	28.8	4.8	4.3	-0.4	-5.7	31.9	31.5	34.8	37.8
Lu	-2.2	-2.6	-6.4	-10.7	25.8	25.3	27.1	28.3	4.2	3.7	-1.0	-6.3	31.6	31.2	34.5	37.4

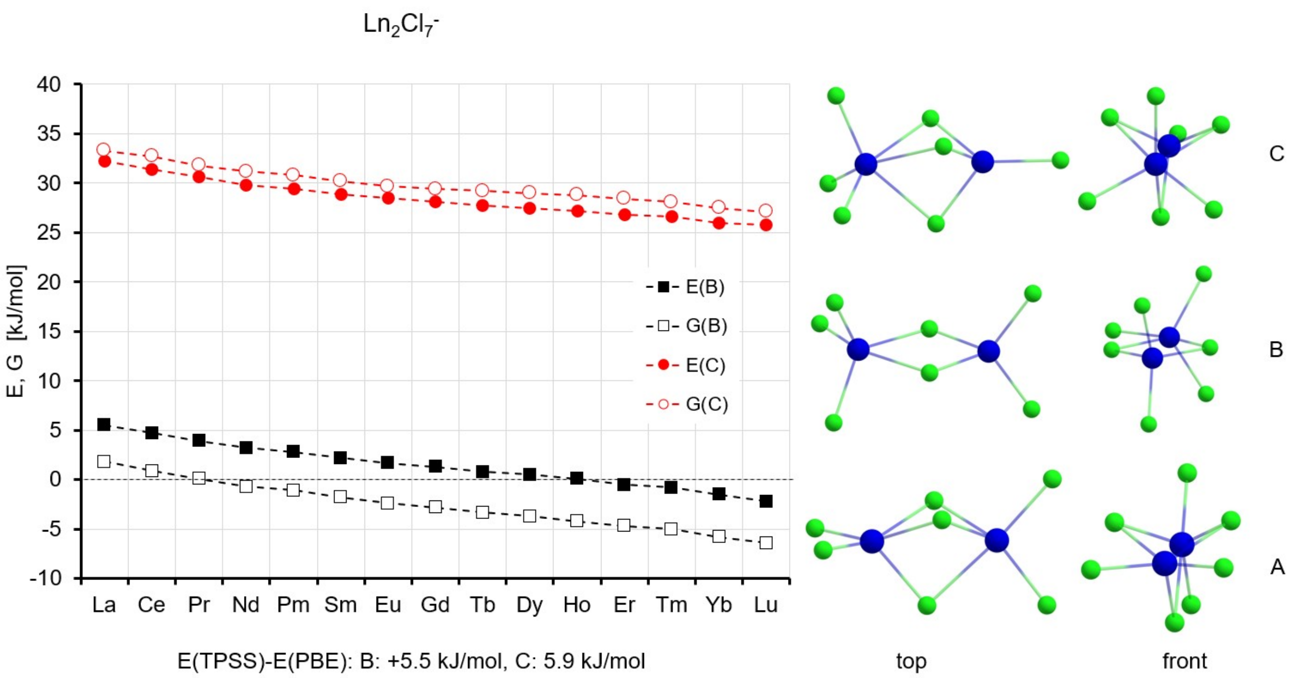


Figure S5. $Ln_2Cl_7^-$: Energies, E, and Gibbs free energies, G, at 300 K of isomer B and C relative to isomer A for La-Lu at levels PBE/ECP/TZVP and TPSS/ECP/TZVP.

Table S4. Relative energies and Gibbs free energies of isomers of $Ln_3Cl_{10}^-$, see also **Table S3**.

	PBE								TPSS							
	B				C				B				C			
	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}
La	17.8	17.2	10.9	3.9	24.8	24.7	15.9	7.1	22.1	21.6	15.8	9.5	20.5	20.6	15.9	11.3
Ce	17.6	17.1	10.5	3.2	25.1	25.0	16.0	7.1	22.3	21.6	15.2	8.2	20.7	20.8	14.9	9.2
Pr	17.5	16.9	10.4	3.2	25.8	25.7	17.5	9.2	22.5	21.7	14.8	7.1	21.6	21.5	14.8	8.0
Nd	17.4	16.8	10.2	2.8	26.3	26.2	18.0	9.8	22.8	22.0	13.1	3.3	22.0	21.9	14.4	6.8
Pm	17.2	16.6	10.0	2.7	26.2	26.1	17.4	8.6	22.8	22.0	15.2	7.5	21.9	21.8	12.7	3.6
Sm	17.0	16.4	10.2	3.4	26.3	26.1	16.4	6.5	22.8	22.0	15.4	8.0	21.9	21.8	12.8	3.8
Eu	16.8	16.2	9.5	2.2	26.6	26.1	14.0	1.6	22.9	22.1	14.4	5.8	22.3	22.1	13.0	3.7
Gd	16.7	16.1	9.5	2.2	25.8	25.1	10.8	-4.0	23.0	22.2	14.7	6.5	22.1	22.0	14.0	5.9
Tb	16.7	16.0	9.4	2.2	25.1	24.5	12.3	-0.4	23.2	22.3	14.8	6.5	21.9	21.5	12.2	2.7
Dy	16.8	16.1	9.6	2.4	24.5	23.9	12.6	0.9	23.6	22.7	15.8	8.0	21.7	21.1	11.5	1.5
Ho	16.6	15.9	9.2	1.9	23.9	23.2	12.6	1.3	23.6	22.7	15.6	7.5	21.2	20.6	10.6	0.0
Er	16.2	15.5	9.0	1.7	23.0	22.4	12.1	1.2	23.5	22.5	14.1	4.8	20.4	19.8	8.9	-2.5
Tm	16.2	15.5	8.7	1.1	22.3	21.7	11.8	1.3	23.7	22.7	14.2	4.7	20.0	19.3	7.9	-4.0
Yb	15.6	14.8	7.9	0.3	21.4	20.9	11.1	0.9	23.2	22.2	14.3	5.4	19.2	18.5	6.9	-5.3
Lu	14.9	14.2	7.3	-0.4	20.6	20.1	10.6	0.6	22.6	21.5	13.0	3.5	18.5	17.7	5.9	-6.6

