A Study of Hydrated Rare Earth Ions

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Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

Hydrated lanthanide(III) ions $Ln^{3+}(H_2O)_8$ with $Ln^{3+} = La^{3+}$ to Yb^{3+} have been studied using ab-initio methods. The binding energy as a function of ion-water distance and position of the ion in the rare earth series is discussed. The calculations are related to recent experimental results elucidating the hydration behaviour of lanthanide(III) ions. Since no S-shape behaviour is found for complex binding energies or metal-oxygen distance, the calculations indicate that observed thermodynamic anomalities should come from hydration number changes due to the different ionic radii within the series.

The non-additivity of the ion-water interactions has been calculated and it is found that its relative importance increases from 26% for La^{3+} to 32% for Ln^{3+}.

The S-shape behaviour in many physical properties of solutions of rare earth ions is known since a long time [1]. Briefly spoken, it means that for many thermodynamic and transport properties the plot of the property versus the nuclear charge results in a linear dependency for the light rare earth ions and in a separate one for the heavy ones with a discontinuity in between. It has been discussed whether a change of the hydration number within the series could be responsible for this. There is an ongoing discussion about the hydration number of the rare earth ions and its concentration dependence ([2] and references therein). Various recent studies have employed X-ray diffraction, EXAFS [3] and neutron diffraction [4] techniques. While some authors believe that a change from coordination number 9 to 8 occurs within the series ([3] and references therein, [5]), this question has not been settled yet [2].

In the present study Hartree-Fock calculations on octahydrates of all rare earth ions are presented. The ion-oxygen distance has been optimized and the binding energy of the water molecules has been calculated. Additionally, full geometry optimizations on 1:1 complexes have been performed on the Hartree-Fock and MP2 (second order perturbation theory) levels of theory.

The main aim of the study is to show whether an S-shape behaviour exists for distances or interaction energies between the water molecules and the Ln^{3+} ions. If such a behaviour is found, then the "two-series"-anomality of the rare earth ions could be explained as primarily caused by differences in the electronic structure of the rare earth elements, if not the ions would rather behave as spheres with decreasing size within the series (La: 1.16 Å; Lu: 1.03 Å) and interact purely electrostatically with the hydration shell water molecules. Then it must be concluded that a change in coordination number, simply due to the decrease in the ionic radii, is the only explanation of the S-shape behaviour.

Method of Calculations

The lanthanide atoms have 57 to 71 electrons. Only recently, ab-initio calculations of molecules including such heavy elements have become possible in a satisfactory way using effective core potentials (ECP's) [6, 7]. Using ECP's, the inner shell electrons do not contribute much to the total computational effort while the accuracy of all-electron Hartree-Fock calculations is retained. Further, the inclusion of relativistic effects, which become important for the heavy elements, is greatly facilitated. Very recently, Preuss and coworkers [8] have published the first complete set of

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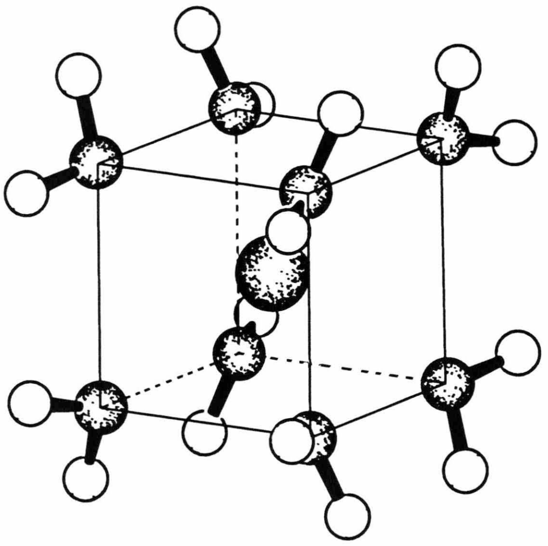

Fig. 1. Structure of $Ln^{3+}(H_2O)_8$.

Gaussian basis sets and ECP's for the rare earth elements and have demonstrated their use in molecular calculations [9]. For the lanthanides with partially filled 4f shell, the inclusion of this energetically low-lying orbitals into the effective potential further facilitates the ab-initio calculations. From the interaction of the 4f subshell with the valence electrons a large number of very similar electronic states arise which would all have to be treated explicitly if the 4f electrons are not included as part of the effective potential interacting with the energetically high-lying 5s 5p valence shell electrons. In our calculations, we have used the energy-adjusted quasi-relativistic effective potentials and optimized (7s 6p 5d)/[5s 4p 3d] GTO valence basis sets mentioned above [8]. For the oxygens of the water molecules the ECP and basis set from Stevens, Basch and Krauss [10] in double zeta quality with one d-type polarization function ($e_d = 1.154$), and for the hydrogens a double zeta basis set from Dunning [11] was used.

