Secondary Sphere Chloro-Ln$_{III}$ Complexes with a 1,3,5-Triazine-based Ligand Supported by Anion-π, π-π and Hydrogen-bonding Interactions.

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Anion-π interactions, π-π interactions secondary sphere interactions, hydrogen-bonding, 1,3,5-triazine, lanthanide; pyridine protonation

ABSTRACT

2,4,6-Dipicolylamine-functionalized 1,3,5-triazine (*dpat*) was isolated. When reacted with $LaCl_3$, compound $[(LaCl_6)(H_3$*dpat*$)][H_2O]_2$ **1** formed, which crystallized in the monoclinic $P2_1/n$ space group with parameters a = 11.47 Å, b = 19.22 Å, c = 20.98 Å, V = 4652.02 Å and β = 90.53°. When reacted with $NdCl_3$, the complex $[NdCl_3(H_2O)_4(H_3$*dpat*$)][Cl]_3(MeOH)_2$ **2** crystallized in the monoclinic $P2_1/n$ space group with unit cell parameters a = 20.05 Å, b = 12.81 Å, c = 20.64 Å, V = 5004.40 Å and β = 110.20°. In both cases, the *dpat* ligand forms a bowl-shaped cavity that partially envelops the Ln$_{III}$-containing central unit, which is anionic in **1** and neutral in **2**. The formation of these outer-sphere complexes is supported by secondary interactions, including π-π stacking, hydrogen bonding and anion-π between the chlorido-Ln^{III} fragment and the electron-deficient 1,3,5-triazine ring. Evidence of the protonation of the pyridine rings in *dpat* was substantiated through isolation of [H$_2$*dpat*][Cl]$_2$ **3**. This compound crystallized in the monoclinic *C*2/c space group with parameters a = 11.93 Å, b = 20.22 Å, c = 15.28 Å, V = 3664.97 Å and β = 94.35°. Four pyridine rings are pairwise protonated in **3**. *dpat* showed a moderate ability to extract La^{III} from aqueous into organic phase, indicating its potential, through judicious manipulation of secondary sphere interactions, as starting point for efficient extractants for Ln^{III} ions.

INTRODUCTION

Lanthanide ions (Ln^{III}) have unique magnetic and spectroscopic properties that are useful in fields as diverse as medicine and renewable energies.[1-2] Ln^{III} are also present in spent nuclear fuel, and thus reprocessing of spent nuclear fuel is desirable, among other reasons, to recover these economically important materials.[3-4] In this process, the used nuclear fuel is dissolved in acid, followed by extraction of the Ln^{III} with chelating agents, such as TOPO (tri(octyl)phosphineoxide) or TBP (tri-butyl phosphate), which directly bind the *f* element and extract it from the aqueous into an organic layer.[5-6] It is recognized that outer-sphere interactions[7-10] also play an important role in the actinide/lanthanide separation and lanthanide extraction,[11-13] and knowledge of and control over these interactions is desirable, since they will open new avenues for the efficient extraction and separation of Ln^{III}.

Outer-sphere interactions are frequently encountered in host-guest chemistry, and have been reported to help stabilize reactive intermediates, and are central in the sensing of chemical species and modeling of biological systems, among others.[14-25] Among these secondary sphere interactions are hydrogen bonding,[26-28] and anion-π interactions.[29] The latter support spatial interactions in biological systems and the assembly of supramolecular materials, and, in this role, were first described by Demeshko *et al.*[30] and de Hoog *et al.*[31] They are paramount in the rational design of anion receptors or hosts[29, 31-35] and of catalysts.[36-39] The π-systems involved are electron-deficient aromatics such as N-heterocycles, fluoroarenes or trinitrobenzene, for which short contacts between the ring centroid or edge and anions such as halides and nitrates are observed.[40-45]

Since $\mathrm{Ln^{III}}$ ions are hard acids, they tend to dissociate their counter-ions in polar organic solvents and easily coordinate to heteroatoms of organic ligands, such as dipicolylamine, tris(picolylamine) and other N-heterocycles; the counter-ions are then present in the structure but not bound to the metal ion[46-66] $\mathrm{Ln^{III}}$ ion complexes are relevant in a variety of applications such as magnetic resonance imaging, shift reagents and as structural probes in enzymes and biomolecules, with a myriad of spatial interactions;[1, 67] yet, only few examples of fully encapsulated or partially encapsulated outer-sphere complexes are known. Wang *et al.*[68] isolated a tetragonal prismatic complex in which a $[\mathrm{Ln_2L_4(H_2O)_2}]^+$ cage encapsulates $[\mathrm{Ln(H_2O)_8}]^{3+}$ (L = 4-amino-1,2,4-triazole-bridged 3,3'-biphenylcarboxylato); the complex is stabilized by hydrogen-bonding between the amine groups and the cationic $\mathrm{Ln^{III}}$ unit. This same cation was encapsulated in the pores of a metal-organic framework; again, hydrogen-bonding interactions to the water molecules bound to $\mathrm{Ln^{III}}$ stabilize the structure.[69] This complex cation $[\mathrm{Ln(H_2O)_8}]^{3+}$ is further involved in outer-sphere interactions with 15-crown-5 and 18-crown-6 ethers, as described by Rogers and co-workers,[70-72] and Pilkington and co-workers,[73] and cucurbituril ligands as described Shen and co-workers.[74] However, in these examples the cations are not fully encapsulated by a single ligand. Instead, hydrogen-bonding of the water molecules with several surrounding ligands stabilizes the cation and leads to outer-sphere complexes. Pecoraro and co-workers, on the other hand, observed that 15-crown-5 was able to directly bind to $\mathrm{Ln^{III}}$, and, interestingly, the complex structures formed a cavity that encapsulated selected anions; this process was supported through secondary sphere interactions.[75]

