Anion-π and H-Bonding Interactions Supporting Encapsulation of $[Ln(NO_3)_{6/5}]^{3-/2-}$ (Ln = Nd, Er) with a Triazine-based Ligand

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ABSTRACT

Reaction of Nd^{III} and Er^{III} nitrate salts with a 1,3,5-tris(dipicolylamine)-triazine (*dpat*) ligand yielded two unprecedented examples of $[Ln(NO_3)_{6/5}]^{3-/2-}$ (Ln = Nd, Er) moieties completely encapsulated by the ligands. They are found in the two new complexes, $[(H_3\textit{dpat})_2][(Nd(NO_3)_6)_2]\cdot 2CH_3CN$ **1**, and the related $[(H_3\textit{dpat})_2][(Er(NO_3)_5)_3]\cdot 3CH_3CN\cdot 2H_2O$ **2**. The structures of the complexes are similar and they crystallize in the triclinic P-1 space group with a = 12.1630(3), b = 12.2694(3), c = 17.6357(5) Å, V = 2611.10(12) $Å^3$, and a = 14.3372(4), b = 17.1271(4), c = 25.2207(7)Å, V = 5934.7(3) $Å^3$, respectively. Anion-π interactions, which are reported here for the first time for Ln^{III} ion complexes, hydrogen bonding interactions and π-π stacking support the formation of the encapsulated species. Evidence of the protonated *dpat* ligand

in **1** and **2** was found through isolation of $(H_2dpat)(NO_3)_2$. Finally, the pH-dependent ability of the ligand to extract La^{III} and nitrate ions from aqueous into toluene solution is demonstrated.

INTRODUCTION

Host-guest chemistry, which frequently involves the formation of outer-sphere complexes, has applicability in stabilization of reactive intermediates, sensing of chemical species and modeling of biological systems, among others. As such, it has been the target of an increasing number of studies in recent years.[1-12] Hydrogen bonding is an important type of interaction supporting the formation of outer-sphere complexes,[13-15] as are anion-π interactions, first described in this context by Demeshko *et al.*[16] and de Hoog *et al.*[17] The latter support spatial interactions in biological systems and the assembly of supramolecular structures,[18-22] and have gained increasing attention in catalysis.[23-26] Known examples involve electron deficient aromatics such as N-heterocycles, fluoroarenes or trinitrobenzene interacting with mono and poly-anions.[27-32] Interactions leading to outer-sphere complexes of lanthanide [Ln^{III}] ions have been studied due to the importance of these ions in magnetic resonance imaging, shift reagents and as structural probes in enzymes and biomolecules in general.[33-34] Further, outer-sphere interactions also play an important role in the actinide/lanthanide separation in nuclear reprocessing.[35-37] However, examples where the Ln^{III}-bearing species is completely enveloped by a ligand moiety are extremely rare, since in the presence of other coordinating ligands the counter-ions or water molecules of hydration dissociate and the ligands, such as N-heterocycles, bind through their heteroatoms.[38-53] Nonetheless, Wang *et al.*[54] recently reported the formation of a tetragonal prismatic complex in which $[Ln(H_2O)_8]^{3+}$ enclosed in a $[Ln_2L_4(H_2O)_2]^{+}$ cage; L is 4-amino-1,2,4-triazole-bridged 3,3'-biphenylcarboxylato. The carboxylato groups coordinate two Ln^{III} ions, forming the capsule, and the amine moiety hydrogen-bonds the cationic guest. This same cation has been recently encapsulated into the pores of a metalorganic framework, to which it is connected through hydrogen bonding of the water molecules.[55] Further, the $[Ln(H_2O)_8]^{3+}$ cluster is present and involved in outer-sphere interactions in 15-crown-5 complexes, such as the ones described by Rogers *et al.*[56-57] where the crown-ether hydrogen bonds to the water molecules coordinated to the metal, leading to a sandwich type structure.