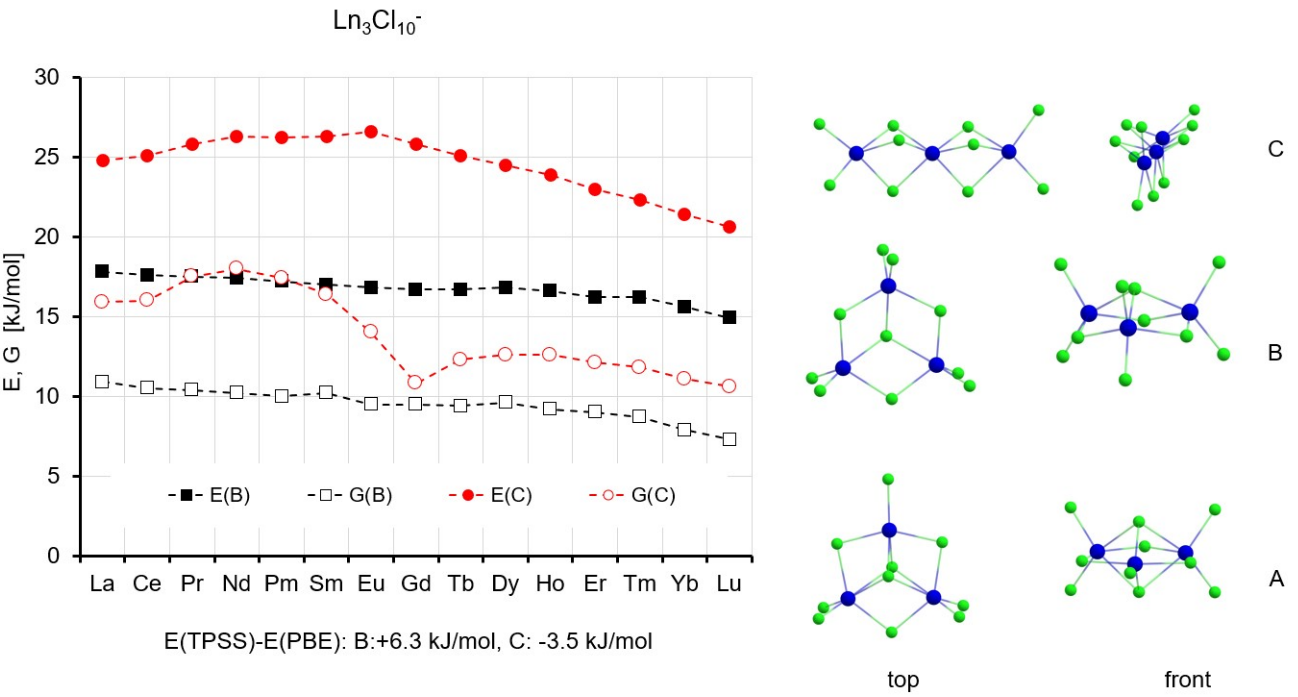
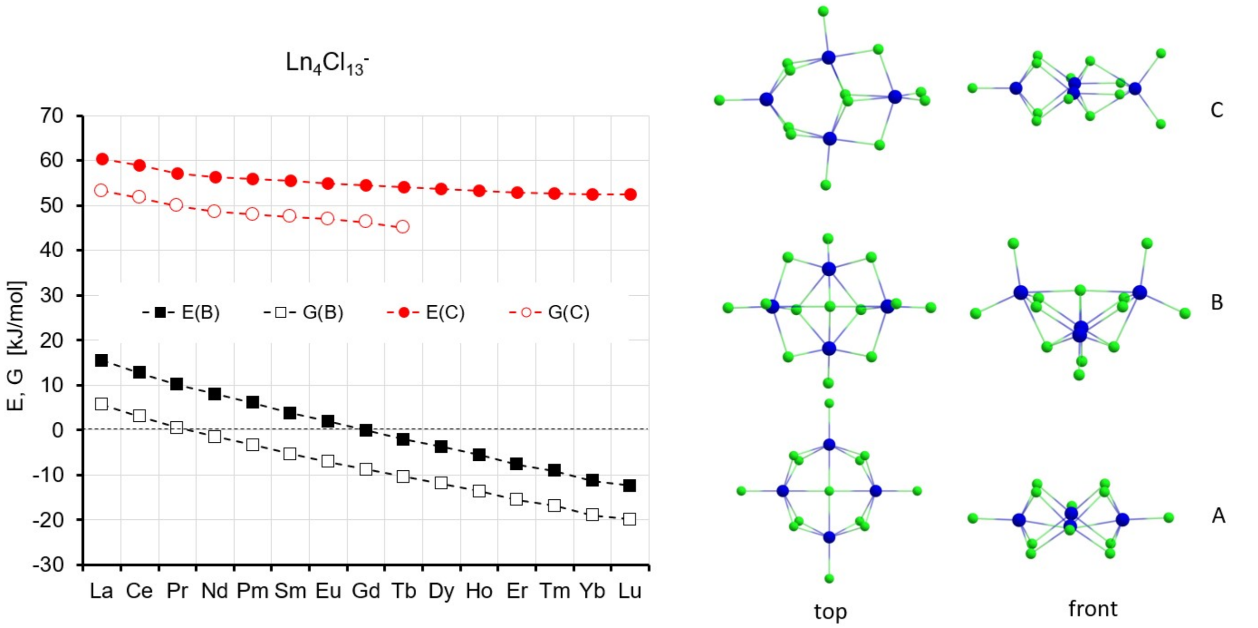


Figure S6. $Ln_3Cl_{10}^-$: Energies, E, and Gibbs free energies, G, at 300 K of isomer B and C relative to isomer A for La-Lu at levels PBE/ECP/TZVP and TPSS/ECP/TZVP.

Table S5. Relative energies and Gibbs free energies of isomers of $Ln_4Cl_{13}^-$, see also **Table S3**. Italic numbers indicate an imaginary frequency for the corresponding isomer.

	PBE								TPSS							
	B				C				B				C			
	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}
La	15.5	14.7	5.7	-4.2	60.4	60.2	53.2	45.9	23.7	22.4	11.9	0.1	69.8	69.2	62.4	55.0
Ce	12.7	11.9	3.1	-6.6	58.9	58.7	51.7	44.5	20.8	19.6	9.5	-1.8	68.0	67.5	61.2	54.3
Pr	10.1	9.3	0.5	-9.1	57.2	57.1	49.9	42.4	18.0	16.9	7.2	-3.6	65.9	65.6	59.7	53.4
Nd	8.0	7.2	-1.5	-11.1	56.3	56.2	48.6	40.9	15.9	14.9	5.5	-4.9	64.7	64.5	58.7	52.7
Pm	6.1	5.3	-3.3	-12.8	55.9	55.7	48.0	40.1	13.9	12.9	3.7	-6.6	63.9	63.7	57.8	51.6
Sm	3.8	3.1	-5.3	-14.5	55.4	55.3	47.5	39.5	11.7	10.7	1.5	-8.8	63.3	63.0	56.9	50.5
Eu	1.9	1.2	-7.0	-15.9	54.9	54.8	47.0	39.0	9.6	8.6	-0.6	-10.9	62.5	62.2	56.0	49.5
Gd	-0.1	-0.8	-8.7	-17.4	54.5	54.4	46.3	38.0	7.5	6.5	-2.5	-12.6	61.9	61.6	55.5	49.0
Tb	-2.1	-2.7	-10.4	-18.9	54.0	54.0	45.0	35.8	5.4	4.5	-4.2	-13.9	61.2	61.0	55.0	48.9
Dy	-3.7	-4.2	-11.9	-20.2	***53.6***	***53.5***	***54.4***	***58.6***	3.7	2.8	-5.6	-14.9	60.5	60.3	54.5	48.4
Ho	-5.5	-6.1	-13.6	-21.8	***53.2***	***53.1***	***54.0***	***58.1***	1.6	0.9	-7.3	-16.3	59.8	59.7	53.6	47.3
Er	-7.6	-8.2	-15.5	-23.5	***52.9***	***52.8***	***53.6***	***57.7***	-0.6	-1.4	-9.3	-18.0	59.4	59.3	52.5	45.5
Tm	-9.1	-9.6	-16.8	-24.8	***52.7***	***52.6***	***53.3***	***57.3***	-2.1	-2.8	-10.7	-19.3	59.0	58.8	51.0	42.9
Yb	-11.3	-11.8	-18.9	-26.6	***52.4***	***52.3***	***53.0***	***56.9***	-4.6	-5.3	-13.0	-21.5	***58.6***	***58.3***	***59.2***	***63.2***
Lu	-12.4	-12.9	-19.8	-27.4	***52.5***	***52.4***	***53.0***	***56.8***	-5.8	-6.6	-14.2	-22.6	***58.6***	***58.2***	***58.9***	***62.7***



E(TPSS)-E(PBE): B:+7.5 kJ/mol, C: +7.5 kJ/mol

for Ho-Lu isomer C is a saddlepoint

Figure S7. $Ln_4Cl_{13}^-$: Energies, E, and Gibbs free energies, G, at 300 K of isomer B and C relative to isomer A for La-Lu at levels PBE/ECP/TZVP and TPSS/ECP/TZVP.

Table S6. Relative energies and Gibbs free energies of isomers of $Ln_5Cl_{16}^-$, see also **Table S3**.

	PBE								TPSS							
	B				C				B				C			
	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}
La	-1.3	-0.6	10.6	22.5	-1.2	0.3	11.7	24.6	-4.6	-4.0	5.2	15.1	-10.5	-8.9	1.7	13.8
Ce	2.4	3.2	14.5	26.7	4.0	5.5	16.9	29.8	-1.6	-0.9	9.2	20.1	-6.0	-4.3	6.8	19.5
Pr	6.1	6.9	18.5	31.0	9.3	10.7	22.2	35.0	1.2	2.1	12.9	24.7	-1.5	0.3	11.9	25.1
Nd	10.0	10.8	22.7	35.4	14.7	16.2	27.5	40.3	4.6	5.5	16.3	28.1	3.5	5.2	16.7	29.9
Pm	13.9	14.8	26.7	39.6	20.2	21.6	32.8	45.3	8.1	9.0	19.7	31.4	8.7	10.4	21.5	34.3
Sm	17.8	18.7	30.9	44.1	25.7	27.1	38.2	50.7	11.7	12.6	23.5	35.3	14.1	15.7	26.6	39.1
Eu	21.8	22.8	35.3	48.9	31.4	32.8	44.0	56.6	15.3	16.3	27.5	39.7	19.4	21.1	32.0	44.4
Gd	25.6	26.6	39.7	53.8	36.7	38.1	49.7	62.6	18.9	19.9	31.5	44.2	24.6	26.3	37.4	50.1
Tb	29.9	30.9	44.8	59.7	42.5	43.9	56.1	69.8	22.9	24.0	36.0	49.2	30.3	32.0	43.4	56.4
Dy	33.8	34.9	51.2	68.8	48.1	49.5	64.0	79.9	26.5	27.7	40.5	54.4	35.7	37.5	49.4	62.9
Ho	38.1	39.3	59.7	81.3	53.8	55.4	73.6	93.3	30.5	31.9	52.3	74.1	41.4	43.3	62.7	84.0
Er	42.2	43.5	64.5	86.9	59.6	61.1	79.7	99.7	34.7	36.0	55.4	76.1	47.3	49.2	67.3	87.2
Tm	46.2	47.4	65.3	84.5	65.1	66.4	81.5	98.0	38.8	40.2	52.3	62.4	53.0	54.9	65.5	74.5
Yb	50.3	51.4	68.1	86.1	70.7	71.9	85.3	99.9	42.9	44.3	57.1	67.9	58.8	60.7	71.6	80.8
Lu	53.3	54.5	70.5	87.8	75.1	76.3	88.5	101.8	46.3	47.6	68.4	90.5	63.9	65.5	84.0	104.2

