

Evidence of Different Stoichiometries for the Limiting Carbonate Complexes across the Lanthanide(III) Series

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Abstract The stoichiometries of limiting carbonate complexes of lanthanide(III) ions were investigated by solubility measurements of hydrated $\text{NaLn}(\text{CO}_3)_2$ solid compounds ($\text{Ln} = \text{La, Nd, Eu}$ and Dy) at room temperature in aqueous solutions of high ionic strength ($3.5 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$) and high CO_3^{2-} concentrations (0.1 to $1.5 \text{ mol}\cdot\text{kg}^{-1}$). The results were interpreted by considering the stability of carbonate complexes, with limiting species found to be $\text{La}(\text{CO}_3)_4^{5-}$, $\text{Nd}(\text{CO}_3)_4^{5-}$, $\text{Eu}(\text{CO}_3)_3^{3-}$ and $\text{Dy}(\text{CO}_3)_3^{3-}$. TRIFS measurements on the Eu and Dy solutions confirmed the predominance of a single aqueous complex in all the samples. Equilibrium constants were determined for the reaction $\text{Ln}(\text{CO}_3)_3^{3-} + \text{CO}_3^{2-} \rightleftharpoons \text{Ln}(\text{CO}_3)_4^{5-}$: $\log_{10} K_{4,\text{La}}^{3.5\text{m NaClO}_4} = 0.7 \pm 0.3$, $\log_{10} K_{4,\text{Nd}}^{3.5\text{m NaClO}_4} = 1.3 \pm 0.3$, and for $\text{Ln} = \text{Eu}$ and Dy , $\log_{10} K_{4,\text{Ln}}^{3.5\text{m NaClO}_4} \leq -0.4$. These results suggest that tetracarboxylate complexes are stable only for the light lanthanide ions in up to $1.5 \text{ molal CO}_3^{2-}$ aqueous solutions, in agreement with our recent capillary electrophoresis study. Comparison with literature results indicates that analogies between actinide(III) and lanthanide(III) ions of similar ionic radii do not hold in concentrated carbonate solutions. $\text{Am}(\text{CO}_3)_3^{3-}$ was previously evidenced by solubility measurements, whereas we have observed that $\text{Nd}(\text{CO}_3)_4^{5-}$ predominates in similar conditions. We may speculate that small chemical differences between $\text{Ln}(\text{III})$ and $\text{An}(\text{III})$ could result in macroscopic differences when their coordination sphere is complete.

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1 Introduction

Many publications related to nuclear fields have focused particular attention the speciation of actinides (An) in aquatic systems, typically to evaluate their environmental behavior (disposal of radioactive wastes, contaminated sites, nuclear fuel reprocessing, sequestering and decorporation). Among the research areas, the thermodynamic stabilities of An species in their various possible oxidation states has been of great concern. Reducing conditions favor the +III oxidation state for Am, Cm and potentially Pu. Because measuring data for these radioactive elements requires (i) potentially harmful manipulations of radioactive matter only possible with dedicated facilities and (ii) generates radioactive wastes, chemical analogies, either among An(III) themselves or with lanthanide (Ln) ions in the same oxidation state, are often used to avoid additional experimentation and to complete data bases about soluble and solid compounds [1–6].

The aqueous speciations of Ln(III) and An(III) in carbonate solutions have been extensively studied, since these cations form strong aqueous complexes with carbonate ligands. Various techniques have been used: partition [7–18], solubility [19–25], spectroscopy [26–38] or electromotive force measurements [39]. Most of the studies concern MCO_3^+ and $\text{M}(\text{CO}_3)_2^-$, which could be predominant in natural brines and groundwaters. Consequently, numerous data are available for their formation constants β_1 and β_2 , respectively [18, 40, 41]. There are many fewer data on the limiting carbonate complexes, which are less relevant for environmental issues, but of fundamental importance in the coordination chemistry of actinides.

In concentrated carbonate solutions the relevance of analogies between Ln(III) and An(III) ions is a topic still being discussed. The $\text{M}(\text{CO}_3)_4^{5-}$ stoichiometry has been proposed for $\text{M}^{3+} = \text{La}^{3+}$ [19], Ce^{3+} [20], Pr^{3+} [19, 26], Nd^{3+} [19, 26, 27], Sm^{3+} [19], Eu^{3+} [7, 8, 19], Gd^{3+} [19] and Cm^{3+} [28, 29], whereas other authors have considered that $\text{M}(\text{CO}_3)_3^{3-}$ would be the limiting aqueous complex for $\text{M}^{3+} = \text{Nd}^{3+}$ [21],¹ Eu^{3+} [22, 30], Er^{3+} [26], Am^{3+} [3, 23, 24], and Cm^{3+} [31]. These observations may suggest that the main parameter that controls the stoichiometry of the limiting carbonate complexes of the Ln^{3+} ions is their ionic size. The Ln contraction is typically reflected by (i) a regular decrease of the distance between the central Ln^{3+} aquo ion and the oxygen atoms of the water molecules in the first hydration layer with increasing atomic numbers, typically from $d_{\text{La-OH}_2} = 2.55 \text{ \AA}$ to $d_{\text{Lu-OH}_2} = 2.31 \text{ \AA}$ as obtained by averaging EXAFS results [42–45]; (ii) a decrease of the hydration numbers of the Ln^{3+} ions from 9 water molecules to 8 across the Ln series as recently discussed and reproduced by classical molecular dynamics simulations [46].

Chemical differences between light and heavy Ln^{3+} ions in concentrated carbonate solutions should be confirmed by investigating several f-element ions with the same technique.

¹Rao et al. measured the solubility of $\text{NaNd}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$ over a wide range of free carbonate concentrations ($0.1 \text{ mol}\cdot\text{L}^{-1} \leq [\text{Na}_2\text{CO}_3]_{\text{initial}} \leq 2 \text{ mol}\cdot\text{L}^{-1}$ and $0.1 \text{ mol}\cdot\text{L}^{-1} \leq [\text{NaHCO}_3]_{\text{initial}} \leq 1 \text{ mol}\cdot\text{L}^{-1}$) [21]. The ionic strength of the various samples was not constant and thermodynamic modelling is required to calculate the aqueous speciation of Nd^{3+} for each sample. We tried to fit their experimental data with a model including $\text{Nd}(\text{CO}_3)_4^{5-}$. The residual sum of squares of the regression analysis was reduced by 30%. This interpretation gives $\log_{10} K_4^0 = -2.2 \pm 0.9$, which is in good agreement with our results ($\log_{10} K_4^0 = -2.1 \pm 0.9$) (see Sect. 6.1 in Appendix).

In a single solubility study, the $\text{Ln}(\text{CO}_3)_4^{5-}$ complex was proposed as the limiting aqueous complex for all the Ln^{3+} ions [9], but this interpretation might be biased by kinetic effects [47]. We have therefore studied carbonate solutions of Ln(III) ions for the whole 4f-series by capillary electrophoresis coupled to ICP-MS, and found that the variation of the electrophoretic mobility supported a change in the Ln speciation between the light Ln ions and the heavier ones [48].

The reviews by the NEA thermochemical data base project did not select any formation constant for the Np(III) and Pu(III) limiting carbonate complexes, and recommended estimating them by analogy with Am(III) [4], for which $\text{Am}(\text{CO}_3)_3^{3-}$ was considered to be the limiting stoichiometry according to experimental data [3]. More recently, $\text{Cm}(\text{CO}_3)_4^{5-}$ was proposed as the limiting stoichiometry of Cm(III) carbonate complexes from spectroscopic data [28, 29]. The chemical difference with Am(III) in such a highly charged complex was supposed to originate from very small differences in the ionic radii of Am^{3+} and Cm^{3+} [5]. According to their ionic radii, an opposite behavior would be expected by comparison with the 4f-series ions. It should be pointed out that medium effects and stoichiometry changes are hardly distinguishable because the ligand is at high concentration and necessarily interacts with metal species at short distance. Hence, interpretations should be made with appropriate methodologies for taking into account medium effects.

The stoichiometry of the limiting complex also depends on the maximum activity that can be experimentally obtained for the ligand in aqueous solutions. The stoichiometries and structures of carbonate complexes of Ln(III) ions have also been investigated in the solid state. Among the number of synthesized Ln solid compounds containing carbonate, only a few may be representative of the structure of the aqueous complexes stable in highly concentrated carbonate solutions. The guanidinium [49] and cobalt hexamine [50–52] cations have shown good properties for precipitating Ln(III) limiting carbonate complexes. Nd(III) [49, 51], Sm(III) [50] and Ho(III) [52] were proposed to be coordinated to four carbonate ligands according to single-crystal X-ray diffraction. Absorbance spectra of Nd(III) in concentrated guanidinium carbonate aqueous solutions are in fair agreement with diffuse reflectance spectra of the stoichiometry in the solid compound, where the Nd coordination is expected to be $\text{Nd}(\text{CO}_3)_4(\text{H}_2\text{O})^{5-}$ [49]. Consequently, $\text{Nd}(\text{CO}_3)_4^{5-}$ has been proposed to be the most probable stoichiometry in solution where it could be partially dissociated. The $\text{Ho}(\text{CO}_3)_4^{5-}$ anion has been stabilized in a crystal matrix, and the Raman spectrum of the crystalline powder was compared with the one of a $0.01 \text{ mol}\cdot\text{L}^{-1}$ Ho(III)/ $2.5 \text{ mol}\cdot\text{L}^{-1}$ Na_2CO_3 solution [52]. The Raman shifts were found to be slightly different, which was interpreted as indicating the coexistence of the tetracarboxato complex and lower carbonate complexes in the solution. Other reported structures from solid-state analyses have shown both monodentate and bidentate carbonates, and also bridging ligands [50, 51], which are hardly comparable with aqueous complexes. Solid state methods provide useful structural information, but a definite conclusion about the stoichiometry of the aqueous complexes is difficult to draw.

