



## Solvent phase characterization of lanthanide and americium complexes with malonamide and terpyridine ligands. Comparison with single crystals.

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### Abstract

This work presents our latest results on the coordination polyhedron of the trinitrato lanthanide complexes with aza and carboxy ligands. Structures in the solid state have been determined by X-ray single crystal diffraction and solution studies have been carried out by X-ray Absorption Spectroscopy at the cation L<sub>III</sub> edge. Comparison is made with the Am cation.

### Article

Fundamental data on the actinide ions in the solvent phase have always been a subject of interest. Ionic versus covalent relative character across the series, inner or outer sphere complexation mechanism in various solvent phases or structural characterization of the actinide polyhedra are some of the problems to be addressed. On the other hand, the actinide solvent phase behavior has found some recent developments in the field of nuclear waste reprocessing and in particular with the selective extraction of the minor actinides (Am, Cm) *versus* the lanthanides of the nuclear fuels. Given the physical - chemical similarities between the lanthanide and minor actinide ions, one of the major challenge is to fine tune the selective extractant properties in order to optimize the separation. Such task can only be achieved by comparing the solvent phase behaviors of the two families, even though working with Am and Cm ions is limited by the radiological hazards. X-ray Absorption Spectroscopy applied to actinide species has undergone a strong development for the past decade and has been shown to be a very powerful technique to probe the actinide coordination sphere. Numerous studies have reported on the lanthanide and actinide polyhedron in aqueous media and in solvent phases. In particular, many papers have been devoted to the aquo Ln<sup>3+</sup> ions and to its coordination mode across the series in non complexing Cl<sup>-</sup> or ClO<sub>4</sub><sup>-</sup> aqueous solutions. Thus, the occurrence of inner or outer sphere complexes has been often discussed and has shown to highly depends on the medium.

Our laboratory has been working in the field of complexation studies of the trinitrato lanthanide and actinide ions with chelating donor ligands such as carboxylamine or aza molecules. At the starting point of this study, we investigated the solvation structure of the Ln ions in pyridine phase. This ligand represents indeed the elementary unit of promising aza molecules, as the 2,2':6,2" terpyridine (Tpy) one that has been shown to be a good candidate for the lanthanide - actinide separation. Thus, the behavior of the trinitrato Ln species in such solvent, and further comparison with the Am ion is the first step in the investigation of Ln-An coordination ability to aza ligands.

We first investigated the solid state complexes of a series of trinitrato lanthanide complexes with the Tpy ligands, as exemplified by the solid state structure of  $[\text{Gd}(\text{NO}_3)_3(\text{H}_2\text{O})\text{Tpy}]\cdot 3\text{py}$  (Figure 1). All the complexes show the 1:1 Tpy/Ln ratio with a contraction of the Ln coordination sphere as the atomic number of the cation increases (lanthanidic contraction).