Relative intensities for the $La_5Cl_{16}^-$ isomers:

With the PBE functional the free energy of isomer B at 300 K is 10.6 kJ/mol above isomer A, isomer C is 11.7 kJ/mol higher. This translates into relative intensities of 98% for isomer A, 1% for B and 1% for C, respectively. With the TPSS functional the free energies are 5.2 kJ/mol and 1.7 kJ/mol, respectively (see also table S6). This in turn translates into relative intensities of 61% for isomer A, 8% for B and 31% for C. Both functionals differ by 5-10 kJ/mol and we cannot safely predict which isomer is preferred. For the later lanthanides, isomer A is strongly favoured.

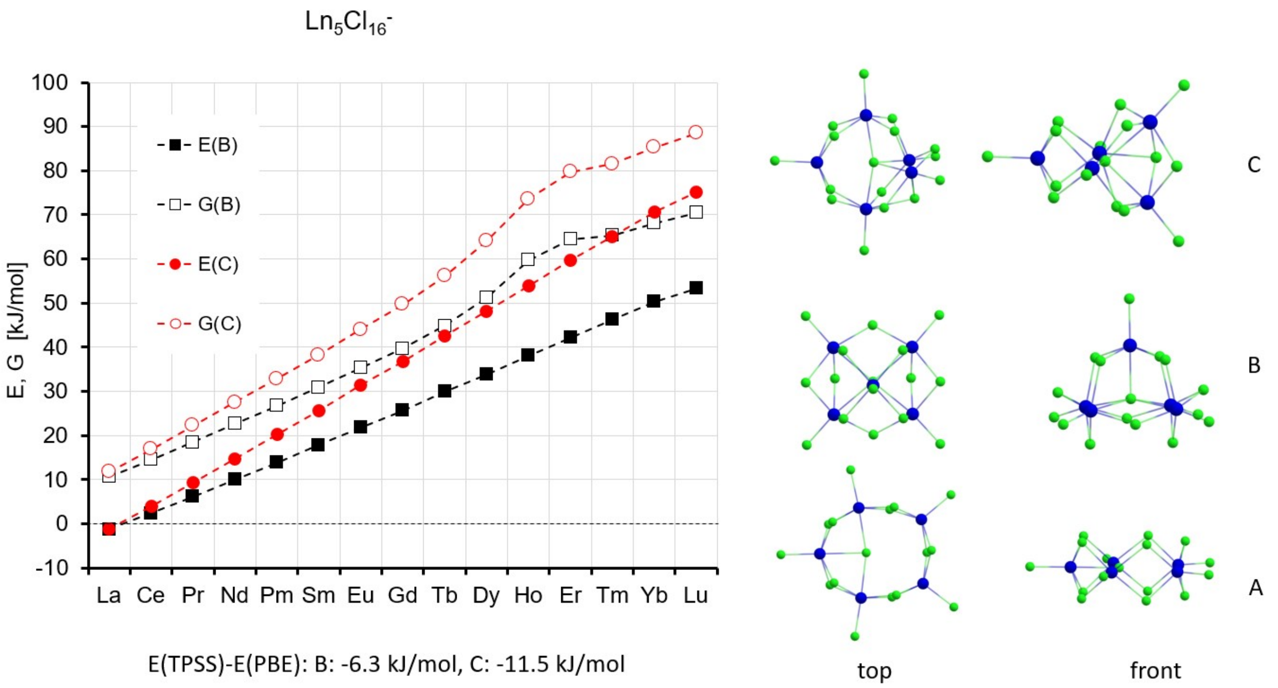


Figure S8. $Ln_5Cl_{16}^-$: Energies, E, and Gibbs free energies, G, at 300 K of isomer B and C relative to isomer A for La-Lu at levels PBE/ECP/TZVP and TPSS/ECP/TZVP.

Table S7. Relative energies and Gibbs free energies of isomers of $Ln_6Cl_{19}^-$, see also **Table S3**.

	PBE								TPSS							
	B				C				B				C			
	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}	E	G_0	G_{300}	G_{600}
La	21.3	21.2	6.9	-7.5	33.7	34.8	22.6	11.4	19.8	19.9	10.2	0.6	13.7	14.8	2.0	-9.9
Ce	20.3	20.0	1.4	-17.6	35.7	36.7	25.0	14.3	19.3	19.0	6.3	-6.7	16.3	17.2	4.2	-8.0
Pr	19.5	19.4	5.5	-8.6	38.7	39.5	28.1	17.5	18.9	18.7	6.3	-6.4	19.9	20.7	7.4	-5.3
Nd	18.5	18.3	5.2	-8.2	40.2	41.0	29.5	18.8	18.1	17.9	6.0	-6.1	21.9	22.7	10.4	-1.2
Pm	17.5	17.4	4.8	-8.1	41.0	41.8	30.2	19.4	17.3	17.2	5.8	-5.8	23.2	24.0	12.7	2.0
Sm	16.5	16.3	4.0	-8.6	41.8	42.5	31.0	20.1	16.3	16.3	5.1	-6.2	24.5	25.4	14.1	3.6
Eu	15.6	15.4	3.2	-9.2	43.2	43.9	32.2	21.1	15.6	15.5	4.2	-7.4	26.5	27.4	15.9	5.2
Gd	14.5	14.3	2.3	-9.9	43.7	44.3	32.5	21.2	14.7	14.5	2.7	-9.3	27.7	28.4	16.8	5.8
Tb	13.5	13.3	1.5	-10.6	44.6	45.1	33.0	21.4	13.9	13.5	1.4	-11.1	29.2	29.8	17.8	6.3
Dy	12.9	12.6	1.0	-11.0	45.9	46.3	33.9	21.9	13.6	13.1	0.6	-12.3	31.5	31.8	19.2	6.9
Ho	12.0	11.8	0.3	-11.4	46.9	47.2	34.6	22.3	12.9	12.3	-0.2	-13.3	33.2	33.2	18.6	4.0
Er	11.0	10.8	-0.4	-12.0	47.5	47.8	35.0	22.5	12.1	11.5	-0.9	-13.9	34.6	34.4	19.6	4.6
Tm	10.3	10.1	-1.0	-12.4	48.6	48.8	35.9	23.1	11.6	11.0	-1.2	-14.1	36.5	36.3	22.4	8.2
Yb	9.3	9.1	-1.9	-13.3	49.3	49.4	36.4	23.5	10.7	10.2	-1.8	-14.5	37.9	37.8	23.8	9.8
Lu	8.5	8.2	-2.7	-14.0	49.5	49.5	36.5	23.6	9.9	9.4	-2.6	-15.0	38.4	38.2	24.5	10.7