The stoichiometries of the aqueous complexes can be directly deduced from the solubility of a well-characterized solid phase equilibrated with the aqueous solution. The stoichiometries $\text{Ce}(\text{CO}_3)_4^{5-}$ [20], $\text{Nd}(\text{CO}_3)_3^{3-}$ [21], $\text{Eu}(\text{CO}_3)_3^{3-}$ [22] and $\text{Am}(\text{CO}_3)_3^{3-}$ [23, 24] have been determined from the limiting slopes of solubility curves of double carbonate compounds, under conditions where such solid phases are expected to be stable and control the solubilities [3, 22–24, 53].

Several factors like the crystallinity of the solid, the possible presence of hardly-detectable amorphous phases, possible presence of colloids, and also uncertainties inherent to the measurements may contribute to the difficulty of obtaining an unambiguous interpretation of the solubility curves. The association of the solubility study with a speciation

technique like time-resolved laser-induced fluorescence spectroscopy (TRLFS) can help determining the species present in the solutions, and validate the thermodynamic modelling. In a previous study by both solubility and TRLFS, it was concluded that $\text{Eu}(\text{CO}_3)_3^{3-}$ was the predominant complex in equilibrium with $\text{NaEu}(\text{CO}_3)_2(\text{s})$ [22]. Noticeably, interpretation of only the TRLFS data in a large range of carbonate concentration could have led to misinterpretation by considering $\text{Eu}(\text{CO}_3)_4^{5-}$ in the modelling, because it slightly improved the quality of the fit [30].

In the present study, we have complemented our earlier studies on Eu(III) by investigating the speciation of four Ln(III) ions representative of the 4f-series. The solubility of $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ compounds was measured for Ln = La, Nd, Eu, and Dy in mixtures of sodium perchlorate and sodium carbonate solutions at a constant ionic strength of $3.5 \text{ mol} \cdot \text{kg}^{-1}$. The results are interpreted by taking into account appropriate activity corrections. TRLFS was used to investigate the Eu and Dy aqueous speciation in the solutions equilibrated with their respective solids, and validate the thermodynamic modelling of the solubility curves. The stoichiometries and the stepwise formation constants of the limiting carbonate complexes are determined and discussed by comparison with available data for Ln and An solutions.

2 Experimental Details

2.1 Materials

All of the experiments were performed at room temperature ($22 \pm 1^\circ\text{C}$). Millipore deionized water (Alpha-Q, $18.2 \text{ M}\Omega \cdot \text{cm}$) was used throughout the experiments. The solubility solutions were prepared from weighed amounts of Na_2CO_3 (VWR, Normapur $\geq 99.9\%$), NaHCO_3 (VWR, Normapur $\geq 99.5\%$), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), and NaCl (Labosi, $\geq 99.9\%$) which were used without further purification. The $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ solid compounds were prepared from weighed amounts of the sodium salts and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (VWR, Rectapur $\geq 99.99\%$), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Johnson Matthey $\geq 99.9\%$), $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Aldrich $\geq 99.99\%$) and $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Johnson Matthey $\geq 99.9\%$). HNO_3 65% (Merck, Suprapur) was used for Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES, Optima 2000 DV, Perkin Elmer) measurements.

2.2 Preparation of the Solid Compounds

The $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ solid compounds were prepared by precipitation from mixtures of concentrated Na_2CO_3 or NaHCO_3 solutions with $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ solutions. 0.32 mL of 2.25 to $2.39 \text{ mol} \cdot \text{L}^{-1}$ $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ aqueous solutions were added into 8 mL of a $0.5 \text{ mol} \cdot \text{L}^{-1}$ NaHCO_3 solution and mixed thoroughly, for the 3 heavier lanthanides: Nd, Eu and Dy. This general procedure was slightly modified for La: 1 mL of $0.7 \text{ mol} \cdot \text{L}^{-1}$ $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added into 8 mL of a $1 \text{ mol} \cdot \text{L}^{-1}$ Na_2CO_3 solution, and mixed thoroughly. The polyethylene bottles containing the solid compounds were shaken on an orbital shaker for 92, 120, 481 and 636 days for La, Nd, Eu, and Dy, respectively. The suspensions were then filtered through nitrocellulose Whatman 0.2 μm membranes. This pore size is similar to that used in previously published solubility studies using similar lanthanide or americium solid compounds under similar experimental conditions [23, 24, 49]. The presence of colloidal particles in such conditions has never been observed so far, but particles smaller than 0.2 μm , if any, may induce some errors on the solubility. The precipitates were washed with deionized water prior to being characterized. The precipitates were found to be $\text{NaLa}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{NaNd}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, $\text{NaEu}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$, and $\text{NaDy}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$

according to analyses by ICP-OES, thermogravimetry (SETARAM TAG 24), and powder X-ray diffraction (XRD, X'Pert pro Panalytical diffractometer, CoK α 1). The solid compounds are reasonably well crystallized as shown by their powder XRD patterns monitored before and after solubility measurements (see Fig. 6 in Appendix). Details on the synthesis and characterization of the solid compounds have been reported in a previous paper [54]. The number of water molecules for the solid La compound was chosen arbitrarily, it has an influence only on the ionic strength corrections, but this influence is very small.

2.3 Solubility Measurements

Batch experiments were performed for the four double carbonate solid compounds in various Na₂CO₃–NaHCO₃–NaClO₄–NaOH solutions with $\{\text{Na}^+\} = 3.5 \text{ mol}\cdot\text{kg}^{-1}$ (where braces indicate molal concentrations, mol·kg⁻¹, see Table 4 in Appendix). One additional batch was prepared for each Ln that contained NaCl at 3.2 mol·kg⁻¹ instead of NaClO₄, to check if the counter anion (Cl⁻ or ClO₄⁻) has any influence on the medium effect. The samples were placed in 50 mL polypropylene tubes, each containing an excess of NaLn(CO₃)₂·xH₂O. The tubes were closed and continuously shaken with reciprocating motion. At different times of contact $-\log_{10}[\text{H}^+]$ (where brackets indicate molar concentrations, mol·L⁻¹) were measured and aliquots were taken out and filtered with 0.2 μm nitrocellulose membranes. The first filtered 0.7 mL of solution was discarded. The analyses were carried out on the following filtered few milliliter samples. The aliquots were diluted in 0.5 mol·L⁻¹ HNO₃ and the Ln concentration was determined by ICP-OES. The same HNO₃ solution was used to dilute the commercial standard solutions (Spex, CertiPreps, 2% or 5% HNO₃). Based on the standard deviation, the errors on the Ln concentrations were estimated to be less than 3%.

At the end of the sampling periods, the solid compounds were filtered out and analyzed by XRD. NaLn(CO₃)₂·xH₂O was evidenced in all the samples, except for one La solution with $\log_{10}\{\text{CO}_3^{2-}\} = -0.73 \text{ mol}\cdot\text{kg}^{-1}$. When the solids NaLa(CO₃)₂·5H₂O and NaEu(CO₃)₂·5H₂O were equilibrated in a 3.05 mol·kg⁻¹ Na₂CO₃ solution, the solubility was found to be lower than expected and the diffraction peaks revealed the presence of an additional crystalline compound identified as Na₂CO₃. These additional peaks disappeared after washing the remaining solid compound with water. The presence of a carbonate compound may have altered the free carbonate concentration, and also the Ln concentration if co-precipitation occurred. Moreover, the ionic strengths of such samples were 9.15 mol·kg⁻¹, which may be out of the valid range of the SIT formula, usually 0–4 mol·kg⁻¹. Consequently, these data were not included in the evaluation of the stoichiometry of the limiting complexes. At low free carbonate concentrations ($\log_{10}\{\text{CO}_3^{2-}\} \leq -1.6 \text{ mol}\cdot\text{kg}^{-1}$), the solubility was found to be higher than expected if it were controlled by NaLn(CO₃)₂·xH₂O in equilibrium with carbonate complexes. Such an observation can be attributed to the transformation of the NaLn(CO₃)₂·xH₂O solid compound into a metastable Ln₂(CO₃)₃ solid compound. The kinetics of precipitation of the latter compound seemed to be faster than that of the NaLn(CO₃)₂·xH₂O solid compound [3, 20, 21, 23, 47, 53]. Moreover, under these conditions, a significant hydrolysis of Ln(III) cannot be excluded as calculated from published hydrolysis constants [47, 55–59]. Then, samples containing low carbonate concentrations or a concentration of supporting electrolyte lower than 3.5 mol·kg⁻¹ (about 0.5 and 1 mol·kg⁻¹) are subject to hydrolysis, and the data were discarded for the present analysis. Moreover, the possible formation of colloids under these experimental conditions may contribute to the dispersion of the experimental results. All of these additional data points that were considered unreliable for our purpose but are given elsewhere [47]. Only the results obtained in high ionic strength solutions containing high carbonate concentrations were used in the quantitative thermodynamic interpretation, where precipitation of

secondary solid phases, hydrolysis or formation of colloids can be avoided, and where the limiting solubility results can be indubitably modelled by straight lines. For one sample the supporting electrolyte is NaCl (triangles in Fig. 1), another one is made with Na₂CO₃ to reach high carbonate concentrations (squares in Fig. 1), and for the remaining samples the supporting electrolyte is NaClO₄ (circles in Fig. 1).

Only considering the samples where NaLn(CO₃)₂·xH₂O is the thermodynamically stable solid compound and hydrolysis cannot happen, 4, 5 or 6 samples were selected for each Ln for the quantitative analyses of the experimental results. The values of the total Ln concentrations in solution and the measured $-\log_{10}[\text{H}^+]$ did not vary, within the experimental error, in the last 3 solubility aliquots, indicating that the equilibrium was achieved within 9 days or less for Eu and Dy (see Fig. 5 for example and Table 5 in Appendix). The equilibria for La and Nd were achieved after a longer time, within 19 to 70 days (see Table 6 in Appendix).