Our research in sensitized luminescence of Ln^{III} ions[76-81] prompted us to screen as an antenna the previously reported 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*).[82] The 1,3,5-triazine moiety, which is resistant to radiolysis, is frequently used in nuclear waste separation studies.[64-65, 83-86] By inclusion of the dipicolylamine functional group, we expected both coordination and sensitization of Ln^{III} ions.[87-88] Unexpectedly, we did not observe the characteristic metal-centered emission in solutions of Ln^{III} ion salts in the presence of the ligand. Instead, the crystals that quickly formed, showed the isolation of unprecedented outer-sphere complexes of Ln^{III} ions stabilized by hydrogen bonding, π-π and anion-π interactions, which we discuss in the following.

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. 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. *dpat* (0.0201 g, 30.8 μmols) was placed in a round bottom flask under nitrogen with $ErCl_3$ (0.0084 g, 30.7 μmols), 10 mL of dry MeCN, and 2 mL of dry MeOH. The solution was refluxed for 2 hours and the solvents were then removed under reduced pressure. 0.001 g of the white solid was added to 10 mL of DMSO.

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).[82]

This compound was synthesized following a literature procedure[82] and isolated as a pale-yellow solid in 70.9% yield. ^{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).

Synthesis of $[(LaCl_6)(H_3dpat)][H_2O]_2$ ***1***

dpat (0.0208 g, 30.9 μmol) was added to a flask with methanol (10 mL). $LaCl_3$ (0.0074 g, 30.2 μmol) was added to the solution. The mixture was refluxed for 2 hours and filtered into a diffusion chamber with ethyl acetate. X-ray quality crystals formed within a few days. The yield was not determined, as isolation of bulk material was not attempted.

Synthesis of $[NdCl_3(H_2O)_4(H_3dpat)][Cl]_3(MeOH)_2$ ***2***

dpat (0.0203 g, 30.2 μmol) was added to a flask with methanol (10 mL). $NdCl_3 \cdot 6H_2O$ (0.0118 g, 32.9 μmol) was added to the solution. The mixture was refluxed for 2 hours and filtered into a diffusion chamber with ethyl acetate. X-ray quality crystals formed within a few days. The yield was not determined, as isolation of bulk material was not attempted.

Synthesis of $(H_2dpat)(Cl)_2$ ***3*** *dpat* was suspended in about 10 ml of deionized water. Enough 0.1 M HCl 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.

Extraction procedure for $LaCl_3$ with dpat – La^{III} extraction

The pH of a 60 mL aqueous solution of 0.01 M $LaCl_3 \cdot 6H_2O$ (0.2118 g, 59.97×10^{-5} mol) was adjusted with 0.01 M HCl to 4.01 and the La^{III} concentration determined by titrating with EDTA using xylenol orange as indicator.[89] *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 (0.0339 g, 5.04×10^{-5} mol), 2:1 (0.0680 g, 10.11×10^{-5} mol), 3:1 (0.1015 g, 15.10×10^{-5} mol), and 4:1 (0.1349 g, 20.06×10^{-5} mol). 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 remaining La^{III} was determined by titrating with EDTA using xylenol orange as indicator. The final pH of each solution was determined. Each experiment was run in triplicate and at constant temperature of 25.0±0.1°C.

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[90] software and refined using SAINTPlus[91] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus[91] software. Absorption corrections were applied using SADABS.[92] The structures were solved by direct methods and refined by least square methods on F^2 using the SHELXTL[93] 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 complexes with water molecules of crystallization or bound water molecules, the hydrogen atoms could not be located on the difference map and could not be added geometrically and have been omitted, although the formulas are correct. Complex **2** was refined as a non-merohedral twin with 2 components using Cell Now.[94] CCDC 1923141, 1923143, and 1923142 contain the supplementary crystallographic data for this manuscript for compounds **1**, **2** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

NMR spectroscopy

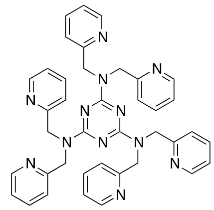
All NMR spectra were recorded on Varian 400 and 500 MHz spectrometers with chemical shifts reported (*δ*, ppm) in deuterated DMSO against tetramethylsilane (TMS, 0.00 ppm) at 25.0 ± 0.1 ^{o}C. Samples for the NMR spectra were prepared by mixing in 1:1 stoichiometry the ligand and the metal ion in the deuterated solvent.