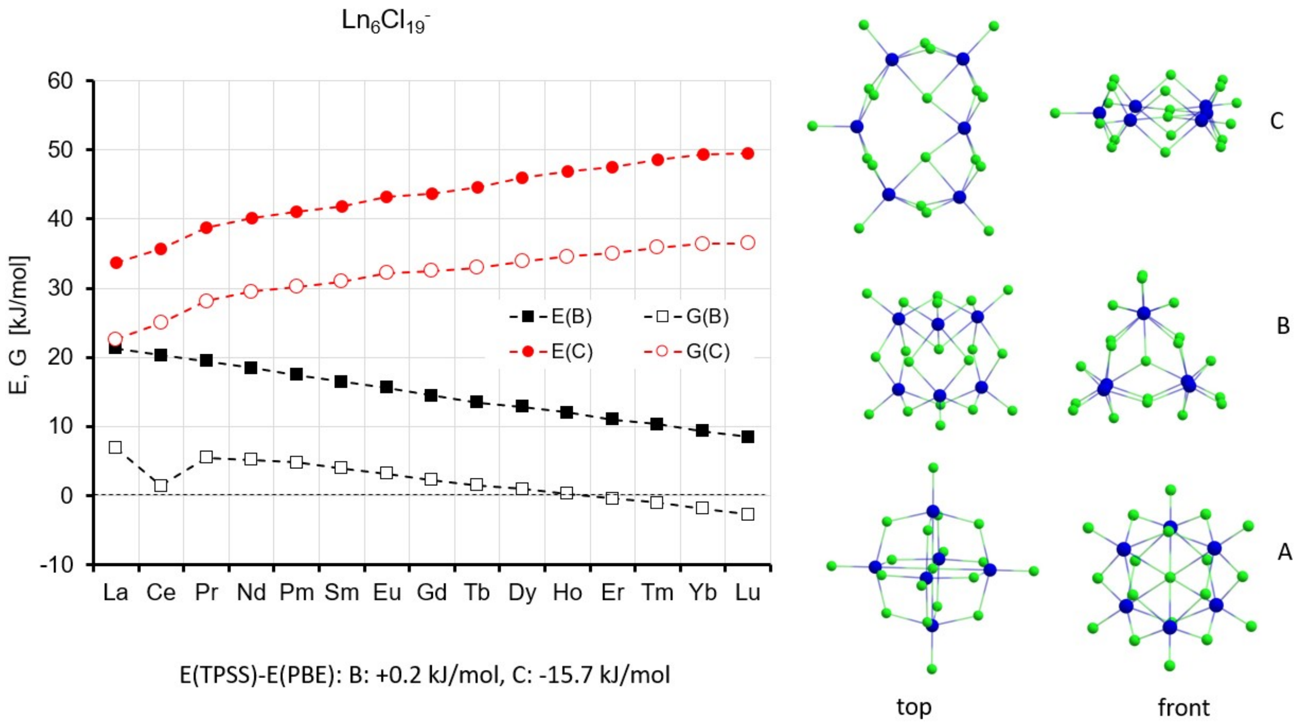


Figure S9. $Ln_6Cl_{19}^-$: Energies, E, and Gibbs free energies, G, at 300 K of isomer B and C relative to isomer A for La-Lu at levels PBE/ECP/TZVP and TPSS/ECP/TZVP.

Reaction pathways and transition states. In the **Figures S10-S13** we graphically show the result of the reaction path optimizations at level PBE/lcecp-1-TZVP for Ln=La in case of x=3,4,5 and Ln=Lu for x=6. All maxima show a single imaginary frequency already after this first step. Data for the transition states after final optimization (same convergence criteria as for the minima) are listed in **Tables S8** and **S9**. We note that the energies of the finally optimized transition states differ by that of the maxima in the path optimization typically by only ~1 kJ/mol. For x=5, the pathways A→C and C→B were optimized separately and combined for the figure afterwards; we were not able to identify a direct path from A to B with low barrier.

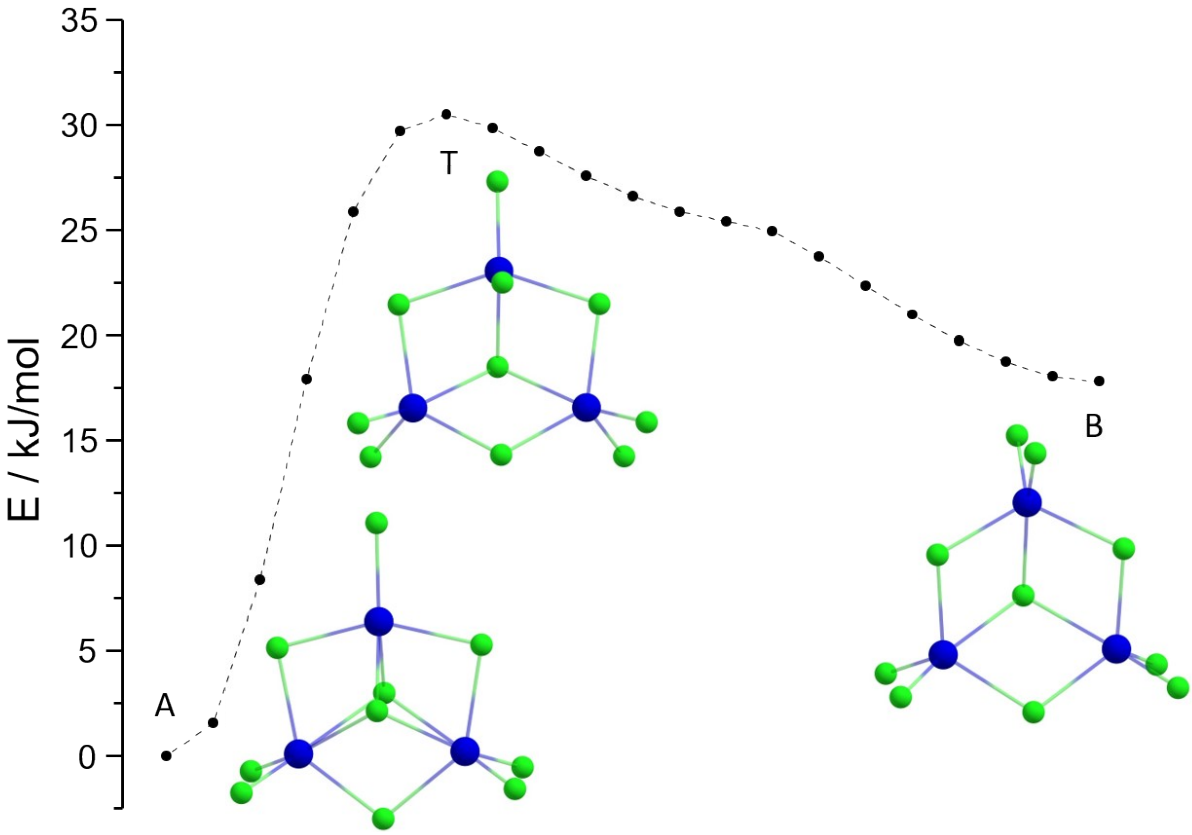


Figure S10. Optimized pathway from isomer A to isomer B for $La_3Cl_{10}^-$ obtained at level PBE/lcecp-1-TZVP. Data for the finally optimized transition state for Ln=La-Lu are listed in **Table S8**.