2.4 pH and [CO₃²⁻] Determinations

The [H⁺] was measured with a combined glass electrode (Radiometer Analytical, XC161) modified with a 3.5 mol·kg⁻¹ NaClO₄ reference solution as detailed elsewhere [22]. The same tailor-made electrode was used for measuring [H⁺] in 3.2 mol·kg⁻¹ NaCl solutions. The junction potential of the electrode was evaluated with 3.5 mol·kg⁻¹ NaClO₄ and 3.2 mol·kg⁻¹ NaCl solutions at the same [H⁺]. The measured $-\log_{10}[\text{H}^+]$ in the 3.2 mol·kg⁻¹ NaCl solutions were lowered by 0.14 to correct for the junction potential.

Some measurements were performed outside of the range of calibration due to the high alkalinity of the working solutions, which can cause errors on the measured $-\log_{10}[\text{H}^+]$. These values were compared to calculated $-\log_{10}[\text{H}^+]$ (see Tables 5, 6 and 7 in Appendix). The difference reached 0.6 at the most, but contributed to only a small part in the uncertainty of the free carbonate concentration ($\{\text{CO}_3^{2-}\}$). The $-\log_{10}[\text{H}^+]$ values measured in each sample after different equilibration periods, remained almost constant during the entire experiment (see Tables 5 and 6 in Appendix).

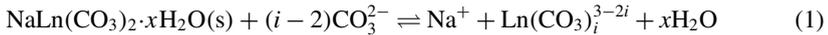
2.5 TRLFS

The TRLFS experiments were performed on the filtered solutions in a 4 mL quartz cell after the solubility reached a constant value. The excitation wavelengths were set at 394.8 nm and 388.0 nm for Eu(III) and Dy(III), respectively, using a Nd-YAG laser (Surelite II) pumped optical parametric oscillator system (Panther Ex OPO, Continuum, USA). The laser delivered 1.5 mJ of energy with a repetition rate of 10 Hz and a pulse duration of about 5 ns. The fluorescence spectra from the solution samples were collected with a detection system as detailed elsewhere [60]. The spectra were recorded with a gate delay (D) of 10 μs and a gate width (W) of 1200 μs for Eu(III), and D = 0.5 μs and W = 30 μs for Dy(III), in order to collect the largest part of their fluorescence in the solutions. The fluorescence spectra were normalized to the total Ln concentrations. The fluorescence lifetimes were derived from the decay of the intensity with increased gate delays at a constant gate width, 50 μs for Eu and 2 μs for Dy. The decay curves were fitted with exponential functions [60]. Uncertainties of 5% in the measured intensities were estimated from measurements of the fluorescence of Eu(III) and Dy(III) reference solutions.

3 Data Treatment

3.1 Medium Effects

The reactions occurring in the samples are described as follows:



They correspond to the dissolution equilibrium of $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ solid compounds in carbonate solutions and

$$K_{s,i}^m = \frac{\{\text{Ln}(\text{CO}_3)_i^{3-2i}\}\{\text{Na}^+\}}{\{\text{CO}_3^{2-}\}^{i-2}} \quad (2)$$

is the constant of Eq. 1 in molal units (superscript m), $K_{s,i}^m = K_s^m \beta_i^m$ with $\beta_i^m = \frac{\{\text{Ln}(\text{CO}_3)_i^{3-2i}\}}{\{\text{Ln}^{3+}\}\{\text{CO}_3^{2-}\}^i}$ being the overall carbonate complexing constants and $K_s^m = K_{s,0}^m$ is the solubility product of $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$. The auxiliary numerical values we used are given in Appendix (see Tables 7, 8 and 9). $K_i^m = \beta_i^m / \beta_{i-1}^m = K_{s,i}^m / K_{s,i-1}^m$ is the i^{th} stepwise carbonate complexation constant.

When a single carbonate complex predominates in a lanthanide solution, {Ln}, the solubility of $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ is approximatively the concentration of this complex:

$$\begin{aligned} \log_{10}\{\text{Na}^+\} + \log_{10}\{\text{Ln}\} &\approx \log_{10}\{\text{Na}^+\} + \log_{10}\{\text{Ln}(\text{CO}_3)_i^{3-2i}\} \\ &= \log_{10} K_{s,i}^m + (i - 2) \log_{10}\{\text{CO}_3^{2-}\} \end{aligned} \quad (3)$$

The plot of $\log_{10}\{\text{Na}^+\} + \log_{10}\{\text{Ln}\}$ versus $\log_{10}\{\text{CO}_3^{2-}\}$ is a straight line with slope $(i - 2)$ when $\log_{10} K_{s,i}^m$ is constant, i.e., when the activity coefficients of the ions are constant. In this case, it is possible to determine the stoichiometric coefficient i , i.e. the stoichiometry of the predominant aqueous complex.

Because the solutions were made of mixtures of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ and $\text{NaClO}_4/\text{NaCl}$ salts, the activity coefficients of the ions were not strictly constant. Hence, all the experimental concentrations were corrected for activity effects by taking a pure 3.5 mol·kg⁻¹ NaClO_4 solution as a reference since it is close to our experimental conditions. Such a (small) correction enables to use Eq. 3 to determine $\log_{10} K_{s,i}^{3.5\text{m NaClO}_4}$ and the stoichiometry of the predominant aqueous complex. This reference medium is also used for the graphical representations, the slope analyses and the other treatments of the data. Values of $\log_{10}\{\text{Na}^+\}^{3.5\text{m NaClO}_4} + \log_{10}\{\text{Ln}\}^{3.5\text{m NaClO}_4}$ and $\log_{10}\{\text{CO}_3^{2-}\}^{3.5\text{m NaClO}_4}$ were determined from experimental CO_3^{2-} , Ln and Na^+ molar concentrations along with corrections for ionic medium variations δ_x , the abscissa correction, and δ_y , the ordinate correction:

$$\log_{10}\{\text{CO}_3^{2-}\}^{3.5\text{m NaClO}_4} = \log_{10}(p^{3.5\text{m NaClO}_4}) + \log_{10}[\text{CO}_3^{2-}]^{\text{exp}} + \delta_x^M \quad (4)$$

$$\begin{aligned} \log_{10}\{\text{Na}^+\}^{3.5\text{m NaClO}_4} + \log_{10}\{\text{Ln}(\text{CO}_3)_i^{3-2i}\}^{3.5\text{m NaClO}_4} \\ = 2 \log_{10}(p^{3.5\text{m NaClO}_4}) \\ + \log_{10}[\text{Na}^+]^{\text{exp}} + \log_{10}[\text{Ln}(\text{CO}_3)_i^{3-2i}]^{\text{exp}} + \delta_y^M \end{aligned} \quad (5)$$

where the { } and [] notations discriminate between molal and molar concentrations, and the superscripts exp and 3.5m NaClO_4 discriminate between the experimental medium and

the reference medium

$$\delta_x^M = \log_{10} \frac{p^{\text{exp}} \gamma_{\text{CO}_3^{2-}}^{\text{exp}}}{p^{3.5\text{m NaClO}_4} \gamma_{\text{CO}_3^{2-}}^{3.5\text{m NaClO}_4}} \quad (6)$$

$$\delta_y^M = \log_{10} \frac{(p^{\text{exp}})^2 \gamma_{\text{Na}^+}^{\text{exp}} \gamma_{\text{Ln}(\text{CO}_3)_i^{3-2i}}^{\text{exp}}}{(p^{3.5\text{m NaClO}_4})^2 \gamma_{\text{Na}^+}^{3.5\text{m NaClO}_4} \gamma_{\text{Ln}(\text{CO}_3)_i^{3-2i}}^{3.5\text{m NaClO}_4}} \quad (7)$$

where γ , the activity coefficients, were calculated with the SIT formula [3], and p is the [molar]-to-[molal] conversion factor. Numerical values of p were tabulated by Silva et al. [3]; those for NaHCO_3 and NaOH have been calculated from solution densities [61]. For mixtures of electrolytes, p^{exp} was estimated as the concentration-weighted mean of tabulated values (see Table 9 in Appendix). If Eq. 1 correctly describes the system, then the plots of $\log_{10}\{\text{Na}^+\}^{3.5\text{m NaClO}_4} + \log_{10}\{\text{Ln}\}^{3.5\text{m NaClO}_4}$ versus $\log_{10}\{\text{CO}_3^{2-}\}^{3.5\text{m NaClO}_4}$ should give exact slopes of $(i - 2)$, and intercepts $\log_{10} K_{s,i}^{3.5\text{m NaClO}_4}$.