Mass Spectrometry

Electrospray ionization mass spectra (ESI-MS) were collected in positive and negative ion modes on a Waters Micromass ZQ quadrupole in the low-resolution mode for the ligands and on an Agilent model G6230A with a QTOF analyzer in the high-resolution mode for the metal complexes. The samples were prepared by mixing the ligand and metal ion in 1:1 stoichiometry in acetonitrile, diluting to a concentration of ∼1 mg/mL and passing through a 0.2 mm microfilter.

RESULTS AND DISCUSSION

dpat is synthesized in 71% yield by refluxing dipicolylamine in toluene with cyanuric chloride in the presence of base (Scheme 1) following a published procedure.[82]



Scheme 1. Structure of *dpat*

An outer-sphere complex with the molecular formula $[(LaCl_6)(H_3dpat)][H_2O]_2$ **1** was obtained when reacting $LaCl_3$ with *dpat*. The compound crystallized in the monoclinic P21/n space group with parameters a = 11.47 Å, b = 19.22 Å, c = 20.98 Å, V = 4625.02 Å and β = 90.53°. In this complex, a trianionic $[LaCl_6]^{3-}$ moiety is partially encapsulated by one *dpat* ligand, as shown in Figure 1a.

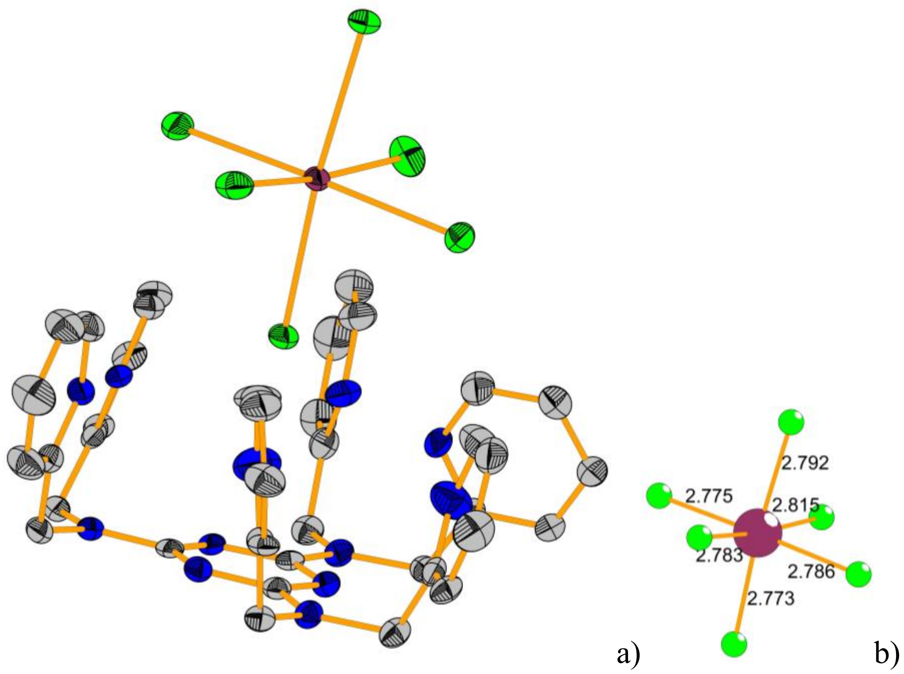


Figure 1. a) Thermal ellipsoid plot of $[(LaCl_6)(H_3$*dpat*$)][H_2O]_2$ **1**. Hydrogen atoms and water molecules of crystallization are omitted for clarity. Thermal ellipsoids at 50% probability. b) Octahedral coordination environment around the La^{III} ion showing La-Cl bond lengths [Å].

This structure is different from the complexes with nitrate salts of Ln^{III} isolated and characterized by us.[95] In those complexes, we observed full encapsulation of nitrato-Ln^{III} anionic species by two triply protonated *dpat* ligands. In this case, the La^{III} ion is in an octahedral geometry surrounded by six Cl^- ions with La-Cl distances ranging from 2.773 to 2.815 Å (Figure 1b). All pyridine rings of the ligand point inwards towards each other with N···N distances of 2.785, 2.732, and 3.383 Å (Figure 2a). Due to the orientation of the *dpat* and the lack of any other species involved in charge balance, it is reasonable to assume that the ligand is triply protonated. While the protons cannot be found in the electron difference map, evidence of their presence is provided by the fact that the pyridine rings point inwards and towards each other (*vide infra*).