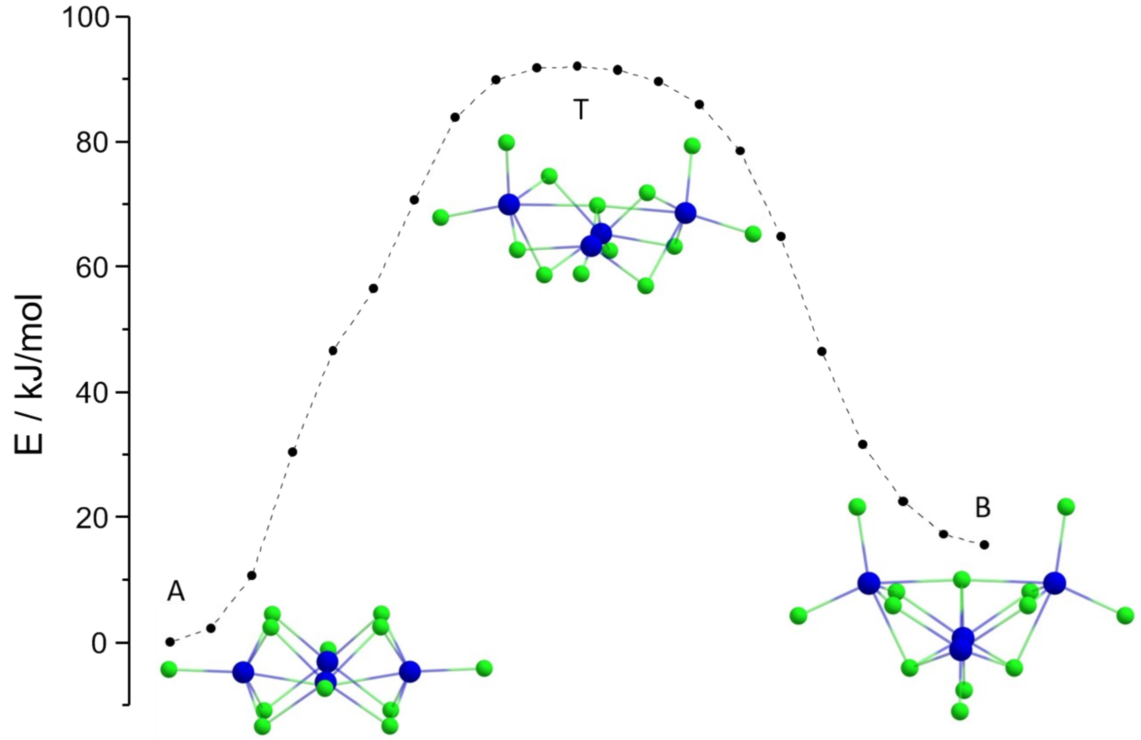


Figure S11. Optimized pathway from isomer A to isomer B for $La_4Cl_{13}^-$ obtained at level PBE/lcecp-1-TZVP. Data for the finally optimized transition state for Ln=La-Lu are listed in **Table S8**.

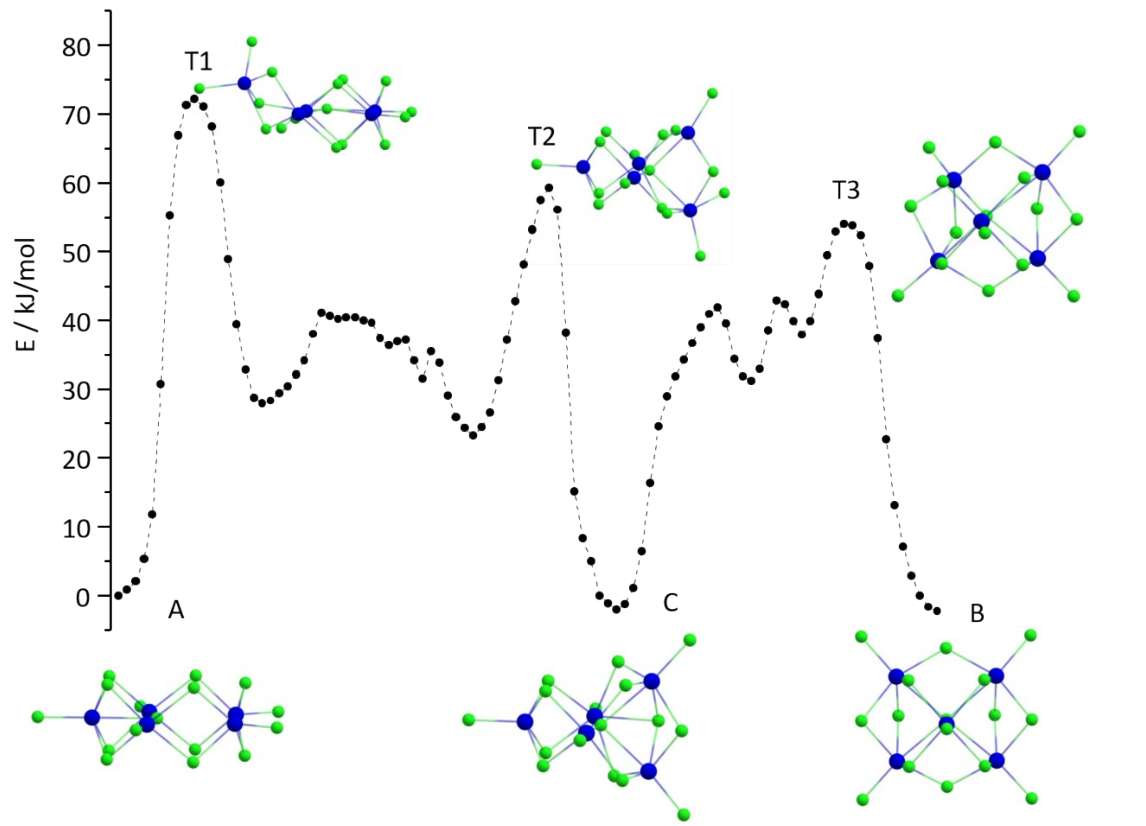


Figure S12. Optimized pathway from isomer A to isomer B via isomer C to isomer B for $La_5Cl_{16}^-$ obtained at level PBE/lcecp-1-TZVP. Data for the finally optimized transition states T1 and T2 for Ln=La-Lu are listed in **Table S9**.

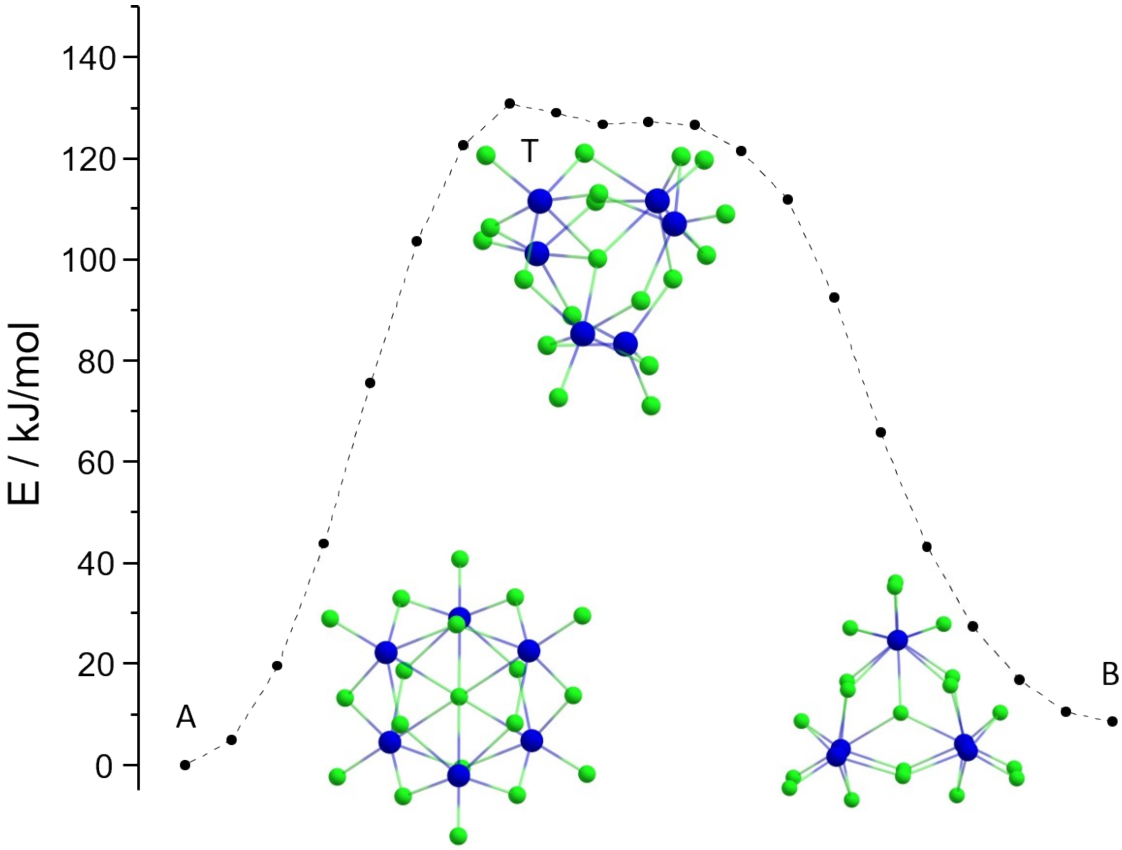


Figure S13. Optimized pathway from isomer A to isomer B for $Lu_6Cl_{19}^-$ obtained at level PBE/lcecp-1-TZVP. Data for the finally optimized transition state for Ln=La-Lu are listed in **Table S8**.

Table S8. Energies (in kJ/mol) of the transition state from A to B relative to isomer A at level PBE for x=2-4, 6, i.e. $Ln_2Cl_7^-$, $Ln_3Cl_{10}^-$, $Ln_4Cl_{13}^-$ and $Ln_6Cl_{19}^-$.