The dependence of the equilibrium constant on the ionic medium was calculated by using the SIT formula [3]

$$\begin{aligned} \log_{10} K^m &= \log_{10} K^0 - \Delta_r \log_{10} \gamma \\ &= \log_{10} K^0 + \Delta_r z^2 D - \Delta_r (\epsilon m) - \nu_{\text{H}_2\text{O}} \log_{10} a_{\text{H}_2\text{O}} \end{aligned} \quad (8)$$

where $\log_{10} K^m = \log_{10} K^M + \Delta_r \log_{10} p$ (superscript M refers to the molar units $\text{mol}\cdot\text{L}^{-1}$). The Δ_r notation refers to the summation weighted by the stoichiometric coefficients (ν_i) of a chemical reaction, D is the Debye-Hückel term $D = \frac{A\sqrt{I_m}}{1 + Ba_i\sqrt{I_m}}$ where $A = 0.509$ and $Ba_i = 1.5$ at 25°C , z is the ion charge, ϵ is the specific interaction coefficient between an anion and a cation, m is the molality of the 1:1 electrolyte and $a_{\text{H}_2\text{O}}$ is the activity of water (see Sect. 6.4 in Appendix). $\Delta_r z^2$ and $\Delta_r (\epsilon m)$ refer to the corresponding equilibrium and to the composition of the solution. For Eq. 1:

$$\Delta_r z^2 = z_{\text{Na}^+}^2 + z_{\text{Ln}(\text{CO}_3)_i^{3-2i}}^2 - (i - 2)z_{\text{CO}_3^{2-}}^2 = 1 + (3 - 2i)^2 - 4(i - 2) \quad (9)$$

In the reference medium $3.5 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$, $\Delta_r (\epsilon m)$ can be simply expressed using the SIT formula for this 1:1 background electrolyte:

$$\Delta_r (\epsilon m)_{3.5\text{m NaClO}_4} = ((2 - i)\epsilon_{\text{Na}^+, \text{CO}_3^{2-}} + \epsilon_{\text{Na}^+, \text{Ln}(\text{CO}_3)_i^{3-2i}} + \epsilon_{\text{Na}^+, \text{ClO}_4^-}) \{\text{NaClO}_4\} \quad (10)$$

All the ϵ values used in this study are taken from previously published data (see Table 8 in Appendix) except $\epsilon_{\text{Na}^+, \text{Ln}(\text{CO}_3)_4^{5-}} = -(0.35 \pm 0.22) \text{ kg}\cdot\text{mol}^{-1}$ which was estimated by fitting the data for $\text{Cm}(\text{CO}_3)_4^{5-}$ formation from [29] using the SIT formula instead of Pitzer's equation, originally used by the authors.

4 Results and Discussion

4.1 Solubility Measurements

The La and Nd experimental data approached limiting slopes of 2 at high aqueous carbonate concentrations (see Fig. 1). This slope evidences the formation of $\text{Ln}(\text{CO}_3)_4^{5-}$ complexes.

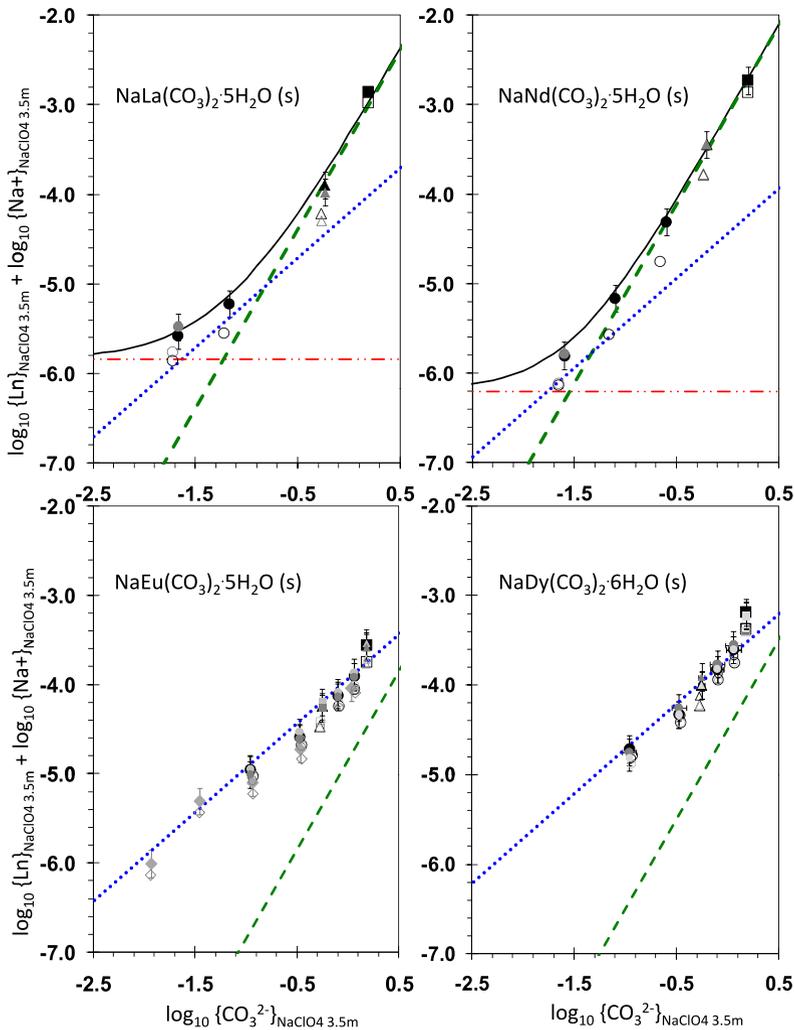


Fig. 1 Solubilities of lanthanides measured in carbonate solutions (*open symbols*) with different background electrolytes: NaClO₄ (*circles, rhombs*), NaCl (*triangles*) and Na₂CO₃ (*squares*). The data were corrected for a 3.5 mol·kg⁻¹ NaClO₄ medium (*closed symbols* at different equilibration times (*clear grey to black*) for La and Nd at 70 and 119 days, and for Eu and Dy at 9, 15, 19 and 29 days). Previously published results on Eu(III) [22] were extrapolated to the same reference medium (*grey solid rhombs*). $\log_{10}\{\text{Ln}(\text{CO}_3)_2\}^{3.5\text{m NaClO}_4} + \log_{10}\{\text{Na}^+\}^{3.5\text{m NaClO}_4}$ (*red irregular and horizontal dashed line*), $\log_{10}\{\text{Ln}(\text{CO}_3)_3\}^{3.5\text{m NaClO}_4} + \log_{10}\{\text{Na}^+\}^{3.5\text{m NaClO}_4}$ (*blue dotted line*) and $\log_{10}\{\text{Ln}(\text{CO}_3)_4\}^{3.5\text{m NaClO}_4} + \log_{10}\{\text{Na}^+\}^{3.5\text{m NaClO}_4}$ (*green dashed line*) were also represented, as well as the calculated solubility when the existence of the various complexes is verified (*black solid line*)

At lower carbonate concentrations the curvature can be fitted by adding straight lines with slopes of 1 or 0, which correspond to partial dissociation of the limiting complexes into Ln(CO₃)₃³⁻ and Ln(CO₃)₂⁻ aqueous complexes. For the heavier lanthanides Eu and Dy, different interpretations were tested. However, the predominance of one unique complex was

Table 1 Solubility constants in molal units in the 3.5 mol·kg⁻¹ NaClO₄ reference medium, and extrapolated values to zero ionic strength

	La	Nd	Eu	Dy
$\log_{10} K_{s,2}^{3.5m \text{ NaClO}_4}$	-5.8 ± 0.5	-6.2 ± 0.5		
$\log_{10} K_{s,2}^0$	-6.7 ± 0.6	-7.1 ± 0.6		
$\log_{10} K_{s,3}^{3.5m \text{ NaClO}_4}$	-4.1 ± 0.2	-4.4 ± 0.2	-3.9 ± 0.2	-3.7 ± 0.2
$\log_{10} K_{s,3}^0$	-6.1 ± 0.3	-6.4 ± 0.3	-5.8 ± 0.3	-5.5 ± 0.3
$\log_{10} K_{s,4}^{3.5m \text{ NaClO}_4}$	-3.4 ± 0.2	-3.1 ± 0.2	≤ -4.3	≤ -4.5
$\log_{10} K_{s,4}^0$	-8.8 ± 0.8	-8.5 ± 0.8	≤ -10.1	≤ -9.7

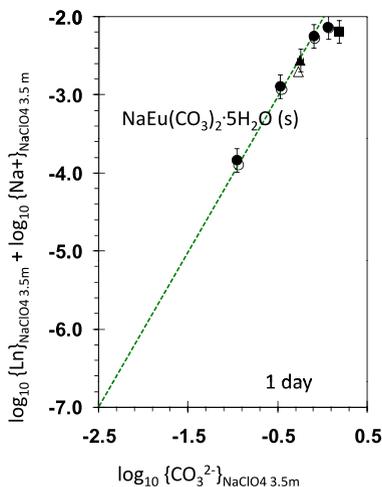
supported by the TRLFS results (see Sect. 4.2). Consequently, a single straight line was used to fit the data, and a slope of 1 was finally considered as the most probable. The experimental data in the most concentrated carbonate solution is slightly above these straight lines. Then, the fit could be improved by adding a straight line with slope of 2 reflecting the possible presence of the $\text{Ln}(\text{CO}_3)_4^{5-}$ aqueous complex as a minor species ($\leq 20\%$). The data obtained in the NaCl media fall on the same line of those obtained in the NaClO₄ media, confirming that no chloride complexes were formed in these samples and exchanging the Cl⁻ and ClO₄⁻ anions has a negligible influence as already observed for similar systems [30].

Vercouter et al. measured the solubility of NaEu(CO₃)₂·5H₂O in NaClO₄ supporting electrolyte using the same methodology as in the present study [22]. Their results are plotted as grey rhombs on Fig. 1, and they coincide fairly well with our data.