There are π-π interactions present between adjacent parallel triazine rings with a centroid-to-centroid distance of 3.623 Å (Figure 2b).[96-97] It is interesting to note that the adjacent, stacked 1,3,5-triazine rings are not only offset, but there is a 60° rotation, leading to a configuration in which each nitrogen atom is on top of a carbon atom and vice-versa. Buda and co-workers indicated that this configuration is preferred and contributes to strengthening associated anion-π interactions, which are discussed below.[97]

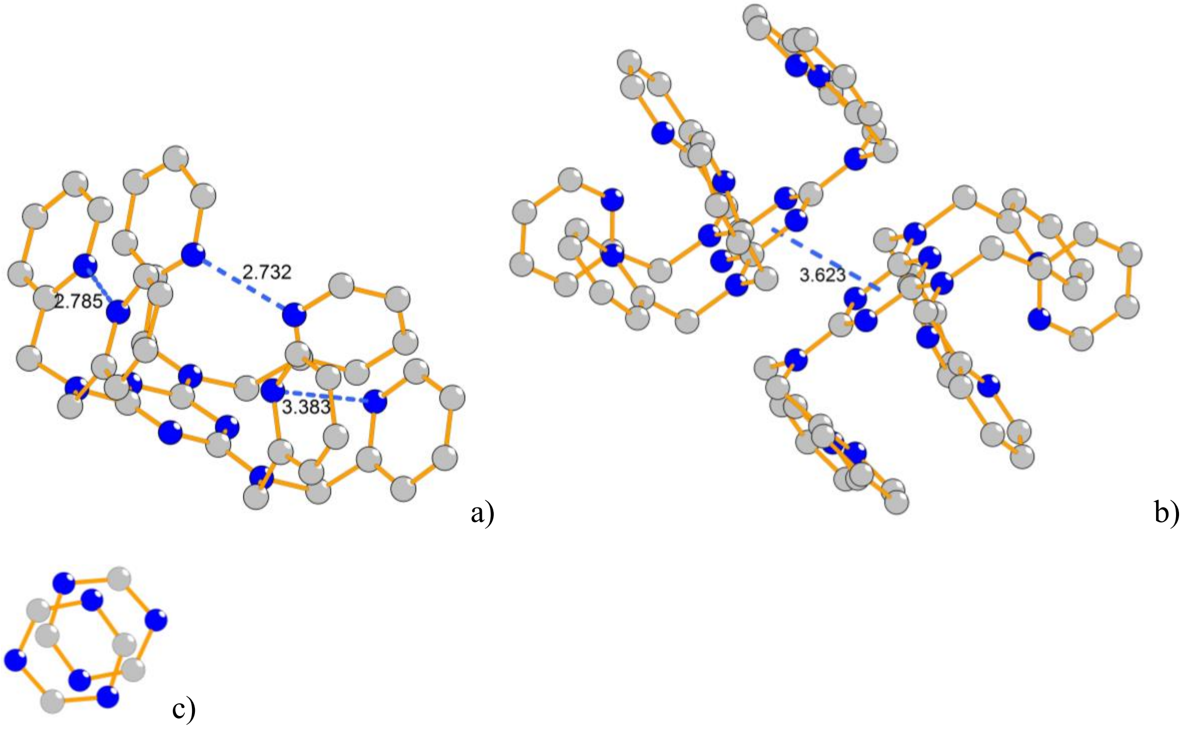


Figure 2. Ball-and-stick diagram of the *dpat* moiety in **1** showing a) the N···N short contacts with distances [Å] between pairs of pyridine rings, b) and π-π stacking interaction between adjacent *dpat* moieties with distance [Å] and c) detail of the 60° rotation off-set of the stacked 1,3,5-triazine rings.

Trifurcated hydrogen bonding[98] interactions are present in this complex with distances in the range 3.449-3.812 Å (D···A) between the apical chloride ion on the La^{III} and the pairwise protonated nitrogen atoms of the pyridine rings (Figure 3). These hydrogen bonding interactions are slightly longer, as they involve more than two centers, but within the range of hydrogen-bonding interactions observed between other $[LnCl_6]^{3-}$ anions and organic molecules in close contact. For example, distances of 3.032 Å between $[HoCl_6]^{3-}$ and $[[(CH_3)_2NH_2]_2Cl]^{+}$,[99] 3.72 and 3.75 Å between $[TbBr_6]^{3-}$ and the (NN)-C*sp*2 terminus of an ionic liquid,[100] and 3.185 and 3.196 Å between $[TbCl_6]^{3-}$ and the protonated nitrogen atom of two 3,5-dimethylpyridiniums[101] were described. A weak anion-π interaction is observed between the apical chloride and the 1,3,5-triazine ring, with a centroid···Cl distance of 3.925 Å and a triazine plane-centroid-Cl angle of 87.09° (Figure 3). This centroid···Cl distance is longer than,[102] but comparable to the value of 3.2 Å calculated by Mascal and coworkers[103] for an idealized isolated gas-phase chloride ion interacting with 1,3,5-triazine, while the triazine plane-centroid-Cl angle is smaller than the calculated equilibrium value of 90°. According to Hay *et al.*, for a convincing anion-π interaction, the chloride ion should be located over the arene centroid with a tilt angle of 90 ± 10^{o} and within 3.37 Å of the arene carbon atoms.[102]