	2	3	4	6
	E	E	E	E
La	10.9	25.2	90.5	82.9
Ce	10.2	25.2	87.3	86.3
Pr	9.4	25.1	84.2	90.0
Nd	8.9	25.1	81.6	93.3
Pm	8.6	25.2	79.4	96.6
Sm	8.1	25.2	76.8	99.8
Eu	7.7	25.2	74.4	103.2
Gd	7.4	25.4	72.0	106.1
Tb	7.1	25.5	69.6	109.4
Dy	6.8	25.8	67.5	112.9
Ho	6.4	25.8	65.0	116.1
Er	6.0	25.8	62.4	119.3
Tm	5.8	26.0	60.4	122.5
Yb	5.3	25.6	57.7	125.4
Lu	5.0	25.1	56.2	127.5

Table S9. Energies (in kJ/mol) of the transition states T1-T3 isomer A at level PBE for $Ln_5Cl_{16}^-$, Ln=La-Gd. For the heavier lanthanides T1 converges to A during the optimization.

	T1	T2	T3
	E	E	E
La	71.9	58.9	54.8
Ce	72.6	62.0	57.5
Pr	72.3	65.3	60.3
Nd	73.5	68.9	63.4
Pm	74.6	72.8	66.6
Sm	75.5	76.6	69.6
Eu	76.8	80.5	72.9
Gd	77.9	84.2	75.9

Table S10. Lowest (lo) and highest (hi) vibrational frequencies (in 1/cm) for low energy isomers of $Ln_nCl_{3n+1}^-$ (n = 2-6, Ln = La, Gd ,Lu) A, B and C (for n=5) as well as imaginary (im), lowest and highest vibrational frequency for the connecting transition states (Tr(A-B) etc.).

	A		B		Tr(A-B)										
	lo	hi	lo	hi	im	lo	hi								
n=2															
La	12	291	10	298	-32	12	297								
Gd	13	300	10	308	-35	13	306								
Lu	15	308	11	316	-36	12	313								
n=3															
La	21	302	15	305	-26	16	305								
Gd	24	312	17	316	-25	18	315								
Lu	27	319	18	323	-25	20	322								
n=4															
La	20	307	22	309	-13	15	308								
Gd	24	318	25	320	-11	17	318								
Lu	28	326	27	327	-15	4	326								
n=6															
La	36	318	14	317	-37	16	317								
Gd	40	329	22	327	-39	20	327								
Lu	44	335	27	334	-42	21	333								
n=5															
	A		B		C		Tr1(A-C)			Tr2(A-C)			Tr(B-C)		
La	9	312	20	313	24	313	-20	6	313	-29	14	313	-19	19	314
Gd	12	323	23	324	27	323	-14	9	323	-36	17	324	-18	25	324
Lu	11	330	26	331	28	331	-1	2	326	-41	21	332	-25	30	332

Coordinates (PBE/ECP/TZVP, in Å)

$LaCl_4^-$

La	0.00000	-0.00000	0.00000
Cl	1.54718	-1.54718	1.54718
Cl	-1.54718	1.54718	1.54718
Cl	-1.54718	-1.54718	-1.54718
Cl	1.54718	1.54718	-1.54718

$La_2Cl_7^-$

isomer A

La	0.0393325	1.9941234	0.0342456
La	-0.0546563	-1.9942526	-0.0202587
Cl	2.1010511	0.1809318	0.2129749
Cl	-1.2827735	0.0062668	1.6232989
Cl	-0.6980199	-0.1875816	-1.9943008
Cl	1.9982567	-3.6840657	-0.0042657
Cl	-2.0985110	-3.6806370	0.0622151
Cl	0.4272561	3.6897503	2.0350149
Cl	-0.4319357	3.6754646	-1.9710416

isomer B

La	-0.0159202	2.4237904	-0.0554668
La	0.0116743	-2.0302300	0.0401069
Cl	2.4401933	3.2505990	0.4906635
Cl	0.4984255	-0.0275493	1.7927335
Cl	-0.4840048	-0.0176003	-1.7491287
Cl	2.1097366	-3.5161930	-0.5561431
Cl	-2.0972979	-3.5129446	0.6050371
Cl	-1.8200497	3.2514386	1.6981129
Cl	-0.6427571	3.7689505	-2.2565372

isomer C

La	0.0000000	0.0000000	2.2179740
La	0.0000000	0.0000000	-1.7921214
Cl	0.0000000	0.0000000	4.8924532
Cl	1.0856153	1.8803409	0.6638417
Cl	1.0856153	-1.8803409	0.6638417
Cl	-2.1712307	0.0000000	0.6638417
Cl	-1.2146923	-2.1039088	-2.8508434
Cl	-1.2146923	2.1039088	-2.8508434
Cl	2.4293847	0.0000000	-2.8508434

transition state A-B

La	0.1650438	2.0056446	-0.0223381
La	-0.2992653	-2.2072320	0.0201946
Cl	2.5832290	0.9155576	0.0628229
Cl	-0.7650935	-0.2087044	1.8297752
Cl	-0.6878661	-0.2485048	-1.8532650
Cl	1.8871282	-3.6879243	0.0779475
Cl	-2.3771993	-3.8284277	-0.0016077
Cl	-0.3249392	3.6548711	2.0050331
Cl	-0.1810376	3.6047198	-2.1185626

$La_3Cl_{10}^-$

isomer A

La	0.0000000	-2.2165520	1.0862448
La	-0.0000000	-0.0000000	-2.4260977
La	0.0000000	2.2165520	1.0862448
Cl	0.0000000	-2.7235926	-1.7790184

Cl	-2.0915155	-3.6270305	1.8359722
Cl	-0.0000000	-0.0000000	2.8698144
Cl	2.0915155	-3.6270305	1.8359722
Cl	-0.0000000	-0.0000000	-5.0718876
Cl	-2.0915155	3.6270305	1.8359722
Cl	2.0915155	3.6270305	1.8359722
Cl	1.8141398	-0.0000000	-0.2950529
Cl	0.0000000	2.7235926	-1.7790184
Cl	-1.8141398	-0.0000000	-0.2950529

isomer B

La	1.3329406	2.3087209	-0.0180813
La	1.3329406	-2.3087209	-0.0180813
La	-2.6658813	0.0000000	-0.0180813
Cl	2.1299029	-3.6891000	2.0727217
Cl	0.0000000	0.0000000	-1.3875387
Cl	2.8789027	0.0000000	0.6084345
Cl	2.1299029	3.6891000	2.0727217
Cl	2.0976632	3.6332592	-2.1477982
Cl	-1.4394514	2.4932029	0.6084345
Cl	-4.2598058	0.0000000	2.0727217
Cl	-1.4394514	-2.4932029	0.6084345
Cl	-4.1953264	0.0000000	-2.1477982
Cl	2.0976632	-3.6332592	-2.1477982

isomer C

La	3.9530168	-0.0539669	-0.0025827
La	-0.0000034	0.1241195	0.0000499
La	-3.9530136	-0.0539703	0.0025474
Cl	5.7417853	0.8072444	-1.7508963
Cl	2.0345894	1.1496354	1.7276194
Cl	-1.9155352	-2.0178659	0.1846965
Cl	5.4745764	-1.1277093	1.8711988
Cl	1.9155511	-2.0178430	-0.1847960
Cl	-5.7418890	0.8072025	1.7507812
Cl	-5.4744431	-1.1277107	-1.8713344
Cl	-2.0345921	1.1497925	-1.7274830
Cl	-1.8524279	1.1568452	1.7882803
Cl	1.8523861	1.1570041	-1.7881236

transition state A-B

La	-2.1868550	1.1770192	-0.5381080
La	-0.1611262	-2.5569683	0.5737798
La	2.1883506	1.4238003	-0.2728560
Cl	-2.7708146	-1.5710087	0.0112953
Cl	-4.2816518	2.1401190	-1.8235907
Cl	-0.0522223	3.0343538	-0.9694992
Cl	-1.9513488	1.5865856	2.0428399
Cl	0.4682560	-4.5485487	-1.0086058
Cl	3.9095993	1.2760575	-2.2431347
Cl	3.2798725	2.9909347	1.5312083
Cl	-0.6162952	-3.6181065	2.9337721
Cl	2.0998834	-0.9676202	1.2803548
Cl	0.0743521	-0.3666176	-1.5174558

$La_4Cl_{13}^-$

isomer A

La	-2.0808417	-2.0808417	-0.0262336
La	-2.0808417	2.0808417	-0.0262336
La	2.0808417	2.0808417	-0.0262336
La	2.0808417	-2.0808417	-0.0262336