From the fit to the solubility data, the $K_{s,i}^{3.5m \text{ NaClO}_4}$ equilibrium constants were obtained with $i = 2$ to 4 for La and Nd, and $i = 3$ for Eu and Dy (see Table 1). A ± 0.2 uncertainty is assigned to the $\log_{10} K_{s,i}^{3.5m \text{ NaClO}_4}$ constants for $i = 3$ and 4 from graphical inspection of the fit. The values of $\log_{10} K_{s,2}^{3.5m \text{ NaClO}_4}$ for La and Nd were determined when 10% minimum of the lanthanide is stabilized as the $\text{Ln}(\text{CO}_3)_2^-$ complex in solution. Thus, three experimental results were used to determine these formation constants while all the experimental results were used to determine $\log_{10} K_{s,3}^{3.5m \text{ NaClO}_4}$ and $\log_{10} K_{s,4}^{3.5m \text{ NaClO}_4}$. The few available experimental results and the potential for secondary solid phase precipitation, hydrolysis or colloid formation in the low carbonate concentration region increases the uncertainty assigned to $\log_{10} K_{s,2}^{3.5m \text{ NaClO}_4}$. A ± 0.5 uncertainty was estimated for the $\log_{10} K_{s,2}^{3.5m \text{ NaClO}_4}$ constants. The values of $\log_{10} K_{s,3}^{3.5m \text{ NaClO}_4}$ lie between -4.4 and -3.7 with no clear trend along the Ln series. For the two heavier lanthanides, $\text{Ln}(\text{CO}_3)_3^{3-}$ was highly predominating under our conditions, and only a maximum value of $K_{s,4}^{3.5m \text{ NaClO}_4}$ could be determined from the single data point at the highest $\{\text{CO}_3^{2-}\}$ (Eu-F and Dy-F). These maximum possible values are about 1 order of magnitude lower than the constants determined for the light lanthanides La and Nd. All the thermodynamic constants were extrapolated to zero ionic strength for comparison with literature data (see Table 1). A larger uncertainty was assigned to the extrapolated thermochemical data, which essentially originates from the propagation of the uncertainties of the specific ion interaction coefficients [5].

Surprisingly, the solubility curve for Eu exhibits a limiting slope of 2 after a 1-day equilibration period (see Fig. 2). Though unusual, transient formation of $\text{Eu}(\text{CO}_3)_4^{5-}$ during the solid dissolution followed by a slow dissociation into the stable $\text{Eu}(\text{CO}_3)_3^{3-}$ species cannot be excluded, but is very unlikely since the kinetic formation of aqueous inorganic carbonato

Fig. 2 Europium lixiviation in the $3.5 \text{ mol}\cdot\text{kg}^{-1} \text{ NaClO}_4$ reference medium after 1 day. The green dashed line represents a slope of 2. The batch solutions with NaClO_4 as supporting electrolyte were represented by circles, the ones with NaCl by triangles, and the ones with no supporting electrolyte (Na_2CO_3 only) by squares



complexes is expected to be rapid. Slow kinetics is expected rather for the solid dissolution; the slope of 2 could as well originate from the transient control of solid or surface compounds with an apparent 1:1 stoichiometry for the ratio of Eu^{3+} and CO_3^{2-} stoichiometric coefficients. Equilibrium was eventually achieved between 2 and 9 days. This observation is similar to results obtained by Faucherre et al. who measured the solubility of hydrated $\text{KLn}(\text{CO}_3)_2$ in K_2CO_3 – KHCO_3 – KCl solutions for La, Pr, Nd, Sm, Eu and Gd after an equilibration period of 24 hours [19]. It was concluded according to slope analysis that the predominant aqueous species was $\text{Ln}(\text{CO}_3)_4^{5-}$, while a steady state was probably not achieved for all of the lanthanides.

4.2 Spectroscopic Measurements

The predominance of a unique carbonate complex for Eu and Dy in the experimental solutions was confirmed by TRLFS. The lanthanides exhibit several emission bands at 579, 592, 616 and 650 nm for Eu, and 475, 480, 485 and 575 nm for Dy. The main emissions were observed at 616 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) and 575 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) for Eu(III) and Dy(III), respectively (see Fig. 3). They both correspond to “hypersensitive transitions”, emissions particularly sensitive to variations that occur in the inner coordination sphere of the Ln^{3+} ions. The less sensitive transitions $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ were observed at about 579 and 592 nm for Eu aqueous complexes, and the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition at about 480 nm for Dy. The shapes of the spectra were very similar for all the samples containing the same Ln. This observation would suggest that, whatever the carbonate concentration, a single species predominates in solution, since all the spectra superimposed within the experimental uncertainty after normalization to the concentration of Ln in the solution. These results are consistent with the predominance of $\text{Ln}(\text{CO}_3)_3^{3-}$ for Eu and Dy in the sample containing the highest CO_3^{2-} concentration. The fluorescence lifetimes were identical, whatever the free carbonate concentration: $\tau_{\text{Eu}} = 415 \pm 20 \mu\text{s}$ and $\tau_{\text{Dy}} = 8.3 \pm 0.4 \mu\text{s}$. These values are slightly lower than the ones measured in $3 \text{ mol}\cdot\text{L}^{-1} \text{ K}_2\text{CO}_3$, which ranged from 455 to 466 μs and 9 to 9.5 μs for Eu and Dy respectively [62, 63]. This difference may be attributed to the differences of ionic medium and viscosity. The mean number of remaining water molecules ($n_{\text{H}_2\text{O}}$) in the first coordination sphere of the Ln^{3+} ions is correlated to the lifetime as proposed by Horrocks et al. [64]. The relationships established by Zhang et al. from lifetime

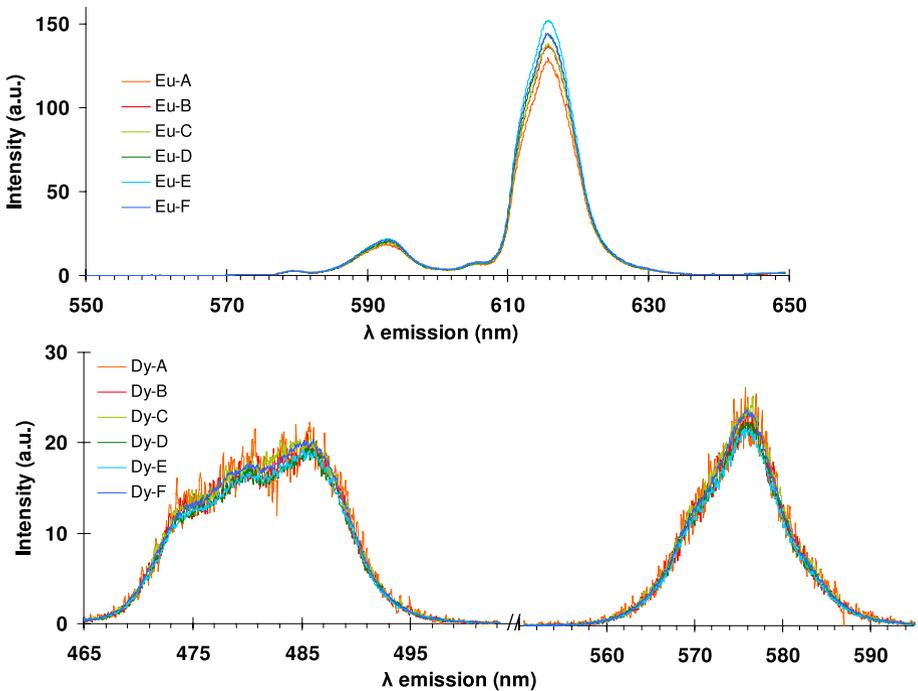


Fig. 3 Normalized TRLF spectra of filtered Eu and Dy solutions from solubility batch experiments. The molal concentrations of CO_3^{2-} initially introduced in the samples are 0.123, 0.357, 0.525, 0.790, 1.084, 1.527 $\text{mol}\cdot\text{kg}^{-1}$ for samples Ln-A, Ln-B, Ln-C, Ln-D, Ln-E and Ln-F, respectively

measurements in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures were used [65]:

$$n_{\text{H}_2\text{O}}^{\text{Eu}} = \frac{1.05}{\tau} - 0.44 \quad (11)$$

$$n_{\text{H}_2\text{O}}^{\text{Dy}} = \frac{0.0211}{\tau} - 0.60 \quad (12)$$

where τ , the mean fluorescence lifetime of the aqueous species, is expressed in milliseconds. From these empirical formulae, the number of remaining species, in the first coordination sphere of Eu(III) and Dy(III) is about 2 in both cases: 2.1 ± 0.5 for Eu and 1.9 ± 0.5 for Dy. Considering that the 3 CO_3^{2-} ligands are bidentate, the coordination numbers of Eu(III) and Dy(III) would be about 8, which is a plausible coordination number, similar to the number of water molecules coordinated to the heavy Ln^{3+} aquo ions.

4.3 Discussion

Only a few studies dealt with Ln carbonate complexes in chemical conditions where the limiting complexes are expected to be stable. To extend the comparison between apparent formation constants and to test if the analogy between f-element trivalent cations is still relevant, the data for the carbonate complexes of An(III), namely Am and Cm, are also reported (see Table 2).