Our research in sensitized luminescence of Ln^{III} ions,[58-63] prompted us to screen as an antenna *dpat*.[64] This ligand, which is N^2,N^2,N^4,N^4,N^6,N^6-hexakis(pyridin-2-ylmethyl)-1,3,5-triazine-2,4,6-triamine, was reported by Maheswari and co-workers; it forms a Zn complex with displays an anion-π interaction between the nitrate anion of a $[Zn(NO_3)_2]$ moiety with the triazine ring.[64] The 1,3,5-triazine moiety itself is frequently used in nuclear waste separation studies, due to the stability towards radiolysis, as well as the stability of the formed complexes.[48-51, 65-66] The additional presence of dipicolylamine led us to expect both coordination and sensitization of Ln^{III} ions with *dpat*, as this functional group has been reported to successfully accomplish this goal. To our surprise, the solutions of Ln^{III} ion salts in the presence of the ligand did not show the desired strong metal-centered luminescence. Non-luminescent crystals of the Nd^{III} analog were quickly grown and showed a remarkable, symmetric and, in our opinion, esthetically highly pleasing structure of an encapsulated Ln^{III}-bearing complex, vaguely reminiscent of the structure of endohedral fullerenes.[67-69] While we are pursuing luminescence sensitization through different triazine derivatives,[70] we became interested in the complexes isolated, as these are a rare example of outer-sphere coordination of Ln^{III} ions with complete encapsulation. The formation of the complex is supported by anion-π as well as hydrogen-bonding interactions between the enveloping ligands and the $[Nd(NO_3)_6]^{3-}$ anion. The metal ion is not coordinated directly to the ligand and is at relatively long distances of ~6 and 7 Å to the pyridine and triazine centroids,[71] thus providing a possible explanation for the weak luminescence. A similar encapsulation complex with Er^{III} was obtained and both compounds are described here. The few examples of anionic Ln^{III} ion-containing species of the type $[Ln(NO_3)_{6/5}]^{3-/2-}$ (Ln = La - Lu) often display hydrogen-bonding with other molecules present in the compounds,[72-80] but partial or full encapsulation or anion-π interactions have not been reported. Since N-heterocycles contain only C, H, N and possibly O atoms, and are therefore interesting for lanthanide/actinide extraction from nuclear waste,[35, 37] the results obtained here give important clues as to the intermolecular interactions pertaining the separation chemistry,[81-83] especially in anion-exchange columns.[84-85] Further, these results point to a new ligand architecture involving the known triazine moiety, which takes advantage of secondary interactions for the potential simultaneous separation of Ln^{III} and nitrate ions.

EXPERIMENTAL SECTION

All commercially obtained reagents were of analytical grade and used as received. Solvents were dried by standard methods. NMR spectra were recorded on Varian 400 and 500 spectrometers with chemical shifts (δ, ppm) reported against tetramethylsilane (TMS). Electrospray ionization mass spectra (ESI-MS) were collected on a Waters Micromass ZQ quadrupole mass spectrometer. The samples were prepared by preparing solutions of the compounds in a concentration of ~1 mg/mL with acetonitrile. All samples were filtered through a 0.2 μm syringe filter before injecting into the mass spectrometer. Elemental analysis was performed at Galbraith Laboratories (Knoxville, TN).

Synthesis

Synthesis of the ligand N^2,N^2,N^4,N^4,N^6,N^6-hexakis(pyridin-2-ylmethyl)-1,3,5-triazine-2,4,6-triamine (dpat) ***iii***.[64]

Cyanuric chloride ***i*** (0.2316 g, 1.26 mmol) was added to a flask with dry toluene (30 mL) and stirred until dissolved. Dipicolylamine ***ii*** (1.1070 g, 5.56 mmol) in 20 mL of toluene was added dropwise to the cyanuric chloride solution and the mixture was stirred for 30 minutes. NaOH (0.1940 g, 4.85 mmol) was added and the mixture was refluxed for 24 hours. After 24 hours the mixture was washed with water (30 mL), the organic layer was dried over magnesium sulfate, and the toluene was removed under reduced pressure. The compound was purified by flash chromatography on silica using 1:1 THF:hexanes as the eluent, yielding a pale yellow solid in 70.9% yield. X-ray quality crystals formed within one month upon dissolution of the compound in THF. ^{1}H NMR (δ, ppm, CD_3CN): 8.39 (ddd, *J*=7.5, 1.4, 1.0 1H), 7.47 (td, *J*=7.6, 1.8 Hz, 1H), 7.10 (td, *J*=4.8, 1.8, 1H), 7.01 (d, *J*= 7.8 Hz, 1H), 4.82 (s, 2H). ^{13}C NMR (δ, ppm, CD_3CN): 166.8, 159.7, 149.7, 137.2, 122.8, 122.4, 52.9. ESI-MS(+) m/z: 673.59 amu [H*dpat*]$^+$ (calc. 673.33 amu). Elemental analysis found (calc.): C 69.17% (69.62%), H 5.25% (5.39%), N 24.82% (24.98%).

Synthesis of $[(H_3dpat)_2][(Nd(NO_3)_6)_2]\cdot 2CH_3CN$ ***1***

dpat (0.0075 g, 11.2 μmol) was added to a flask with acetonitrile (10 mL). $Nd(NO_3)_3\cdot 6H_2O$ (0.0017 g, 3.88 μmol) was added to the solution. The mixture was refluxed for one hour. A small amount of methanol was added to aid complete dissolution and the solution was refluxed one additional hour. The mixture was filtered into vials. X-ray quality crystals grew within days through vapor diffusion with diethyl ether. The yield was not determined, as isolation of bulk material was not attempted.