Cl	-3.2361407	0.0000000	-1.6526881
Cl	0.0000000	3.2361407	-1.6526881
Cl	-2.7133056	0.0000000	1.8190772
Cl	0.0000000	-3.2361407	-1.6526881
Cl	0.0000000	-2.7133056	1.8190772
Cl	0.0000000	2.7133056	1.8190772
Cl	-3.9381809	-3.9381809	0.0977385
Cl	-0.0000000	0.0000000	-0.6453617
Cl	2.7133056	0.0000000	1.8190772
Cl	3.9381809	-3.9381809	0.0977385
Cl	-3.9381809	3.9381809	0.0977385
Cl	3.2361407	0.0000000	-1.6526881
Cl	3.9381809	3.9381809	0.0977385

isomer B

La	0.0000000	-2.1558852	-1.0415380
La	0.0000000	2.1558852	-1.0415380
La	3.1482405	0.0000000	0.9967481
La	-3.1482405	0.0000000	0.9967481
Cl	-0.0000000	0.0000000	1.1619702
Cl	0.0000000	-3.9451541	-2.9538963
Cl	2.2789901	-2.7099893	0.4831470
Cl	-2.2789901	-2.7099893	0.4831470
Cl	1.7654254	0.0000000	-1.8943174
Cl	2.2789901	2.7099893	0.4831470
Cl	3.5606112	0.0000000	3.5831557
Cl	5.5260811	0.0000000	-0.1067280
Cl	-1.7654254	0.0000000	-1.8943174
Cl	0.0000000	3.9451541	-2.9538963
Cl	-2.2789901	2.7099893	0.4831470
Cl	-3.5606112	0.0000000	3.5831557
Cl	-5.5260811	0.0000000	-0.1067280

isomer C

La	-0.0000000	2.2824108	-0.1084416
La	0.0000000	-0.0000000	-3.5969426
La	-0.0000000	-2.2824108	-0.1084416
La	0.0000000	-0.0000000	3.5680398
Cl	0.0000000	-0.0000000	-6.2196653
Cl	-1.7419308	1.8133691	-2.3466642
Cl	-0.0000000	4.8902970	-0.3686627
Cl	1.7419308	-1.8133691	-2.3466642
Cl	1.7419308	1.8133691	-2.3466642
Cl	-0.0000000	2.7041399	2.6735263
Cl	1.6778530	-0.0000000	0.8490927
Cl	-1.7419308	-1.8133691	-2.3466642
Cl	-0.0000000	-2.7041399	2.6735263
Cl	-1.6778530	-0.0000000	0.8490927
Cl	2.1199321	-0.0000000	5.1307173
Cl	-2.1199321	-0.0000000	5.1307173
Cl	-0.0000000	-4.8902970	-0.3686627

transition state A-B

La	-2.3924360	1.4477244	-0.5907738
La	1.9969498	2.5090548	0.5164490
La	2.3895811	-1.4446479	-0.6099109
La	-1.9944417	-2.5116421	0.5132037
Cl	0.9753541	3.2240963	2.8325607
Cl	3.4775846	0.1565718	1.3779855
Cl	-0.3741681	3.3560414	-0.8870903
Cl	-3.4710128	-0.1637363	1.3939853

Cl	-2.3068786	-0.8358153	-2.0485697
Cl	2.2967926	0.8463875	-2.0554014
Cl	-4.4313922	2.8871972	-1.3831543
Cl	0.0015027	-0.0016519	0.6341914
Cl	0.3698559	-3.3514378	-0.9061355
Cl	-3.8236710	-4.2926737	-0.0959500
Cl	3.8233138	4.2930573	-0.0925411
Cl	-0.9615756	-3.2384488	2.8206524
Cl	4.4246415	-2.8800770	-1.4195012

$La_5Cl_{16}^-$

isomer A

La	-0.0000000	0.0000000	3.7785299
La	0.0000000	-3.0698976	1.1054878
La	0.0000000	-2.1535486	-3.0650452
La	0.0000000	2.1535486	-3.0650452
La	0.0000000	3.0698976	1.1054878
Cl	-0.0000000	0.0000000	0.5818248
Cl	-0.0000000	0.0000000	6.4003010
Cl	-1.8183734	2.0502523	3.0230045
Cl	1.8096329	-3.0340573	-1.1271081
Cl	1.8183734	-2.0502523	3.0230045
Cl	0.0000000	-5.6293341	1.6548052
Cl	-1.8183734	-2.0502523	3.0230045
Cl	-1.8096329	-3.0340573	-1.1271081
Cl	-1.7773103	0.0000000	-3.5298466
Cl	1.7773103	0.0000000	-3.5298466
Cl	0.0000000	-3.7453250	-5.1323985
Cl	0.0000000	3.7453250	-5.1323985
Cl	-1.8096329	3.0340573	-1.1271081
Cl	0.0000000	5.6293341	1.6548052
Cl	1.8183734	2.0502523	3.0230045
Cl	1.8096329	3.0340573	-1.1271081

isomer B

La	-2.4138740	2.0475805	0.7102564
La	-2.4138740	-2.0475805	0.7102564
La	2.4138740	-2.0475805	0.7102564
La	0.0000000	0.0000000	-2.7938970
La	2.4138740	2.0475805	0.7102564
Cl	-4.1442359	0.0000000	-0.2112343
Cl	-4.0886602	-3.9472682	1.3501686
Cl	-4.0886602	3.9472682	1.3501686
Cl	-2.3255931	0.0000000	2.7123217
Cl	0.0000000	-3.3708154	1.4555061
Cl	4.0886602	-3.9472682	1.3501686
Cl	2.3255931	0.0000000	2.7123217
Cl	0.0000000	0.0000000	0.1942516
Cl	1.8454079	-2.0820703	-2.0694925
Cl	-1.8454079	-2.0820703	-2.0694925
Cl	0.0000000	0.0000000	-5.4147994
Cl	1.8454079	2.0820703	-2.0694925
Cl	4.1442359	0.0000000	-0.2112343
Cl	0.0000000	3.3708154	1.4555061
Cl	4.0886602	3.9472682	1.3501686
Cl	-1.8454079	2.0820703	-2.0694925

isomer C

La	2.2658670	-0.2982282	2.1054322
La	2.2658670	-0.2982282	-2.1054322

La	0.0629929	2.8870142	-0.0000000
La	-3.5097589	0.5698569	-0.0000000
La	-1.1012181	-2.9376944	-0.0000000
Cl	0.7181766	-2.6870716	2.2206824
Cl	-1.7419916	-5.4757487	-0.0000000
Cl	3.9445321	-0.5080941	4.0996361
Cl	0.9862441	2.1048265	-2.6994953
Cl	-2.2670464	2.4006297	-1.7023493
Cl	2.9338335	1.6702132	-0.0000000
Cl	0.9862441	2.1048265	2.6994953
Cl	-0.0421488	-0.1086326	-0.0000000
Cl	3.9445321	-0.5080941	-4.0996361
Cl	3.5904842	-1.6566030	-0.0000000
Cl	-2.2670464	2.4006297	1.7023493
Cl	0.7181766	-2.6870716	-2.2206824
Cl	-2.8976203	-1.5888562	1.7567640
Cl	-6.0978404	0.9571544	-0.0000000
Cl	-2.8976203	-1.5888562	-1.7567640
Cl	0.4527612	5.4735416	-0.0000000

first transition state A-C

La	4.2652558	-0.0553833	-0.8188320
La	1.0300635	-2.7430861	0.3939741
La	-3.1198346	-2.1927520	-0.1396273
La	-3.0492087	1.9670927	-0.1023839
La	0.7571022	2.9799754	0.7903168
Cl	-0.3507696	0.2452155	0.1190620
Cl	6.8036751	-0.5946083	-0.4400809
Cl	3.4569055	2.3543099	0.5337090
Cl	-0.9514005	-3.1367502	-1.6356073
Cl	2.7654082	-2.2495731	-1.7828925
Cl	1.8817399	-5.0943133	1.1329828
Cl	2.8487045	-0.9998801	1.5941053
Cl	-1.3806278	-2.8781279	1.9479576
Cl	-4.0489852	-0.1065523	1.5309564
Cl	-3.4430855	-0.0787402	-2.0102056
Cl	-5.0652594	-3.9184192	-0.3649177
Cl	-5.0710655	3.5866956	-0.4292581
Cl	-1.6437878	2.8134867	2.2326028
Cl	1.2939461	5.3023554	1.8442747
Cl	3.9606049	1.2611708	-3.0774546
Cl	-0.9393810	3.5378842	-1.3186816

second transition state A-C

La	2.1833877	1.2945341	-2.1040161
La	1.2191943	-2.8328049	0.4825686
La	-2.9696882	-2.0720443	0.1679779
La	-2.1943848	2.0290597	-0.6023800
La	1.5636419	1.4150070	2.2771050
Cl	0.0860834	0.0379138	0.0419403
Cl	2.3760342	3.8760801	-1.5767037
Cl	3.6227025	1.3683523	0.5218796
Cl	-0.9249647	-3.3010715	-1.3473218
Cl	2.7406614	-1.6084443	-1.4967197
Cl	2.3575397	-5.1518489	0.8832930
Cl	2.0354453	-1.2945164	2.7786315
Cl	-1.1597126	-2.8616807	2.1467498
Cl	-3.2426851	0.3969479	1.5239285
Cl	-3.3152037	-0.2397791	-1.9325117
Cl	-5.1157168	-3.5512647	0.3494297