Table 2 Comparison of the stepwise formation constants in molar units of $M(\text{CO}_3)_3^{3-}$ and $M(\text{CO}_3)_4^{5-}$ ($t = 25^\circ\text{C}$)

M	Method ^a	Medium	$\log_{10} K_3^m$	$\log_{10} K_4^m$	$\log_{10} K_3^{0b}$	$\log_{10} K_4^{0b}$	Ref.
La	sol	3.5 mol·kg ⁻¹ NaClO ₄	1.7 ± 0.6	0.7 ± 0.3	0.6 ± 0.4	-2.7 ± 0.9	this work
Ce	sol	3.5 mol·kg ⁻¹ NaClO ₄	1.4 ± 0.2 ^c	1.0 ± 0.2 ^c	0.4 ± 0.4	-2.4 ± 0.8	[20]
Nd	sol	3.5 mol·kg ⁻¹ NaClO ₄	1.8 ± 0.6	1.3 ± 0.3	0.7 ± 0.4	-2.1 ± 0.9	this work
Nd	sol	no supporting electrolyte				-2.2 ± 0.9	[21]
Eu	sol	3.5 mol·kg ⁻¹ NaClO ₄		≤ -0.4		≤ -4.3	this work
Eu	TRLFS	0.1 mol·kg ⁻¹ NaClO ₄ ^c	1.4 ± 0.5		1.0 ± 0.5		[30]
Eu	extr	1.05 mol·kg ⁻¹ NaClO ₄ ^c	2.3 ± 0.2	1.9 ± 0.2	1.5 ± 0.2	-0.7 ± 0.3	[8] ^d
Eu	extr	1.05 mol·kg ⁻¹ NaClO ₄	2.1	1.9	1.3 ± 0.2	-0.7 ± 0.3	[7] ^d
Dy	sol	3.5 mol·kg ⁻¹ NaClO ₄		≤ -0.8		≤ -4.2	this work
Am	sol	3.5 mol·kg ⁻¹ NaClO ₄ , 20 °C	2.45 ± 0.2 (2.41 ± 0.40 ^e)	≤ -1.47	1.4 ± 0.3 (1.3 ± 0.5)	≤ -4.9	[23]
Am	sol	0.1 mol·kg ⁻¹ NaClO ₄ , 20 °C	1.84 (2.1 ± 0.5 ^{e,f})		1.4 (1.7 ± 0.5)		[30]
Am	sol	0.1 mol·kg ⁻¹ NaCl, 20 °C ^c	1.6 ± 0.4 (2.3 ± 0.3 ^e)		1.2 ± 0.5 (1.9 ± 0.3)		[24]
Am	sol	4.4 mol·kg ⁻¹ NaCl, 20 °C ^c	2.1 ± 0.4 (1.8 ± 0.4 ^e)		0.9 ± 0.5 (0.6 ± 0.5)		[24]
Am	sol	5.6 mol·kg ⁻¹ NaCl ^c	3.2 ± 0.5		2.0 ± 0.7		[66]
Am	sol	I → 0	2.9 ± 0.5				[67]
Am	Review	I → 0	2.8 ± 0.4				[3]
Am	Review	I → 0	2.1 ± 0.8				[5]
Cm	TRLFS	1 mol·kg ⁻¹ NaCl	2.9	0.99	2.1 ± 0.2	-1.6 ± 0.3	[28]
Cm	TRLFS	1–6 mol·kg ⁻¹ NaCl			1.9 ± 0.5	-1.7 ± 0.6	[29]
Cm	TRLFS	3.5 mol·kg ⁻¹ NaClO ₄	1.94 ± 0.05		0.87 ± 0.05		[31]

^asol = solubility, extr = solvent extraction, TRLFS = time laser resolved fluorescence spectroscopy

^bAll extrapolations to zero ionic strength were performed with the SIT parameters used in the present work and are available in Appendix

^cThe authors gave the formation constant in molar units, they were recalculated on the molar scale

^dRao and Chatt proposed values for the formation constants of aqueous EuCO_3^+ , $\text{Eu}(\text{CO}_3)_2^-$, $\text{Eu}(\text{CO}_3)_3^{3-}$ and $\text{Eu}(\text{CO}_3)_4^{5-}$ in $\text{NaHCO}_3\text{--NaClO}_4$ solutions ($I=1 \text{ mol}\cdot\text{L}^{-1}$), by solvent extraction [7, 8]. However, the free carbonate concentration never exceeded $0.02 \text{ mol}\cdot\text{L}^{-1}$, which seems not to be enough to observe $\text{Eu}(\text{CO}_3)_4^{5-}$ in significant concentration [22]

^eThe raw results have been reinterpreted by Vercouter [30]

^fMaster's thesis of Robouch cited in Vercouter's Ph.D. thesis, who has shown that $\text{Am}(\text{CO}_3)_4^{5-}$ aqueous complexes can be neglected in speciation calculations under these particular experimental conditions [30]

The constant directly determined from the solubility data is $\log_{10} K_{s,i}$. However, the crystallinity of the solid compounds depends on aging and on the sizes of the grains, which are not controlled in solubility experiments. This can contribute to the scattering over about 1.5 orders of magnitude in the published values extrapolated to zero ionic strength ($\log_{10} K_{s,3,Ce}^0 = -6.9 \pm 0.3$ [20], $\log_{10} K_{s,3,Nd}^0 = -6.22$ [21], $\log_{10} K_{s,3,Eu}^0 = -6.1 \pm 0.3$ [22], $-6.1 \pm 0.3 < \log_{10} K_{s,3,La,Nd,Eu,Dy}^0 < -5.5 \pm 0.3$ in this study). Conversely, when comparing the stepwise complexation constants, the influence of the solid phase cancels out.

The comparison of the published formation constants of the carbonate complexes extrapolated to zero ionic strength are scattered over about 2 orders of magnitude (see Table 2), which approximately corresponds to the scattering obtained for $\log_{10} K_1^0$ and $\log_{10} K_2^0$ for the Ln series [18, 40, 41]. A general trend for the variation of $\log_{10} K_3^0$ and $\log_{10} K_4^0$ across the Ln series can hardly be put forward due to the important uncertainties on these constants. A small increase of $\log_{10} K_3^0$ can be inferred across the Ln series, which could be due to the scattering of the values of $\log_{10} K_2^0$ of over 1.5 orders of magnitude [18, 40, 41]. A small increase of $\log_{10} K_4^0$ can be deduced from La to Nd, while $\log_{10} K_4^0$ clearly decreases for the heavier lanthanides. $\log_{10} K_4^0$ is too small to be measured for Eu and Dy ($\log_{10} K_4^0 \leq -4.2$).

Aqueous carbonate complexes of An ions have already been reviewed. The errors due to glass electrode calibration, activity coefficient, and junction potential, to hydrolysis, and to $\text{CO}_2(\text{g})$ exchanges with the atmosphere have been discussed [3, 4, 6]. Our methodology is aimed at minimizing these systematic errors. It was adapted from that of Grenthe's group. In this group, Ferri et al. studied the solubility of $\text{NaCe}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ in $3 \text{ mol} \cdot \text{L}^{-1}$ NaClO_4 supporting electrolyte [20]. The free carbonate concentrations of their samples ranged up to $0.7 \text{ mol} \cdot \text{L}^{-1}$. This maximum concentration was enough to detect the limiting complex, even though it was always partially dissociated. They determined: $\log_{10} \beta_2^{3\text{MNaClO}_4} = 11.1 \pm 0.1$, $\log_{10} \beta_3^{3\text{MNaClO}_4} = 12.6 \pm 0.2$ and $\log_{10} \beta_4^{3\text{MNaClO}_4} = 13.7 \pm 0.1$ from which we calculated $\log_{10} K_4^{3.5\text{mNaClO}_4} = 1.0 \pm 0.2$, $\log_{10} K_4^0 = -2.4 \pm 0.8$, $\log_{10} K_3^{3.5\text{mNaClO}_4} = 1.4 \pm 0.2$ and $\log_{10} K_3^0 = 0.4 \pm 0.4$. These values overlap with the ones determined in the present work for La and Nd (see Table 2).

Our results are in reasonably good agreement with those determined using the same methodology [20, 22, 24, 30]. Note that the discrepancy on $\log_{10} K_i^0$ is more important for a same element studied by various authors, Am(III) for example, than the uncertainties for various elements studied by the same author (this work).

The increase of $\log_{10} K_i$ ($i = 1$ to 3) with the atomic number is classically attributed to the Ln contraction, which is expected to stabilize the inner-sphere complexes of Ln^{3+} with anionic ligands. However, the reverse effect in contrast can be expected for the limiting complexes; when the coordination sphere is saturated with anionic ligands, their anionic repulsions are more important for the smaller Ln^{3+} . The balance of these two effects can explain the variations of $\log_{10} K_3^0$ and $\log_{10} K_4^0$ across the Ln series. However, the absence of unambiguous monotonic variations of the stepwise formation constants with the atomic number across the Ln series could as well originate from changes of the geometries of the aqueous complexes of the same stoichiometries similar to those for $\text{KLn}(\text{CO}_3)_2$ solid compounds [68].

The change of the 1:4 to 1:3 stoichiometry for the carbonate limiting complex occurs between Nd and Eu, the fourth and the seventh Ln respectively. Moreover,

$\log_{10} K_{3,\text{Am}}^0 \approx \log_{10} K_{3,\text{Ln}}^0$ is observed, which is consistent with the usual analogy between f-block elements at the same oxidation state. Am and Eu are often compared since they are in the same column of the periodic table. Their limiting carbonate complexes are expected to be of the same stoichiometry ($\text{M}(\text{CO}_3)_3^{3-}$). However, Am(III) has a similar ionic radius as Pm(III) for a coordination number of 8, and to Nd(III) for coordination numbers 6 and 9 [69, 70]. Since the hydration numbers vary within the Ln series, the distance, determined by EXAFS, between the central Ln(III) or An(III) cation and the oxygen atom of the water molecules, was chosen in this study rather than the ionic radius, determined for a particular coordination number, to compare lanthanides with actinides. The mean values of $d_{\text{Am-OH}_2}$ is equal to that of $d_{\text{Nd-OH}_2}$ of the aquo ions, calculated from [42–45]. The Am/Nd analogy appears not to be relevant in concentrated carbonate solutions because their limiting complexes, $\text{Am}(\text{CO}_3)_3^{3-}$ [23] and $\text{Nd}(\text{CO}_3)_4^{5-}$, are different as deduced from solubility data under the same conditions (Na_2CO_3 – NaClO_4 solutions with $[\text{Na}^+] = 3 \text{ mol}\cdot\text{L}^{-1}$). A relevant Ln(III) analogue of Cm(III) for concentrated carbonate solutions has not been determined: while Sm(III) would be a good candidate, its ion size is close to those of Nd(III) and Eu(III) for which two different limiting stoichiometries were found. Hence, the increased stabilization of $\text{Cm}(\text{CO}_3)_4^{5-}$ as proposed from spectroscopic measurements in Na_2CO_3 – NaCl solutions may also suggest that there are small but sufficient variations of the Gibbs energy of formation of the tetracarbonate complexes, corresponding to $\log_{10} K_4^0$. It can be concluded that an analogy between 4f and 5f-ions cannot be drawn solely on the basis of ionic radii in concentrated solutions. This difference might be a result of small differences in ion hydration, short-range ion interactions or the lesser hard character of the actinide ions as compared to the lanthanide ions.