It is proposed that the formation of the complex follows the equation:

$$4\ Nd(NO_3)_3\cdot 6H_2O + 2\ dpat + 2\ CH_3CN \rightarrow [(H_3dpat)_2][(Nd(NO_3)_6)_2]\cdot 2CH_3CN + 2\ Nd^{3+} + 6\ OH^- + 18\ H_2O$$

Synthesis of $[(H_3dpat)_2][(Er(NO_3)_5)_3]\cdot 3CH_3CN\cdot 2H_2O$ ***2***

dpat (0.0208 g, 30.9 μmol) was added to a flask with acetonitrile (10 mL). $Er(NO_3)_3\cdot 5H_2O$ (0.0399 g, 90.0 μmol) was placed in 10 mL of acetonitrile and added dropwise to the *dpat* solution. The mixture was warmed to 60 °C for 30 minutes and then filtered into vials. X-ray quality crystals grew within weeks through vapor diffusion with diethyl ether. The yield was not determined, as isolation of bulk material was not attempted.

It is proposed that the formation of the complex follows the equation:

$6\ Er(NO_3)_3\cdot 5H_2O + 2\ dpat + 3\ CH_3CN \rightarrow [(H_3dpat)_2][(Er(NO_3)_6)_3]\cdot 3CH_3CN\cdot 2H_2O + 3\ Er^{3+} + 6\ OH^- + 22\ H_2O$

Synthesis of $(H_2dpat)(NO_3)_2$

dpat was suspended in about 10 ml of deionized water. Enough 0.1 M HNO_3 was added until the *dpat* dissolved. The solution was left to evaporate slowly. X-ray quality crystals formed within a couple of weeks. The yield was not determined, as isolation of bulk material was not attempted.

Aqueous Extraction

Extraction procedure for $La(NO_3)_3$ *with dpat –* La^{III} *extraction*

The pH of a 60 mL aqueous solution of 0.01 M $La(NO_3)_3\cdot 5H_2O$ (0.2504 g, 60.33×10^{-5} mol) was adjusted with 0.01 M HNO_3 to the desired pH and the exact La^{III} concentration was determined by titration with EDTA with xylenol orange as the indicator.[86] *dpat* was placed in four separate round bottom flasks with 10 mL of toluene in order to give the molar ratios (L:M) of 1:1 (0.0333 g, 4.95×10^{-5} mol), and 2:1 (0.0677 g, 10.07×10^{-5} mols) in the initial solutions. 5 mL of La^{III} solution was added to each flask and stirred vigorously. After 2 hours, the aqueous layer was separated and the amount of La^{III} remaining in the aqueous layer was determined by titration with EDTA in the presence of xylenol orange as the indicator.[86] The final pH of each solution was determined. Each experiment was run in triplicate and at constant temperature (25.0±0.1 ^{o}C).

Extraction procedure for $La(NO_3)_3$ with dpat – NO_3^- extraction

The previous procedure was followed for 1:1 and 2:1 stoichiometry of *dpat* and metal salt in the initial solutions. The NO_3^- concentration was monitored before and after the extraction experiment in the aqueous phase with a nitrate-sensitive electrode (VWR symPhony pH/ISE meter with nitrate ion selective electrode). The extraction experiments were run in the pH range 1-4.

Spectroscopy

Singlet and triplet state measurements

Fluorescence and phosphorescence spectra were obtained on a Perkin Elmer LS-55 spectrometer. The triplet-state measurements were performed at 77 K, as described by Crosby,[87] all other measurements were performed at 25.0 ± 0.1^{o}C. The Gd(III) salt was dried under reduced pressure and heating and kept in a glove box under controlled atmosphere ($O_2 < 0.2$ ppm, $H_2O <$ 2 ppm). The complex solutions were diluted to a final concentration of 1.0×10^{-4} M after mixing of the ligand and salt in 1:1 stoichiometry. The solutions were allowed to equilibrate for at least 2 to 3 hours. Slit widths for emission measurements were 5 and/or 10 nm and a scan rate of 250 nm/sec was used. The data were collected in phosphorescence mode with a delay of 0 ms, a cycle time of 16 ms and a gate time of 0.05 ms and then increasing delay times for the triplet state measurements.

