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# Ce<sup>3+</sup> and La<sup>3+</sup> ions in ethylammonium nitrate: a XANES and molecular dynamics investigation

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## Abstract

Diluted solutions of Ce(NO<sub>3</sub>)<sub>3</sub> and La(NO<sub>3</sub>)<sub>3</sub> in ethylammonium nitrate (EAN) were investigated using molecular dynamics (MD) simulations and X-ray absorption near edge structure (XANES) spectroscopy. New La-O and Ce-O Lennard-Jones parameters were optimized to provide an accurate atomistic description of the nitrate complexes at low computational cost. XANES spectra analysis, along with radial and combined distance-angle distributions from MD simulations, indicate that the main metal species in solution is an icosahedral nitrate complex with a 12-fold cation-oxygen coordination and an equilibrium between monodentate and bidentate ligands.

**Keywords:** Molecular Dynamics simulations, X-ray absorption spectroscopy, ion solvation, coordination geometries, ionic liquid, XANES, lanthanoid ions

## 1. Introduction

Lanthanoid-based compounds have seen a wide array of applications, from medical diagnostic to organic synthesis, giving rise to a significant scientific interest in their solvation chemistry.[1, 2, 3, 4] A major challenge is to efficiently separate the lanthanoid (Ln) series metals, which is a frequent issue in nuclear waste management. The usual method to achieve this task is the dissolution of the Ln<sup>3+</sup> ions in solvents with different polarity.[5] Although conventional organic solvents have been the main choice in the past to extract Ln<sup>3+</sup> ions from the aqueous phase, the possibility of employing ionic liquids (ILs) is being explored due to their safer and environmental-friendly nature.[6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16] Therefore, an accurate atomistic description of the Ln<sup>3+</sup> ion solvation structures in IL media is an important piece of information to improve the efficiency of extraction procedures. Among ILs, ethylammonium nitrate (EAN) is one of the oldest and more studied so far. It belongs to the class of protic ILs, meaning that it can form water-like hydrogen bond networks, as well as self assembly in a bicontinuous sponge-like nanostructure.[17] As a solvent, EAN can efficiently solubilize metal cations by forming metal-nitrate complexes, which are also found to be the main complexed species in Ln extraction processes that use concentrated HNO<sub>3</sub>. [18, 19] For these reasons, the study of Ln(III) nitrate salts in EAN is an excellent starting point to reach an understanding of the microscopic interactions that

characterize the Ln-nitrate complexes in IL media. Several recent investigations on mixtures of aprotic ILs with inorganic salts have been published,[20, 21, 22, 23] most of which involve Li<sup>+</sup> salts due to the interest in their use for electrochemical devices.[24, 25, 26, 27] A few papers have dealt with the structural characterization of protic IL mixtures with inorganic salts, finding that the perturbation of the ILs macroscopic arrangement upon salt addition depends significantly on the salt concentration.[28, 29, 30, 31] Moreover, two previous papers have focused on the solvation structure of La<sup>3+</sup> and Ce<sup>3+</sup> in EAN. The former work is a purely theoretical study of the La<sup>3+</sup>-nitrate complexes by means of DFT-based molecular dynamics (MD),[32] while the latter investigation on Ce<sup>3+</sup> in EAN employs a combination of MD and extended X-ray absorption fine structure (EXAFS) spectroscopy.[33] In the former investigation La<sup>3+</sup> was found to be coordinated by 10 oxygen atoms of 5 bidentate nitrate anions, while in the latter a different coordination was shown for Ce<sup>3+</sup>, which is bound by 12 oxygen atoms of mainly monodentate ligands.[32, 33] Taking into account the similarity in the chemical properties of La<sup>3+</sup> and Ce<sup>3+</sup> it is surprising to find such major differences in the coordination structure of their nitrate complexes. Furthermore, the increase in the oxygen coordination number from 10 to 12 is not in agreement with the well-known contraction of the Ln<sup>3+</sup> ionic radii along the series.[34] To better understand the source of this inconsistency, one should look into the possible limitations in the methods employed in Ref 32 and 33. As concerns the theoretical side of investigating Ln<sup>3+</sup> ion solvation structures in EAN, it should be stressed that in such systems the dynamics is very slow due to the high viscosity of the IL. A proper

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