5 Conclusion

By studying the solubilities of $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ solid compounds containing four different lanthanides with decreasing radius, two different limiting stoichiometries have been evidenced under similar experimental conditions. The limiting complexes of the lighter lanthanides, La and Nd, are $\text{Ln}(\text{CO}_3)_4^{5-}$, whereas they are $\text{Ln}(\text{CO}_3)_3^{3-}$ for the heavier ones, Eu and Dy, up to a carbonate concentration of about $1.5 \text{ mol}\cdot\text{kg}^{-1}$. Modelling the experimental solubilities enabled us to determine the formation constants of the limiting carbonate complexes $\text{La}(\text{CO}_3)_4^{5-}$ and $\text{Nd}(\text{CO}_3)_4^{5-}$ as well as the formation constants of the dissociated $\text{La}(\text{CO}_3)_3^{3-}$ and $\text{Nd}(\text{CO}_3)_3^{3-}$ complexes. These formation constants are in agreement with the previously published data that used similar procedures for Ln(III) or An(III) cations. According to the available experimental data for Am(III) and Cm(III), which need confirmation, the analogy of K_4 formation constants based on the ion sizes of the metal ions would be questionable. The relative stabilities of the tetracarbonato complexes could be induced by other parameters. However, this difference could originate in very small energy differences that may be evident only in specific cases as observed here for limiting complexes of a few elements.

Acknowledgements We are grateful to M. Tabarant from CEA/DEN/DANS/DPC/SCP/LRSI for his help with the ICP-OES measurements.

Appendix: Supplementary Materials

6.1 Reinterpretation of Rao et al. Raw Data on Nd [21]

Rao et al. measured the solubility of $\text{NaNd}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$ over a wide range of free carbonate concentrations ($0.1 \text{ mol}\cdot\text{L}^{-1} \leq [\text{Na}_2\text{CO}_3]_{\text{initial}} \leq 2 \text{ mol}\cdot\text{L}^{-1}$ and $0.1 \text{ mol}\cdot\text{L}^{-1} \leq [\text{NaHCO}_3]_{\text{initial}} \leq 1 \text{ mol}\cdot\text{L}^{-1}$) [21]. The ionic strengths of the various samples were not constant and the thermodynamic modelling requires calculation of the aqueous speciation of Nd^{3+} for each sample while adjusting the values of the formation constants of the various aqueous complexes using the same auxiliary data as used in this study (Appendix 6.3). We tried to fit their experimental data, obtained in Na_2CO_3 solutions, with a model including $\text{Nd}(\text{CO}_3)_4^{5-}$. Their last point was neglected since the carbonate concentration is close to the solubility and precipitation of Na_2CO_3 may have occurred. Figure 4 presents the experimental solubility data and the fitted curve. Table 3 presents the experimental conditions and the calculated compositions of the solutions using the following fitted constants: $\log_{10}\beta_{2,\text{Nd}}^0 = 11.54$, $\log_{10}\beta_{3,\text{Nd}}^0 = 13.66$, $\log_{10}\beta_{4,\text{Nd}}^0 = 11.50$ and $\log_{10}K_{\text{NaNd}(\text{CO}_3)_2}^0 = -20.2$.

Fig. 4 Solubility of Nd measured in carbonate solutions (black and grey symbols) by Rao et al. without background electrolyte [21]. The grey symbol, obtained in a very concentrated solution was neglected in the thermodynamic adjustment. The calculated solubility is represented by the black solid line

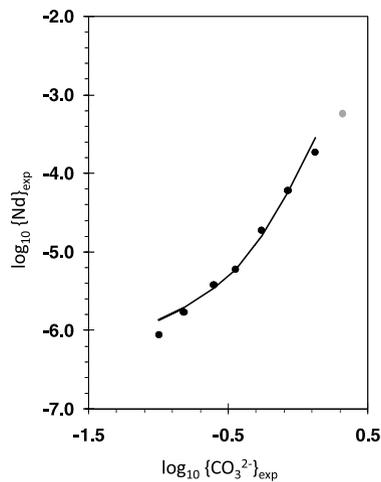


Table 3 Experimental initial carbonate concentrations, calculated Nd total concentrations and compositions of the samples

$\log_{10}\{\text{CO}_3^{2-}\}_{\text{initial}}$ $\text{mol}\cdot\text{kg}^{-1}$	$\log_{10}\{\text{Nd}\}_{\text{calculated}}$ $\text{mol}\cdot\text{kg}^{-1}$	$\text{Nd}(\text{CO}_3)_2^-$ %	$\text{Nd}(\text{CO}_3)_3^{3-}$ %	$\text{Nd}(\text{CO}_3)_4^{5-}$ %
-1.00	-5.86	2	93	5
-0.82	-5.72	1	88	11
-0.61	-5.46	0	72	28
-0.45	-5.22	0	53	47
-0.26	-4.80	0	29	71
-0.07	-4.24	0	13	87
0.12	-3.55	0	4	96

6.2 Solubility Raw Data

Table 4 Experimental conditions of $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ dissolution experiments

Ref.	$\{\text{OH}^-\}^a$	$\{\text{CO}_3^{2-}\}^a$	$\{\text{HCO}_3^-\}^a$	$\{\text{ClO}_4^-\}^a$	p exp	I_m	$-\log_{10}[\text{H}^+]$	$\log_{10}\{\text{CO}_3^{2-}\}$	$\log_{10}\{\text{Ln}\}$
La-A	0.016		0.032	2.988	1.141	3.036	9.61	-1.73	-6.34
La-B	0.051		0.073	2.918	1.135	3.042	10.02	-1.23	-6.03
La-C		0.507		2.033 ^b	1.034	3.556	11.31	-0.27	-4.70
La-D		1.539			1.017	4.623	11.33	0.19	-3.47
Nd-A	0.016		0.033	2.965	1.140	3.013	9.64	-1.66	-6.61
Nd-B	0.051		0.074	2.897	1.134	3.021	10.00	-1.16	-6.05
Nd-C	0.161		0.203	2.674	1.114	3.039	10.31	-0.66	-5.24
Nd-D		0.511		2.029 ^b	1.034	3.563	11.21	-0.24	-4.27
Nd-E		1.535			1.017	4.618	11.21	0.20	-3.35
Eu-A	0.123			3.427	1.168	3.796	10.88	-0.94	-5.58
Eu-B	0.357			2.851	1.168	3.922	11.09	-0.46	-5.17
Eu-C	0.525			2.097 ^b	1.066	3.673	11.33	-0.28	-4.92
Eu-D	0.790			1.802	1.168	4.171	11.27	-0.09	-4.73
Eu-E	1.084			1.083	1.168	4.334	11.37	0.07	-4.52
Eu-F	1.527			0.000	1.017	4.580	11.51	0.18	-4.21
Dy-A	0.123			3.427	1.224	3.796	10.91	-0.94	-5.38
Dy-B	0.357			2.851	1.187	3.922	11.10	-0.46	-4.89
Dy-C	0.525			2.097 ^b	1.049	3.673	11.33	-0.28	-4.62
Dy-D	0.790			1.802	1.126	4.172	11.28	-0.09	-4.40
Dy-E	1.084			1.083	1.083	4.334	11.37	0.07	-4.18
Dy-F	1.527			0.000	1.020	4.581	11.52	0.18	-3.85

^aInitial concentration^bNaCl instead of NaClO₄**Table 5** Solubility data, Ln concentrations and measured $-\log_{10}[\text{H}^+]$, for dissolution experiments of $\text{NaLa}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ and $\text{NaNd}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$

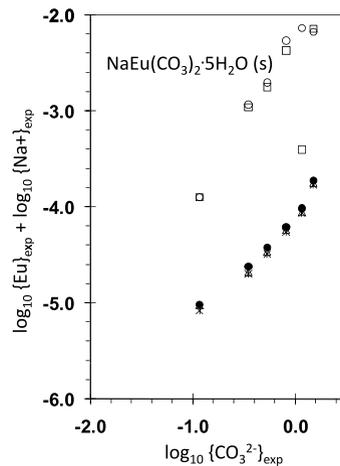
	$\log_{10}\{\text{Ln}\}$						
	1 d	2 d	5 d	9 d	19 d	70 d	119 d
La-A	-5.12	-5.65	-5.85	-6.14	-5.89	-6.25	-6.34
La-B							-6.03
La-C	-4.68	-4.79	-4.75	-4.81	-4.82	-4.78	-4.70
La-D							-3.47
Nd-A	-5.67	-6.11	-5.82	-5.66	-5.62	-6.59	-6.61
Nd-B						-6.05	-6.05
Nd-C						-5.26	-5.24
Nd-D	-4.24	-4.20	-4.17	-4.22	-4.22	-4.26	-4.27
Nd-E						-3.35	-3.35

Table 5 (Continued)