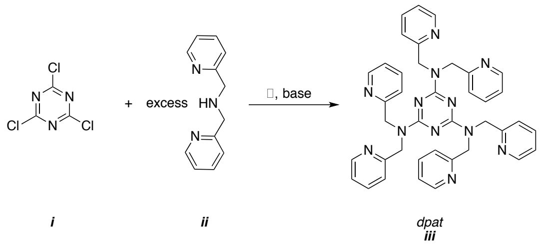
Crystallography

X-ray crystallographic characterization

Crystal data, data collection and refinement details for all three compounds are given in Table S1. Suitable crystals were mounted on a glass fiber and placed in the low-temperature nitrogen stream. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with a low-temperature device, using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Data were measured using a strategy which combines omega and phi scans of 0.3° per frame and an acquisition time of 40 s per frame. Multi-scan absorption corrections were applied. Cell parameters were retrieved using SMART[88] software and refined using SAINTPlus[89] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus[89] software. Absorption corrections were applied using SADABS.[90] The structures were solved by direct methods and refined by least square methods on F^2 using the SHELXTL[91] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added geometrically and their parameters constrained to the parent site. For the complex with water molecules of crystallization, their hydrogen atoms could not be located on the difference map and could not be added geometrically and have been omitted, although the formula is correct. CCDC 780516, 780517, 780518 and 884885 contain the supplementary crystallographic data for this manuscript. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

dpat (***iii***) is synthesized in 71% yield by refluxing dipicolylamine ***i*** in toluene with cyanuric chloride ***ii*** in the presence of base (Scheme 1) following a published procedure.[64]



Scheme 1. Synthesis of *dpat*.

X-ray quality crystals were obtained from THF solution. Details of the synthesis and crystallographic characterization can be found in the Supporting Information (Table S1). *dpat* crystallizes in the monoclinic *C2/c* space group, with six randomly oriented pyridine rings; three are oriented clockwise and the other three counter-clockwise (Figure S1). Further, three of the rings are positioned above the plane of the triazine ring, while the other three are below that plane. Several C-H···π interactions, as well as weak π-π interactions contribute to the three-dimensional packing of this molecule (Figure S2).

Reflux of an acetonitrile solution of $Nd(NO_3)_3$ with *dpat* (experimental details in the Supporting Information) yielded crystals of a complex with the molecular formula $[(H_3\textit{dpat})_2][(Nd(NO_3)_6)_2]\cdot 2CH_3CN$, **1**. In this complex, shown in Figure 1, a $[Nd(NO_3)_6]^{3-}$ anion is enveloped by two now bowl-shaped *dpat* ligands. A second $[Nd(NO_3)_6]^{3-}$ anion is also present but is not encapsulated by any ligands and compensates the charge.

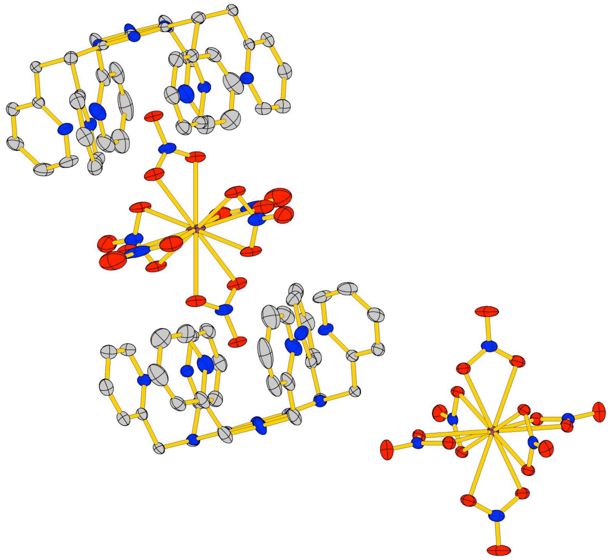


Figure 1. Thermal ellipsoid plot of **1**. Hydrogen atoms and solvent molecules were omitted for clarity. Ellipsoids are shown at 50% probability level.

Both Nd^{III} ions display a coordination number of 12, with a slightly distorted icosahedral geometry, as displayed in Figure 2.

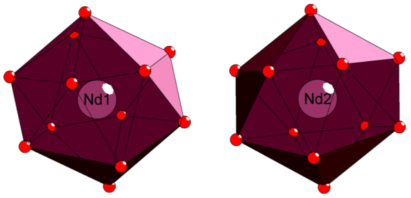


Figure 2. Polyhedral representation of the coordination environment of the two Nd^{III} ions in complex **1**.