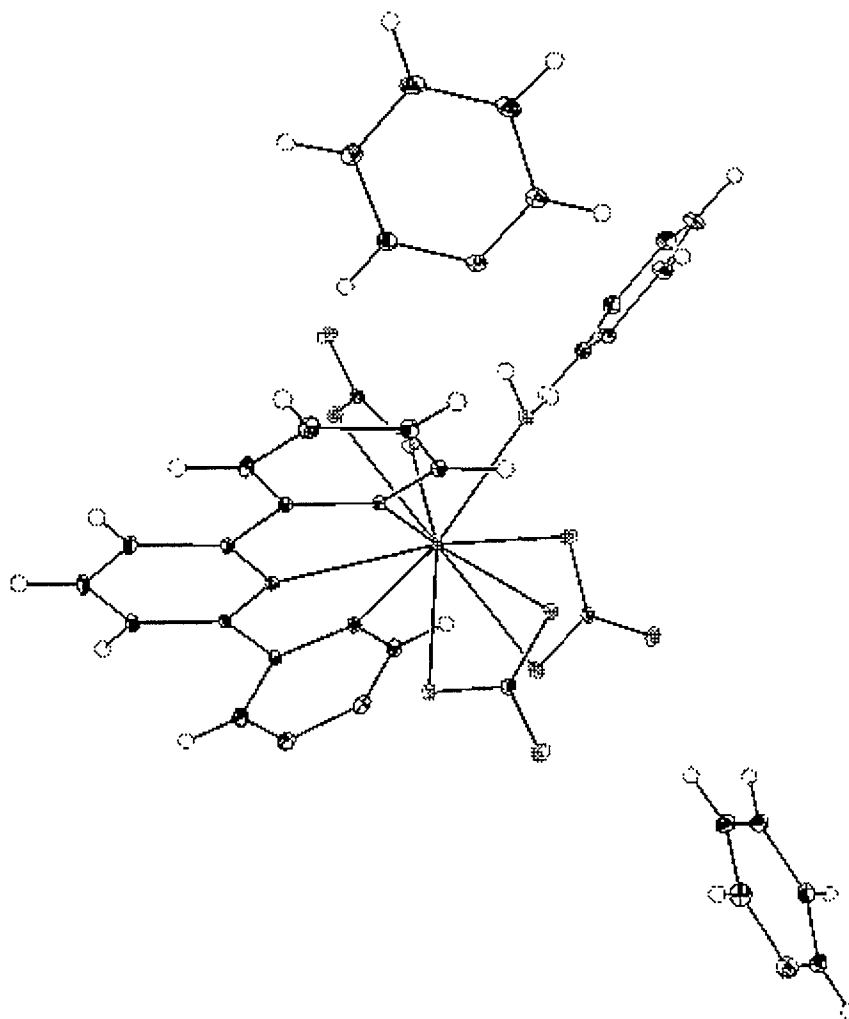


Figure 1 : Solid state structure of  $[\text{Gd}(\text{NO}_3)_3(\text{H}_2\text{O})\text{Tpy}]\cdot 3\text{py}$ .

In the solvent phase (pyridine), there is also a smooth contraction of the lanthanide first coordination sphere as shown in Figure 2 by the evolution of pic I of the PRDF. This peak is related to the cation first neighbors while the second peak, II, is a complex combination of second sphere contributions. It is related to the presence of both nitrate ions and the conformation of the pyridine ligands (if any) in the cation polyhedron.

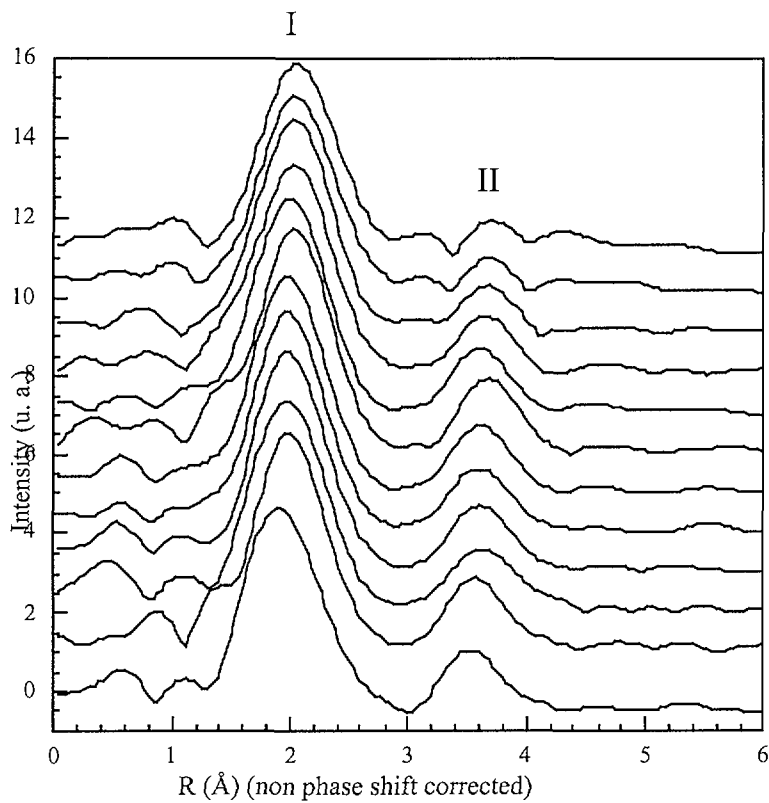


Figure 2 : PFDR at the lanthanide  $L_{III}$  edge of the trinitrato lanthanide complexes in pyridine solvent

The poster describes a precise analysis of these PRDF in relation of the solid state structures of these complexes. The analysis includes the simulations of the lanthanide polyhedron in the multiple scattering formalism.