	$-\log_{10}[\text{H}^+]_m$						$-\log_{10}[\text{H}^+]_c$	
	1 d	2 d	5 d	9 d	19 d	70 d		119 d
La-A	9.67	9.64	9.69	9.72	9.50	9.85	9.61	9.66
La-B	10.01	9.98	10.03	10.07	10.09	10.20	10.02	10.03
La-C	11.34	11.26	11.35	11.36	11.35	11.37	11.31	11.66
La-D	11.44	11.36	11.42	11.41	11.43	11.43	11.33	11.31
Nd-A	9.82	9.71	9.80	9.80	9.75	9.76	9.64	9.65
Nd-B	10.09	10.04	10.15	10.14	10.07	10.11	10.00	10.01
Nd-C	10.34	10.30	10.41	10.42	10.35	10.37	10.31	10.23
Nd-D	11.26	11.23	11.29	11.05	10.93	11.32	11.15	11.66
Nd-E	11.42	11.48	11.30	11.41	11.35	11.35	11.21	11.31

Table 6 Solubility data, Ln concentrations and measured $-\log_{10}[\text{H}^+]$, for dissolution experiments of $\text{NaEu}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ and $\text{NaDy}(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$

	$\log_{10}\{\text{Ln}\}$					$-\log_{10}[\text{H}^+]_m$					$-\log_{10}[\text{H}^+]_c$
	1 d	2 d	9 d	15 d	29 d	1 d	2 d	9 d	15 d	29 d	
Eu-A	-4.46	-4.46	-5.59	-5.64	-5.58	10.69	10.77	10.90	10.89	10.88	11.45
Eu-B	-3.48	-3.51	-5.23	-5.25	-5.17	10.90	10.89	11.11	11.09	11.09	11.70
Eu-C	-3.20	-3.25	-4.96	-4.98	-4.92	11.32	11.14	11.23	11.30	11.26	11.27
Eu-D	-2.80	-2.90	-4.77	-4.79	-4.73	11.25	11.12	11.30	11.27	11.27	11.88
Eu-E	-2.65	-3.91	-4.56	-4.57	-4.52	11.32	11.35	11.40	11.38	11.37	11.96
Eu-F	-2.66	-2.63	-4.23	-4.25	-4.21	11.37	11.49	11.53	11.52	11.51	11.31
Dy-A	-3.36	-3.40	-5.40	-5.44	-5.38	10.84	10.78	10.90	10.91	10.91	11.45
Dy-B	-3.14	-4.82	-4.97	-4.97	-4.89	10.93	11.06	11.10	11.10	11.10	11.70
Dy-C	-2.60	-4.59	-4.72	-4.72	-4.62	11.32	11.19	11.16	11.32	11.26	11.27
Dy-D	-2.92	-4.23	-4.47	-4.47	-4.40	11.26	11.28	11.30	11.29	11.28	11.88
Dy-E	-2.72	-4.03	-4.26	-4.26	-4.18	11.31	11.36	11.41	11.39	11.37	11.96
Dy-F	-4.27	-3.15	-3.87	-3.89	-3.85	11.52	11.47	11.55	11.52	11.52	11.31

Fig. 5 Evolution of the solubility of Eu after 1 day (open circles), 2 days (open squares), 9 days (open triangles), 15 days (crosses) and 29 days (solid circles)

6.3 Auxiliary Data

All the auxiliary data used to determine the aqueous speciation of La, Nd, Eu and Dy in highly concentrated carbonate solutions and constant ionic strength are listed in Tables 7, 8 and 9. It is assumed that only mononuclear aqueous carbonate complexes are of significance. The formation of Ln-perchlorate or Ln-chloride complexes is neglected since no inner-sphere complexes have been evidenced by spectrophotometric measurements on solutions of luminescent lanthanides [71].

Table 7 Formation constants at 25 °C and zero ionic strength used in this study, from [3]

Equilibrium	log ₁₀ <i>K</i>
H ₂ O ⇌ H ⁺ + OH ⁻	log ₁₀ <i>K</i> _w ⁰ = -14.000
CO ₃ ²⁻ + H ⁺ ⇌ HCO ₃ ⁻	log ₁₀ <i>K</i> ₁ ⁰ = 10.329
HCO ₃ ⁻ + H ⁺ ⇌ CO ₂ (aq) + H ₂ O	log ₁₀ <i>K</i> ₂ ⁰ = 6.354
CO ₂ (aq) ⇌ CO ₂ (g)	log ₁₀ <i>K</i> _p ⁰ = 1.472

Table 8 Specific interaction coefficients used to extrapolate published and experimental data to other ionic strengths using the SIT formula

ϵ _{Na⁺,<i>l</i>}	Na ⁺	ϵ _{<i>k</i>,Cl⁻ or ClO₄⁻}	Cl ⁻	ClO ₄ ⁻
Cl ⁻	0.03 ± 0.01 ^a	H ⁺	0.12 ± 0.01 ^a	0.14 ± 0.02 ^a
ClO ₄ ⁻	0.01 ± 0.01 ^a	Ln ³⁺	0.22 ± 0.02 ^a	0.49 ± 0.03 ^a
CO ₃ ²⁻	-0.08 ± 0.03 ^a			
HCO ₃ ⁻	-0.00 ± 0.02 ^a			
OH ⁻	0.04 ± 0.01 ^a			
Ln(CO ₃) ₂ ⁻	-0.05 ± 0.05 ^a			
Ln(CO ₃) ₃ ³⁻	-0.15 ± 0.05 ^a			
Ln(CO ₃) ₄ ⁵⁻	-0.35 ± 0.22 ^b			

^aFrom [3]

^bEstimated from [29]

Table 9 Molar-to molal conversion factor (*p*) used in this study. The following approximation is used for electrolyte *i*, of molar concentration [*i*]: *p* = *a*[*i*]² + *b*[*i*] + *c* and *p* = [*i*]/{*i*} where {*i*} is the molal concentration of *i*

	<i>a</i>	<i>b</i>	<i>c</i>
<i>p</i> _{NaClO₄} ^a	0.0042	0.042	1.0045
<i>p</i> _{Na₂CO₃} ^a	0.0053	0.0018	1.0023
<i>p</i> _{NaHCO₃} ^b	0.042	0.0244	1.0017
<i>p</i> _{NaOH} ^b	0.002	-0.0023	0.9981
<i>p</i> _{NaCl} ^a	0.0012	0.0176	1.0027

^aFrom [3]

^bFrom [61]

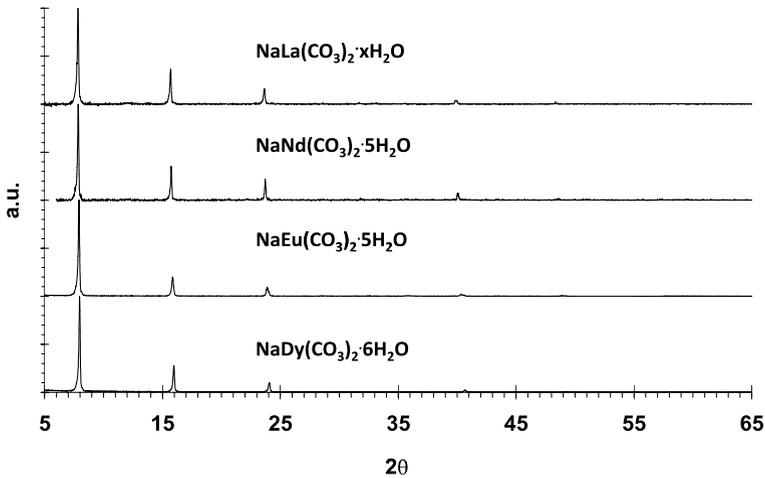


Fig. 6 Powder XRD patterns of $\text{NaLn}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ obtained before the solubility measurements (X'Pert pro Panalytical X-ray diffractometer with $\text{Co K}\alpha 1$ radiation (1.78901 \AA), produced at 45 kV and 40 mA)

For sensitivity analyses, published hydrolysis constants were used [55–58, 72]. All the batch solutions in which hydrolysis was suspected were discarded for the quantitative treatment of data [47].

6.4 Water Activity

$a_{\text{H}_2\text{O}}$ values are tabulated for many 1:1 MX supporting electrolytes, or for the corresponding osmotic coefficient (Φ) defined by:

$$\log_{10} a_{\text{H}_2\text{O}} = \frac{-2m_{MX}\Phi}{55.51\ln(10)}$$

It can also be calculated from the mean activity coefficient calculated from the SIT formula [59] for $M_{v1}X_{v2}$ supporting electrolytes:

$$\Phi = 1 + \frac{\ln(10)(v_1 z_1^2 + v_2 z_2^2)A\sqrt{I_m}}{\nu} F_{(Ba_i\sqrt{I_m})} + \frac{1}{2}(v_1^2 + v_2^2)\epsilon_{(M,X)}\{M_{v1}X_{v2}\} \quad (13)$$

$$F_{(Ba_i\sqrt{I_m})} = \frac{1}{(Ba_i\sqrt{I_m})^3} \left(1 + Ba_i\sqrt{I_m} - 2\ln(1 + Ba_i\sqrt{I_m}) - \frac{1}{1 + Ba_i\sqrt{I_m}} \right) \quad (14)$$

However, we found that the $\frac{\log_{10} a_{\text{H}_2\text{O}}}{\{M_{v1}X_{v2}\}}$ ratio in our chemical conditions is practically constant. This approximation is not less accurate than the SIT formula: $\frac{\log_{10} a_{\text{H}_2\text{O}}}{\{\text{NaClO}_4\}} = -0.0150$, $\frac{\log_{10} a_{\text{H}_2\text{O}}}{\{\text{NaCl}\}} = -0.0154$, $\frac{\log_{10} a_{\text{H}_2\text{O}}}{\{\text{NaHCO}_3\}} = -0.0135$ and $\frac{\log_{10} a_{\text{H}_2\text{O}}}{\{\text{Na}_2\text{CO}_3\}} = -0.0155$ [73]. It allowed to use a simple mixing rule in mixtures of electrolytes, where the osmotic coefficient is assumed to be the mean of the osmotic coefficients of the pure components weighted by their concentrations.

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