The Nd-O distances (Figure S3) are within the range 2.574–2.616 Å (Table S2), similar to the bond lengths described for this anion in other structures.[72, 76-80] Two acetonitrile molecules are also present, but have been omitted from Figure 1. One refined at full occupancy, while two additional ones refined at half occupancy. Due to the presence of the two $[Nd(NO_3)_6]^{3-}$ anions, each ligand is three-fold protonated, as other charged species are absent. Although protons were not found in the difference map, the ligand's bowl conformation, with the nitrogen atoms of the pyridine rings pointing to the Nd-containing anion and each other, is an indication of this protonation. A previously reported protonated dipicolylamine displayed a hydrogen-bonding N···N distance of 2.634 Å between the two proton-sharing pyridines.[92] In the structure described here, the N···N distances are slightly longer in the range 2.706-3.1798 Å, (Table S2 and Figure S4 for comparison) but within the expected for hydrogen-bonding interactions. Overall, these distances and ligand shape are consistent with protonated pyridines, as they compare well with $(H_2$*dpat*$)(NO_3)_2$, which is discussed below.

Additional hydrogen-bond interactions between the pyridine nitrogen atoms are observed with the oxygen atoms of the nitrato anion pointing towards the ligand, with N···O distances in the range 3.100-3.475 Å (Table S2 and Figure 3), an example of trifurcated hydrogen bonds.[93]

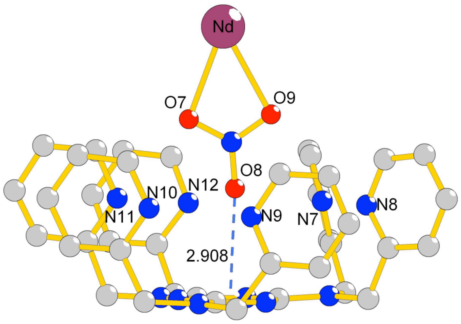


Figure 3. Partial plot of Nd^{III} with a nitrato group in complex **1** in close 2.908 Å anion-π contact with *dpat*.

The uncoordinated oxygen atom of this nitrato anion is at a distance of 2.908 Å from the triazine ring centroid (Figure 3), consistent with an anion-π interaction between the Nd-bound nitrato and the triazine ring. This distance is shorter than the value of 3.006 Å reported by Maheswari *et al.*[64] for the complex of $Zn(NO_3)_2$ with *dpat*. The authors also report an angle of 75.2° between the triazine plane and the centroid-oxygen axis. Here, the magnitude of this angle is 88.2°, which, combined with the short O-centroid distance, indicates a strong anion-π interaction. Gas-phase calculations performed by Zaccheddu and coworkers for an idealized isolated gas-phase nitrate ion interacting with 1,3,5-triazine, show an equilibrium T-shape geometry, in which the nitrate points through one of the oxygen atoms towards the triazine centroid, with an equilibrium O···centroid distance of 3.69 Å.[94]

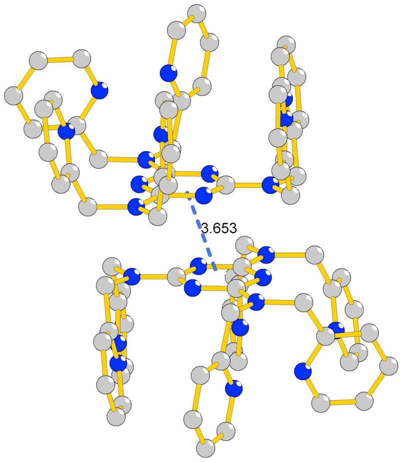


Figure 4. Partial plot of the $[H_3dpat]^{3+}$ moieties in **1**, showing the π-π interaction between the triazine rings and the centroid-centroid distance [Å] as a dashed blue line.

Concurrent π-π stacking of the triazine rings, with a centroid-centroid distance of 3.653 Å and inter-plane distance of 3.332 Å (Figure 4), and a 60° rotation of these rings, with carbon atom on top of nitrogen atom,[95] contributes to the strong anion-π interaction, according to calculations performed by Zaccheddu *et al.*[94] In the Zn-complex[64] with *dpat* π-π stacking of the triazine rings is not observed.

As mentioned above, further evidence for the protonation of the pyridine rings was obtained through comparison of this structure with the structure of the protonated ligand, obtained by addition of HNO_3 to a suspension of *dpat* in water until dissolution of the compound. X-ray quality crystals of a salt, (H_2*dpat*)(NO_3)$_2$, were isolated through slow solvent evaporation of this solution. In this salt (Figure 5), four pyridine rings are paired and share a proton, which was found on the difference map, with N···N distances of 2.6644 and 2.7141 Å. The two non-protonated pyridine rings are on opposite sides of the triazine plane, as in free *dpat*, while the nitrate ions interact through hydrogen-bonding with C-H moieties of the pyridine rings (Figure S4).