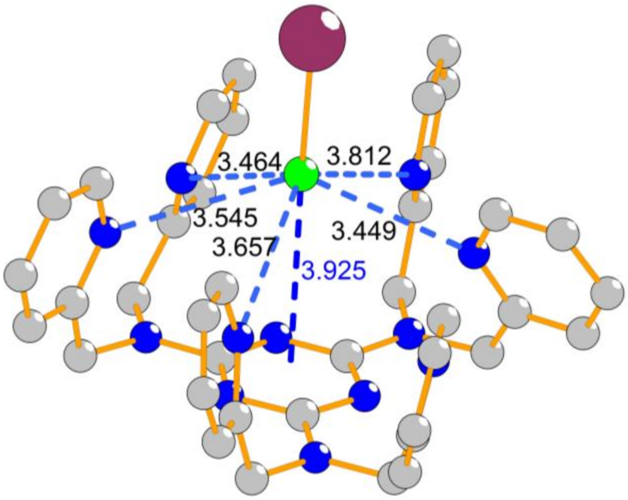
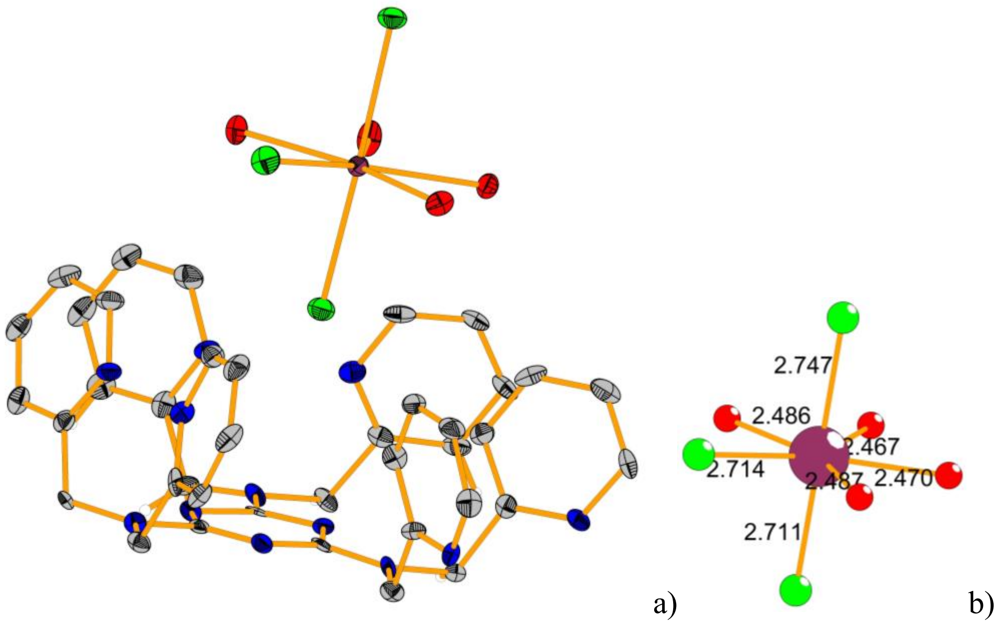


Figure 3. Ball-and-stick diagram showing the N···Cl short contacts [Å] and the Cl···triazine centroid anion-π interaction with corresponding distance [Å] in complex **1**.

Similar interactions have also been seen in transition metal complexes. Meyer and coworkers[30] reported a Cu^{II} chloride complex with dipyridylamine-functionalized 1,3,5-triazine, a ligand related to the one discussed here. In this complex the centroid···Cl^- interaction distance is 3.11 Å and the triazine plane-centroid-Cl^- angle is 87.1°.

Hydrogen-bonding is present within the packing structure of **1** with distances of 2.58-2.80 Å between the chloride ions on the La^{III} metal center and the hydrogen atoms on the pyridine rings.