Cl	-3.9149675	3.9548841	-0.9890897
Cl	-0.5314400	3.1376531	1.4822024
Cl	2.1987729	2.4361254	4.5972845
Cl	3.4893770	1.0204657	-4.3531084
Cl	-0.5040767	1.9464316	-2.8511397

transition state B-C

La	2.1407075	-1.8474170	-0.8665768
La	0.0269128	-0.0511232	3.1357987
La	-2.5183934	-2.0154657	-0.3293054
La	-2.0383518	1.7788801	-1.8058957
La	2.3976672	2.2285327	-0.3981232
Cl	-0.1890615	0.1420910	0.0298852
Cl	4.1014389	0.0393315	-0.0150462
Cl	1.8389908	0.4602417	-2.6204030
Cl	-1.9505918	-2.0720601	2.3849173
Cl	1.8182867	-2.0901677	1.8851208
Cl	0.5594861	-0.5230371	5.6646353
Cl	1.9324555	2.0190306	2.3331350
Cl	-1.8459250	1.8159149	3.0325082
Cl	-3.8235256	0.5559091	-0.0994684
Cl	-2.0652952	-0.7264500	-2.9404102
Cl	-4.4827847	-3.6936960	-0.6977996
Cl	-3.4630302	3.2639945	-3.4079794
Cl	0.0140534	3.5976250	-1.2519245
Cl	4.0679663	4.1653601	-0.9133314
Cl	3.7177385	-3.6343777	-1.9379102
Cl	-0.2387445	-3.4131167	-1.1818267

$La_6Cl_{19}^-$

isomer A

La	3.4080715	-0.0000000	-0.0000000
La	0.0000000	0.0000000	-3.4080715
La	-0.0000000	-3.4080715	0.0000000
La	0.0000000	0.0000000	3.4080715
La	0.0000000	3.4080715	0.0000000
La	-3.4080715	0.0000000	-0.0000000
Cl	0.0000000	-6.0085157	0.0000000
Cl	-0.0000000	-2.7505257	-2.7505257
Cl	6.0085157	-0.0000000	-0.0000000
Cl	2.7505257	-2.7505257	0.0000000
Cl	2.7505257	-0.0000000	-2.7505257
Cl	-0.0000000	-0.0000000	-6.0085157
Cl	-2.7505257	2.7505257	0.0000000
Cl	2.7505257	2.7505257	0.0000000
Cl	-0.0000000	-2.7505257	2.7505257
Cl	-2.7505257	-2.7505257	0.0000000
Cl	0.0000000	6.0085157	0.0000000
Cl	-2.7505257	0.0000000	2.7505257
Cl	0.0000000	0.0000000	0.0000000
Cl	0.0000000	2.7505257	2.7505257
Cl	-6.0085157	0.0000000	-0.0000000
Cl	-2.7505257	0.0000000	-2.7505257
Cl	0.0000000	2.7505257	-2.7505257
Cl	2.7505257	-0.0000000	2.7505257
Cl	-0.0000000	-0.0000000	6.0085157

isomer B

La	-1.4106269	-2.4432775	-2.0692995
La	-1.3740710	2.3799607	2.1419358

La	-1.3740710	-2.3799607	2.1419358
La	-1.4106269	2.4432775	-2.0692995
La	2.7481420	0.0000000	2.1419358
La	2.8212538	0.0000000	-2.0692995
Cl	-2.4609743	-4.2625326	-3.6041254
Cl	-0.1302907	-3.8118691	0.0335069
Cl	-3.2360302	2.0187696	0.0335069
Cl	-2.2730208	0.0000000	-3.1998119
Cl	-2.4388463	4.2242058	3.6427515
Cl	1.1583167	-2.0062633	3.3410323
Cl	-3.2360302	-2.0187696	0.0335069
Cl	-2.4388463	-4.2242058	3.6427515
Cl	-2.4609743	4.2625326	-3.6041254
Cl	0.0000000	0.0000000	0.2071433
Cl	-2.3166333	0.0000000	3.3410323
Cl	-0.1302907	3.8118691	0.0335069
Cl	3.3663209	-1.7930995	0.0335069
Cl	3.3663209	1.7930995	0.0335069
Cl	1.1365104	-1.9684937	-3.1998119
Cl	4.9219487	0.0000000	-3.6041254
Cl	1.1365104	1.9684937	-3.1998119
Cl	4.8776927	0.0000000	3.6427515
Cl	1.1583167	2.0062633	3.3410323

isomer C

Cl	-0.0395803	5.9748182	4.1481633
Cl	-0.0873216	5.9340184	-3.4315175
Cl	0.0000000	0.0000000	-6.2667099
Cl	0.0873216	-5.9340184	-3.4315175
Cl	0.0395803	-5.9748182	4.1481633
La	0.0185317	4.0343448	2.3886289
La	0.0025873	3.9396288	-1.7458230
La	0.0000000	0.0000000	-3.6717778
La	-0.0025873	-3.9396288	-1.7458230
La	-0.0185317	-4.0343448	2.3886289
Cl	-1.8038253	2.0039198	-2.8308350
Cl	-0.2337892	-1.7056283	0.3480216
Cl	-1.7547089	-4.8918089	0.3113998
Cl	-1.7210973	-2.0247820	3.5551816
Cl	-1.8248929	4.6605059	0.3239194
Cl	1.8248929	-4.6605059	0.3239194
Cl	1.8038253	-2.0039198	-2.8308350
Cl	0.2337892	1.7056283	0.3480216
Cl	1.7547089	4.8918089	0.3113998
Cl	1.7210973	2.0247820	3.5551816
Cl	-1.8175415	2.0172133	3.3270825
La	0.0000000	0.0000000	2.5762514
Cl	1.8175415	-2.0172133	3.3270825
Cl	-1.7884547	-2.0914662	-2.9904516
Cl	1.7884547	2.0914662	-2.9904516

transition state A-B

La	3.1863024	0.3265012	0.4413345
La	-0.6473322	-0.1880422	-3.4521983
La	0.1908446	-3.3242946	-0.1425710
La	-0.3142125	-0.6654760	3.9237471
La	0.6835622	3.3711843	-1.3081531
La	-2.8086469	0.4314868	0.6204368
Cl	0.2001736	-5.9180547	-0.3910408
Cl	0.4631787	-2.6994728	-2.9238870

Cl	5.7810234	0.5402048	0.5221033
Cl	2.9031663	-2.4392839	-0.0344326
Cl	2.5475686	1.2799730	-2.2126406
Cl	-1.1363785	-0.7454340	-5.9416431
Cl	-1.9027146	3.0817079	-0.3988326
Cl	2.2958597	2.9832639	0.9428755
Cl	0.2589705	-3.1362578	2.6994469
Cl	-2.4439240	-2.4274336	-0.1769568
Cl	1.2128919	5.8631214	-1.8408072
Cl	-2.9122918	-1.1691156	3.0393458
Cl	0.1014670	-0.0625906	-0.3307401
Cl	-1.0756868	1.6754172	2.6498534
Cl	-5.2971007	1.1679396	0.8541202
Cl	-3.0923369	0.2321190	-2.3353602
Cl	-0.2357369	2.5486510	-3.8601867
Cl	2.3561631	-0.0632686	3.1192308
Cl	-0.3148104	-0.6628458	6.5369558

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