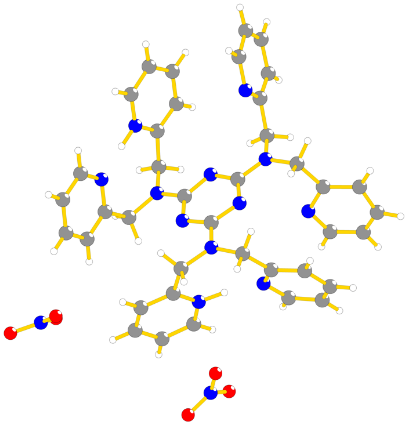


Figure 5. Ball-and-stick diagram of the salt (H_2*dpat*)(NO_3)$_2$.

A complex analogous to **1** was obtained with Er^{III}, [(H_3*dpat*)$_2$][(Er(NO_3)$_5$)$_3$]·3CH_3CN·2H_2O, **2**, shown in Figure 6.

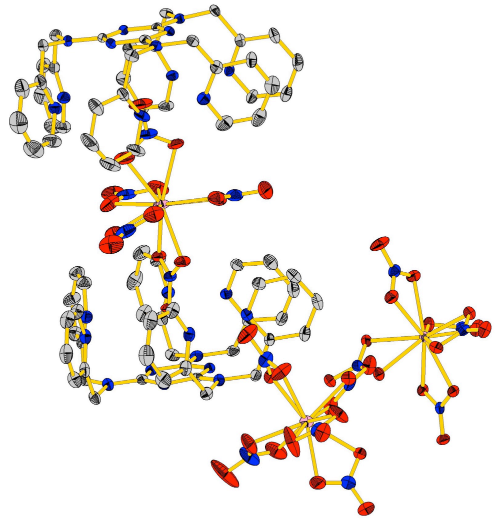


Figure 6. Thermal ellipsoid plot of **2**. Hydrogen atoms and solvent molecules were omitted for clarity. Ellipsoids are shown at 50% probability level.

Crystallographic details are summarized in Table S1. Since Er^{III} is slightly smaller than Nd^{III}, it is coordinated by five nitrato anions to yield a $[Er(NO_3)_5]^{2-}$ moiety. This is in turn encapsulated by the two triply protonated *dpat* ligands. Two additional $[Er(NO_3)_5]^{2-}$ anions are present in the structure, as well as three acetonitrile and two disordered water molecules. The Er^{III} coordination numbers are ten, as shown in Figure 7.

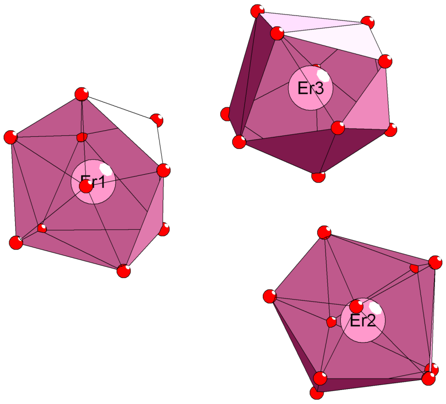


Figure 7. Polyhedral representation of the coordination environment of the three Er^{III} ions in complex **2**.

The Er-O distances (Figure S5), summarized in Table S3, are in the range 2.369-2.549 Å, consistent with the bond lengths seen in the other known structures displaying this complex anion.[96-98]

The encapsulated moiety is within anion-π distance of the triazine ligands, with O-centroid distances of 2.736 and 2.751 Å (Figure 8) and angles between the O-centroid axis and the plane of the triazine are 83.4 and 85.6°, respectively. While the angles are smaller than for the Nd^{III} structure presented above, the O-centroid distances are shorter and very close to the equilibrium distance of 2.75 Å calculated for a free nitrate with an adjacent triazine ring.[64]