Reaction of $NdCl_3$ with *dpat* lead to the isolation of crystals of a compound with the molecular formula $[NdCl_3(H_2O)_4(H_3\textit{dpat})][Cl]_3(MeOH)_2$ **2**. This compound, whose structure is shown in Figure 4a, crystallized in the monoclinic P21/n space group with unit cell parameters a = 20.05 Å, b = 12.81 Å, c = 20.64 Å, V = 5035 Å and β = 110.20°. The Nd^{III} is bound to three chlorido and four water molecules with a coordination number of 7. The coordination geometry is a pentagonal bipyramid, as shown in Figure 4b, with Nd-Cl distances between 2.711 and 2.747 Å and Nd-O distances between 2.467 and 2.487 Å.



a) b)

Figure 4. a) Thermal ellipsoid plot of $[NdCl_3(H_2O)_4(H_3$*dpat*$)][Cl]_3(MeOH)_2$ **2**. Hydrogen atoms and solvent molecules of crystallization are omitted for clarity. Ellipsoids are shown at 50% probability. b) Coordination environment around Nd_{III}, including bond distances [Å] to coordinated water molecules and chlorido.

In analogy to the structure of *dpat* in **1**, four of the six pyridine rings point inwards and towards each other with N···N distances of 2.681 and 2.741 Å (Figure 5a). The remaining two pyridine rings point out, and the nitrogen atoms are in close contact with their symmetry equivalents from a neighboring *dpat* (Figure 5b). This close interaction between the pyridine rings of adjacent *dpat* is concurrent with the absence of stacking of neighboring triazine rings, which was seen in complex **1**. In complex **2**, the triazine ring is located close to a pyridine ring from an adjacent *dpat* ligand; while the centroid-to-centroid distance is relatively short at 3.559 Å (Figure 5c), the planes of the two aromatic rings intersect at an angle of ~13.6$_{o}$, indicating that this is a very weak stacking interaction. Additionally, there is a weak anion-π interaction between the chloride and the centroid of the triazine ring (Figure 6). This interaction displays a centroid···Cl distance of 4.20 Å and a triazine plane-centroid-Cl angle of 93.40°. Comparing these results with the previously mentioned calculated centroid···Cl distance of 3.2 Å and triazine plane-centroid-Cl angle of 90.0°,[103] the distances described here are substantially longer, and longer than for complex **1**, which means there is an even weaker interaction between the chloride ion and the triazine ring.[102] In **1** we observed, in addition to the anion-π interaction, also π-π stacking of the adjacent 1,3,5-triazine rings, which is absent in this structure. This additional secondary interaction, as pointed out by Buda and co-workers, leads to a strengthening of the associated anion-π interactions;[97] it could thus contribute to the longer centroid···Cl distance.