We have restricted ourselves to calculations on the octaaquo and, for comparison, monoaquo-complexes. As mentioned above, it is not at all clear if the coordination number 8 is preferred for all lanthanide ions in dilute aqueous solution or if some ions prefer a higher one. It is very unlikely, however, that some particular trend within the series could only be found for higher hydration numbers than 8, and calculations with more water molecules of the same quality become expensive from the computational viewpoint.

Further, for the octaaquo-complexes a cubic structure (Fig. 1) was assumed. This is a somewhat arbitrary choice since for $Ln^{3+}(H_2O)_8$ also antiprismatic or dodecahedral structures are possible, but from electrostatic considerations [5] it can be assumed that they lead to energetically somewhat more favourable but very similar results. The cubic geometry was chosen because of the large time-savings in the ab-initio calculations due to exploitation of the high symmetry. Nevertheless the ab-initio calculations on the $Ln(H_2O)_8$ clusters took about 40 CPU-minutes per point on an IBM 3090/400 VF computer using a modified version of the program HONDO version 7 [12]. One optimization of an $Ln^{3+}-H_2O$ complex at the level of MP2 perturbation theory took about the same time.

Results and Discussion

The energy as function of $O-Ln^{3+}$ distance has been calculated by pointwise energy calculation and is shown in Figure 2. In these calculations, the water geometry has been fixed at $r_{OH} = 0.957$ Å and $\alpha_{HOH} = 105.4°$. The curve with the lowest minimum at shortest distances corresponds to Lu^{3+} whereas the La^{3+} has the least deep minimum and longest $Ln^{3+}-O$ distance. It can be seen that all minima are not particularly steep, i.e. that a change of the $Ln^{3+}-O$ distance in the order of 0.1 Å does not change the total energy by more than about 2 kcal/mol. Interestingly, the various curves are not spaced completely evenly but at least for the more heavy lanthanides there seems to be a somewhat larger gap between every second element. The significance of this is unclear to us at the moment.

From this diagram the change of $r_{Ln\text{-}O}$ and of the binding energy per water molecule, ΔE, with the nuclear charge of the rare earth elements can be extracted and is shown in Figs. 3 and 4, respectively, together with linear regression lines. One can see that there is definitively no S-shape behaviour in the dependence of energy or distance on the atomic numbers Z. While the energy versus Z curve is quite smooth, the $r_{Ln\text{-}O}$ versus Z plot shows a somewhat larger deviation from the regression line. For La^{3+}, the La–O distance is 2.658 Å, which is about 0.1 Å longer than the value reported in [1 b], which is an indication that a cubic arrangement might not be the energetically most favourable one.

Therefore it can be concluded that it is rather likely that the anomalous behaviour in thermodynamic and