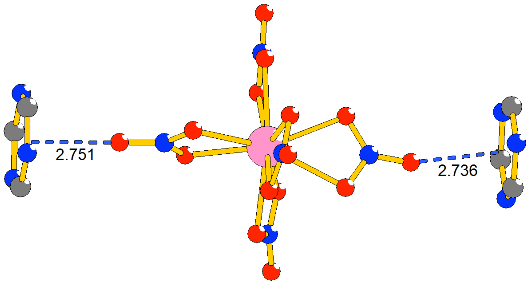
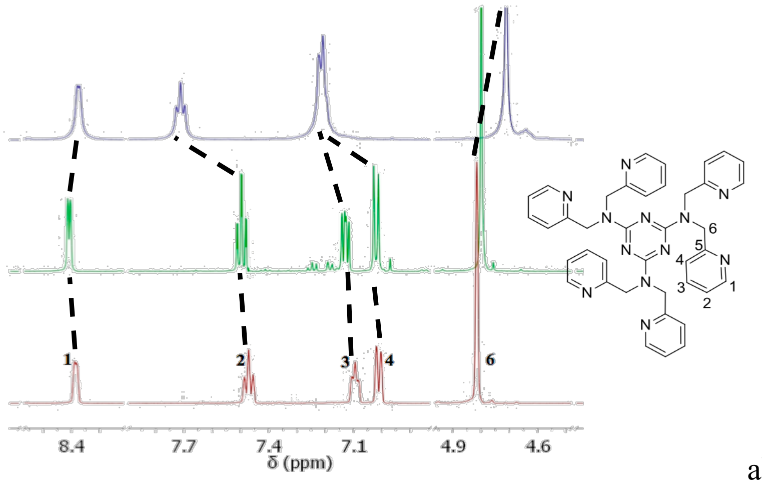


Figure 8. Partial plot of Er^{III} with two nitrato ions in complex **2** in anion-π contact [Å] with the *dpat* ligand (dashed lines).

Interestingly, while the centroid-O distances are shorter, the π-π interaction between adjacent triazine rings is substantially weaker, as these show a centroid-centroid distance of 4.248 Å and the two triazine-containing planes intersect at an angle of 3.4° (Figure S6).[95] Trifurcated hydrogen bonds[93] are seen also for this complex, with N···N distances in the range 2.692-2.701 Å and N···O distances in the range 3.211-3.485 Å (Table S3 and Figure S7).

The presence of these secondary interactions leading to encapsulation in the solid state is possibly present as well in solution. Experimental evidence does not exclude the outer-sphere interaction in solution and efforts to identify it are currently underway. Since the singlet and triplet states of the ligand are located at 32,890 and 26,460 cm^{-1} and well positioned for energy transfer, the lack of emission from any of the visible or near-infrared emitting Ln^{III} ions, as mentioned above, is an indication of the possible absence of metal-ligand coordination.[99-100] Further, the ^{1}H-NMR spectrum of the ligand in the presence of both the non-paramagnetic La^{III} and the paramagnetic Eu^{III} shows small resonance shifts, consistent with the metal interacting weakly with *dpat*. For comparison, the ^{1}H-NMR spectra of dipicolylamine, to which Ln^{III} ions are known to coordinate,[101] in the presence of the two ions were also recorded, displaying much more dramatic resonance shifts (Figure 9). For example, in the *dpat* system, the signal corresponding to proton 1 on the pyridine ring almost does not change upon complexation to La^{III} and shifts a little more upfield upon complexation to Eu^{III}. In the case of the dipicolylamine, the signal corresponding to this proton moves slightly downfield upon complexation to the diamagnetic La^{III}, but significantly upfield upon complexation to the paramagnetic Eu^{III}.[102]



a)

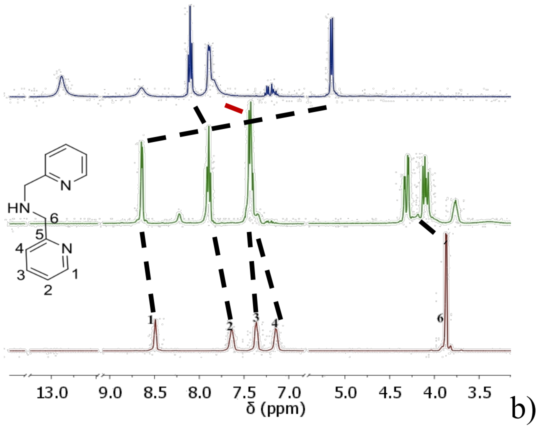


Figure 9. ^{1}H-NMR spectra of a) *dpat* and b) dipicolylamine neat (brown, bottom trace), in the presence of an equimolar amount of La^{III} (green, middle trace) and Eu^{III} (blue, top trace) in acetonitrile. Drawing of ligands with atom numbering shown and dashed lines show tentative changes in chemical shifts upon binding.[102]

ESI-MS data of solutions of these complexes show only the presence of singly and triply protonated ligand, as well as a metal ion containing species, $[Er(NO_3)]^{2+}$, in the case of Er^{III} (Figure S8).