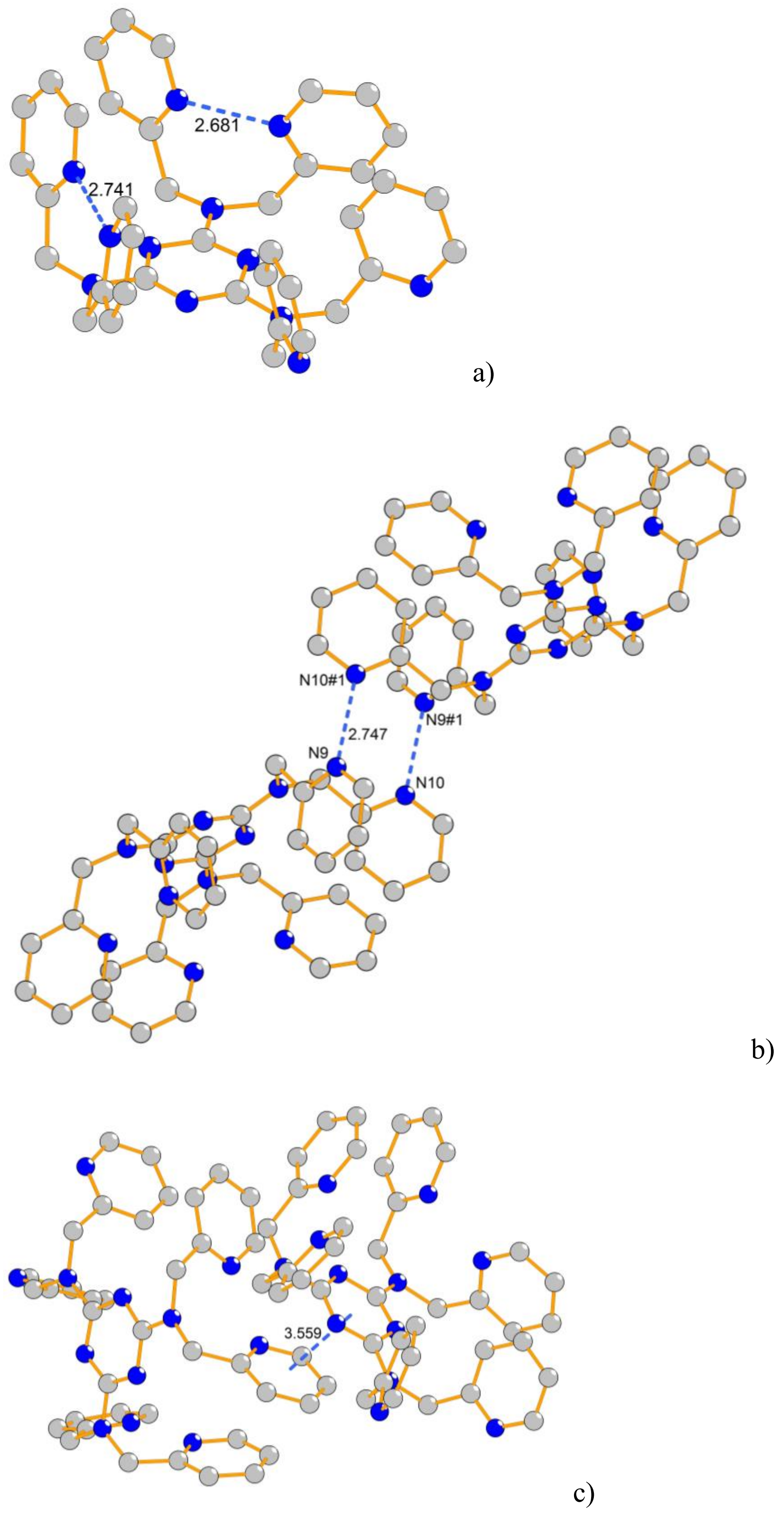

2.681
2.741
a)
N10#1
2.747
N9
N9#1
N10
b)
3.559
c)

Figure 5. Ball-and-stick diagrams for **2** with short contacts [Å] showing a) the pyridine rings pointing towards the center of the *dpat* molecule, b) the out-ward pointing pyridine rings interacting with its symmetry-related neighboring *dpat* (#1 -x,1-y,2-z) and c) the short contact [Å] between the triazine ring and a pyridine ring of a neighboring *dpat*.

Trifurcated hydrogen bonds[98, 104] (Figure 6) are present between a chloride ion on the $[NdCl_3(H_2O)_4]$ and the protons on the pyridine rings that point inwards. Hydrogen-bonding distances (D···A) are in the range 3.860-4.657 Å, quite a bit longer than observed in structure **1**. They are longer that the distances of 3.188 and 3.351 Å observed for a trifurcated hydrogen bond between two chlorido atoms in $[LaCl_6(H_2O)_2]^-$ and the protonated nitrogen atom of a 3,5-dimethylpyridinium, the distances of 3.185 and 3.352 Å in a trifurcated hydrogen bond between two chlorido atoms in $[PrCl_6(H_2O)_2]^-$ and the protonated nitrogen atom of a 3,5-dimethylpyridinium, and the distance of 3.239 Å between a chlorido of the same anion and a second 3,5-dimethylpyridinium.[101]

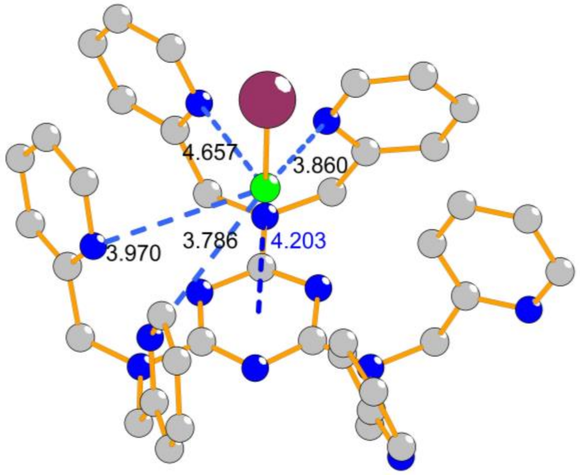


Figure 6. Ball-and-stick diagram showing the anion-π interaction in **2** with distance [Å] between the chloro and the triazine centroid and the contact distances between the chloro and the pyridine nitrogen atoms [Å].

The N···N distances for compounds **1** and **2** (Figures 2a and 5a) are consistent with protonation of the pyridine rings; thus, charge balance is needed, and is provided by three uncoordinated chloride ions present in the structure of **2**. The packing structure of the complex is supported by a large number of hydrogen bonds (Figure S1). The trifurcated hydrogen bonds[98, 104] are present as well between the free chloride ions and hydrogen atoms on the pyridine rings.

The presence of the heavy atoms in **1** and **2**, along with some disordered solvent molecules in the former structure and twinning in the latter, did not allow us to find the hydrogen atoms protonating the pyridine rings in the electron difference map, and we infer their presence from the need to balance charges and from the short N···N contacts. We were though able to find evidence of these protons through the isolation of the compound [H_2*dpat*][Cl]$_2$, which was obtained by treating *dpat* with HCl_{aq}. Its structure is shown in Figure 7. This compound crystallized in the monoclinic *C*2/c space group with parameters a = 11.93 Å, b = 20.22 Å, c = 15.28 Å, V = 3664.97 Å and β = 94.35°. As can be seen in Figure 7a the ligand is two-fold protonated and those protons, which were found in the electron difference map, are located on two nitrogen atoms of two of the pyridine rings, in close contact with the other nitrogen atoms of the companion pyridine rings, with an N···N distance of 2.707 Å and an N-H···N distance of 1.872 Å, as shown in Figure 7b. This is very similar to what is observed for compounds **1** and **2**. Two chloride ions are present in the structure and provide charge balance.