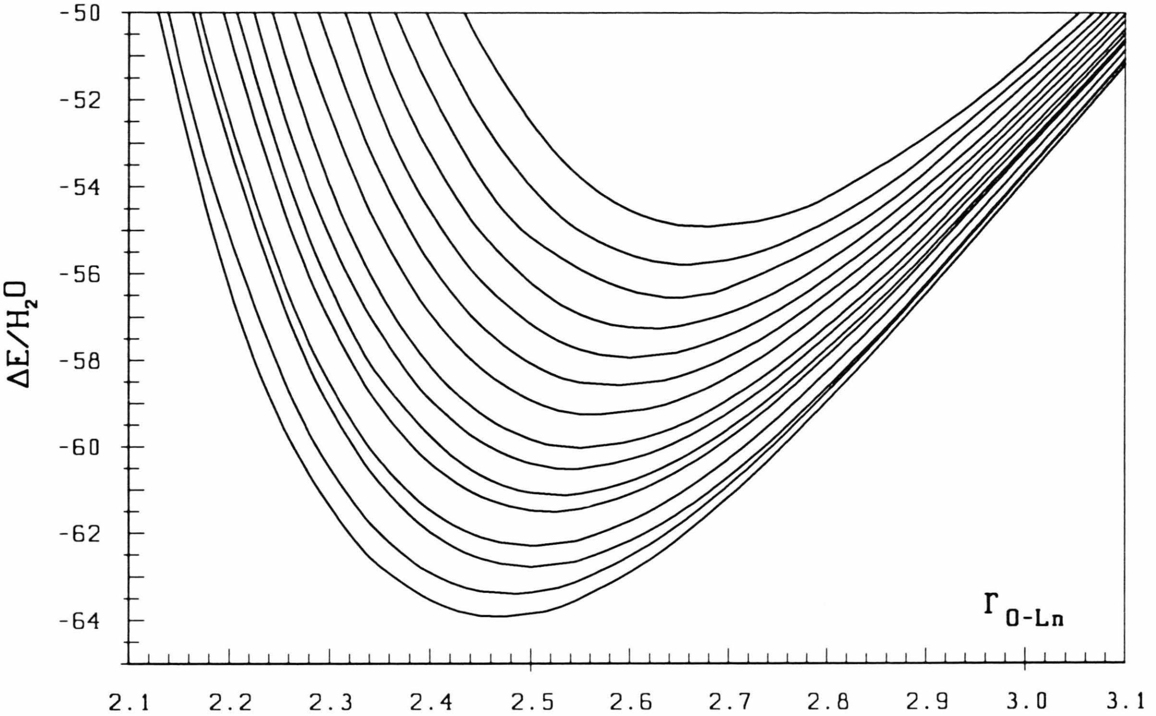

Fig. 2. Binding energy per water molecule as a function of r_{OLn} (distances in Å, energies in kcal/Mol).

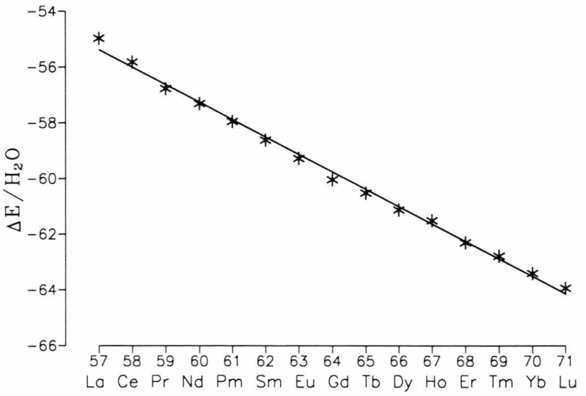

Fig. 3. Binding energies per water molecule in the $Ln^{3+}(H_2O)_8$ complexes (kcal/Mol).

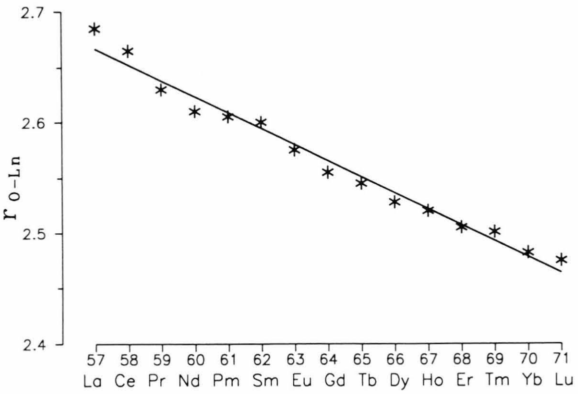

Fig. 4. Optimized values of r_{OLn} in $Ln^{3+}(H_2O)_8$ (Å).

transport properties within the lanthanide series is indeed simply caused by a change in the hydration number due to the different ionic radii within the series and not by differences concerning the electronic structure.

It is reasonable to assume that for hydrated ions the Hartree-Fock level is qualitatively sufficient. While the octahydrated complexes were too big to check the importance of the correlation energy, we have calculated the metal-oxygen distance and binding energy for $Ln^{3+}-H_2O$ by means of Moeller-Plesset second order perturbation theory (MP2). All MP2 results show slightly higher binding energies (Fig. 5) and slightly lower oxygen-metal distances (Fig. 6) than the

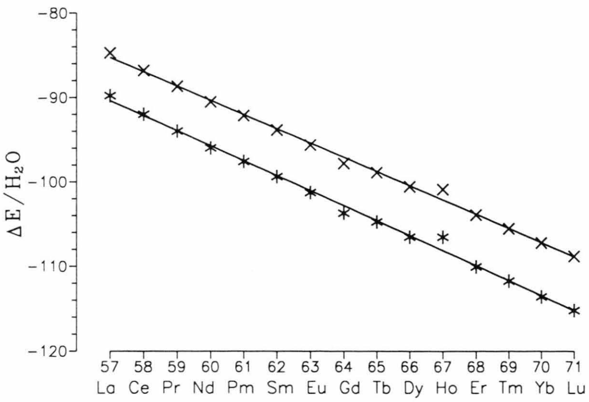

Fig. 5. Binding energy in $Ln^{3+}H_2O$ at the Hartree-Fock (×) and MP2 (∗) level (kcal/Mol).