The interaction of *dpat* with a metal ion-containing species in solution however is still strong enough to allow extraction of La^{III} from aqueous into toluene solution (Figures 10a and S9). Figure 10 shows partition ratios K_D of La^{III} (10a) and NO_3^- (10b) in aqueous and organic phase as a function of pH for 1:1 (squares, black trace) and 2:1 (circles, red trace) ligand-to-metal ion stoichiometries in solution. These results indicate that the partition ratios are dependent on the pH. The best distribution ratios, corresponding to the highest extraction efficiency, are achieved at a pH of 2. Low pH values are desirable for nuclear waste separations, as they are run under highly HNO_3-acidic conditions.[81] At a lower pH of though, the distribution ratios decrease, which is consistent with the ligand protonation observed in the solid-state structures; protonation leads to increased aqueous solubility and thus back-extraction. The co-extraction experiment of the nitrate anion (Figure 10b) shows that nitrate is removed from the aqueous into the toluene phase as well. Again, the partition ratio and thus extraction efficiency is improved as the pH is lowered. Nonetheless, for pH<2, again, most likely due to increased protonation of the ligand, the partition ratio decreases as the protonated ligand is water soluble.

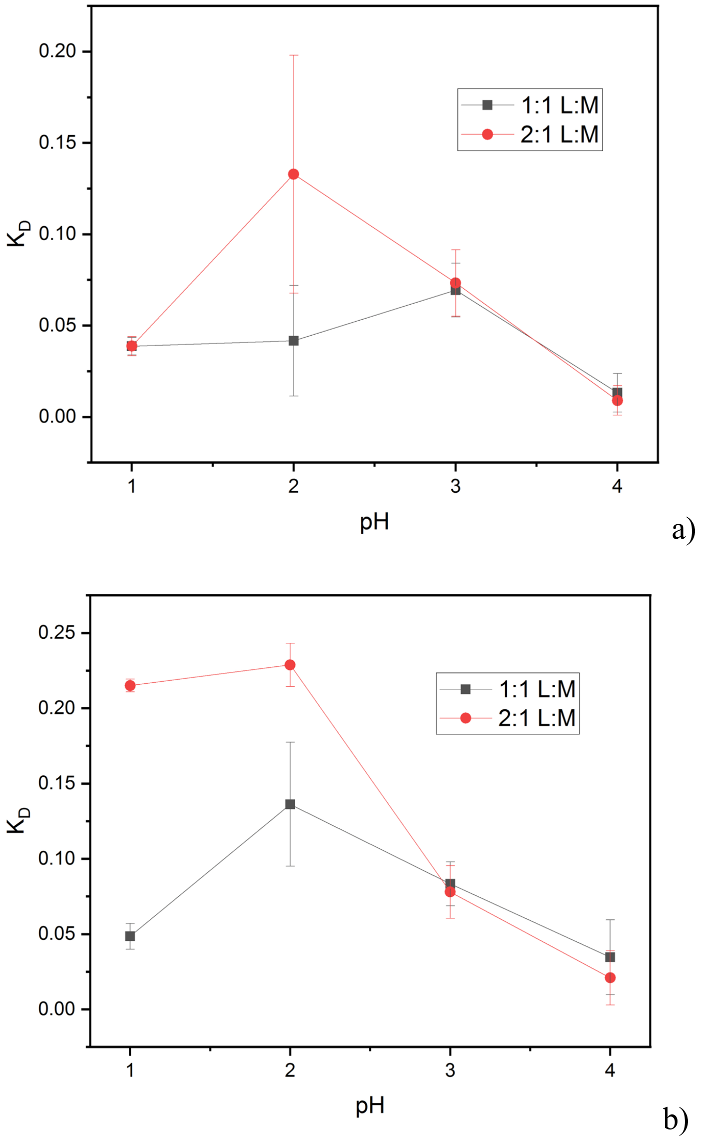


Figure 10. Partition ratios K_D of a) La^{III} and b) NO_3^- in aqueous and toluene solutions as a function of pH for 1:1 (black squares) and 2:1 *dpat*:La^{III} (red circles) stoichiometry.

CONCLUSION

In summary, we have isolated the first encapsulation complexes of $[Ln(NO_3)_{6/5}]^{3-/2-}$ (Ln = Nd, Er) supported by anion-π interactions and hydrogen bonding between the enveloping outer-sphere ligands and the metal-containing species, as well as π-π stacking of the triazine rings. The interplay between the intermolecular interactions, which leads to the formation of the outer-sphere complex, opens the avenue for the design of new ligand systems with improved capabilities for the simultaneous extraction of Ln^{III} ions and counter-anions from aqueous phase in nuclear waste recycling.

ASSOCIATED CONTENT

Supporting Information. ESI-mass spectra, crystallographic details and additional figures are available as supporting information.

The Supporting Information is available free of charge on the ACS Publications website.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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SYNOPSIS