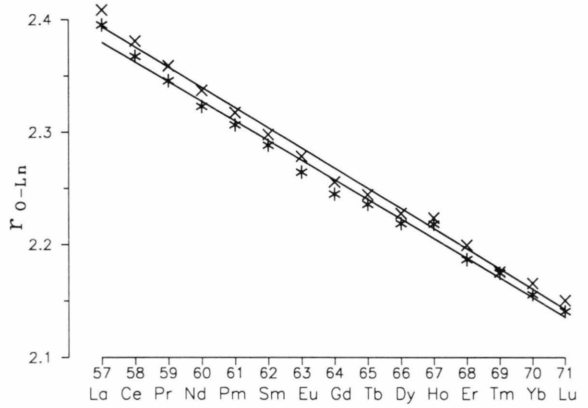

Fig. 6. Optimized Ln–O distance in $Ln^{3+}H_2O$ at the Hartree-Fock (×) and MP2 (∗) level (Å).

Table 1. Binding energies at the Hartree-Fock and pairwise additive level (distances in Å, energies in kcal/Mol).

Ln	Z	$r_{\text{O-Ln}}$	E_{HF}	E_{pair}
La	57	2.685	−54.97	−71.35
Ce	58	2.665	−55.82	−72.83
Pr	59	2.630	−56.77	−74.64
Nd	60	2.610	−57.31	−76.06
Pm	61	2.605	−57.95	−77.03
Sm	62	2.600	−58.62	−77.96
Eu	63	2.575	−59.28	−79.50
Gd	64	2.555	−60.04	−81.55
Tb	65	2.545	−60.52	−82.73
Dy	66	2.528	−61.13	−83.34
Ho	67	2.520	−61.52	−83.73
Er	68	2.505	−62.31	−85.65
Tm	69	2.501	−62.79	−86.60
Yb	70	2.482	−63.41	−87.95
Lu	71	2.475	−63.94	−88.87

Hartree-Fock values. The differences in energy are almost constantly 6 kcal/mol within the series. The differences in metal-oxygen distance are smaller than the differences between neighbouring members of the series.

Since in case of the monohydrates a complete geometry optimization was performed, their effect on the geometry of the water molecules can be studied. The ions cause an elongation of the O–H distance in the water molecule by an average of 0.031 Å. For the MP2-calculations, the r_{OH} value of the free water molecule (0.9649 Å) is stretched upon complex formation between 0.9920 Å (La^{3+}) and 1.001 Å (Lu^{3+}). This is about 1.5 times the effect observed for Mg^{2+} [13].

In the context of water-ion interactions the additivity of the interaction energies is an interesting quantity because it tells how the total binding energy can be modelled by the sum of pair potentials. This in turn is necessary to judge the quality of computer simulations using such potentials. It is reasonable to assume that nonadditive contributions to the total binding energy are mainly due to water-ion interactions whereas nonadditive (water)$_n$ interactions are of minor importance [14, 15]. We have calculated the water-ion binding energy in $Ln^{3+}(H_2O)_8$ in the pair approximation for water-ion interactions according to

$$\Delta E_{\text{pair}} = \{E(Ln^{3+}H_2O) - E(H_2O) - E(Ln^{3+})\} + \{E((H_2O)_8)/8 - E(H_2O)\}\,.$$

ΔE_{pair} is the binding energy per water molecule in the pair approximation, all $E(X)$ values are Hartree-Fock total energies of X. The first term in the equation gives the relative stabilization energy of $Ln^{3+}H_2O$ at an Ln–O distance optimized for $Ln^{3+}(H_2O)_8$ and the second one accounts for the water-water repulsion in the $(H_2O)_8$ cage. Table 1 compares the binding energies of the full Hartree-Fock calculations with the ones obtained as outlined above. The relative magnitude of the nonadditive contribution to the interaction energy is higher than one calculated for Mg^{2+} (ca. 17%) and is in the order found for Al^{3+} (ca. 27%) [15]. It is still much smaller than the one found for Be^{2+} (ca. 60%) [16]. The electric field of the ion at the position of the oxygen is nearly equal in $Mg^{2+}(H_2O)_6$ and $La^{3+}(H_2O)_8$, due to the larger La^{3+}–O distance compared to Mg^{2+}–O. The polarization of the water molecules should therefore be comparable. However, the number of possible three-body terms H_2O-ion-H_2O is larger for octahydrates (27) than it is for hexahydrates (15) and can thus explain the observed difference.

The relative importance of the nonadditive contributions increases towards the more heavy rare earth ions so that e.g. a computer simulation of aqueous Lu^{3+} or a comparative simulation study of different rare earth ions should rather be based on effective pair potentials if the same quality as for main group ions [17] is desired.

Acknowledgement

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