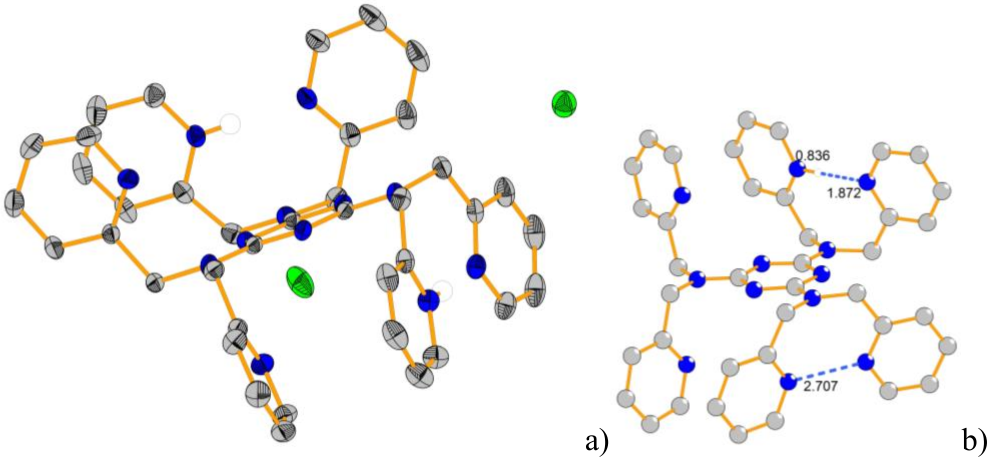


Figure 7. a) Thermal ellipsoid plot of $[\mathrm{H_2}\mathit{dpat}][\mathrm{Cl}]_2$ **3**. Hydrogen atoms, except for protons on pyridine nitrogen atoms and water molecules of solvation removed for clarity. Ellipsoids at 50% probability. b) Ball-and-stick diagram showing the protonated nitrogen atoms on the pyridine rings with N-H, N···H and N···N distances [Å].

To gather preliminary information regarding the presence of these secondary sphere complexes in solution, we were able to record the mass spectrum of a 1:1 solution of *dpat* and erbium$_{\mathrm{III}}$ chloride in DMSO, which is shown in Figure S2. A parent peak for a complex with similar molecular formula as **1** or **2** was not found. Instead, we found evidence of the singly protonated ligand (Figures S2 and S3) in the three peaks present at 673.73, 674.53, and 675.73 amu, whose patterns correlate well with the calculated isotope pattern with the chemical formula of $\mathrm{C_{39}H_{37}N_{12}}$. In addition, a peak corresponding to $[\mathrm{ErCl_5}]_{2-}$ was present in the negative ion mode spectrum, shown in Figure S3, and its experimental isotope pattern correlates well with the calculated one. In contrast to the solid-state structures, the mass spectra obtained do not show direct evidence of direct coordination of the ligand to the Ln$_{\mathrm{III}}$ ion, and open the possibility that outer-sphere coordination is present in solution as well.

To shed additional preliminary light on the solution behavior, the $_1$H spectra of 1:1 solutions of dry *dpat* with dry diamagnetic $LaCl_3$ and dry paramagnetic $EuCl_3$ salts were collected. With the paramagnetic Eu_{III}, if there was direct coordination, we would expect large shifts and broadening of the ligand resonances. The NMR spectra with *dpat* were compared to those of dipicolylamine since this ligand coordinates directly to Ln_{III}.

Figure S4 shows the $_1$H-NMR spectra of *dpat* on its own and in the presence of $LaCl_3$, and $EuCl_3$ in DMSO-d_6 and the analogous spectra with dipicolylamine are shown in Figure S5. The La_{III}-containing solutions don't show large changes when compared to the ligands alone. In the case of the Eu_{III}-containing solutions in turn, the resonance peaks are very broad in both cases, but there is a much more drastic change in the spectrum of dipicolylamine than of *dpat*. These results seem to indicate that, regardless of the Ln_{III} salt, there is interaction with both ligands, and the interaction seems to be weaker with *dpat*. While not conclusive, these results don't exclude the possibility that secondary sphere interactions might be present in solution.

Ligands capable of outer-sphere interactions have been considered for extraction experiments. This was shown for example by Schröder and co-workers; they extracted chloroplatinate$_{IV}$ from acidic aqueous into organic solution with ligands which rely on hydrogen-bonding to bind to the metallic anion.[105-106] These authors described as well the extraction of Zn_{II} and Co_{II} chlorometallates from aqueous solution into organic media through outer-sphere coordination of the metal salts with protonated amidopyridyl ligands.[107-108]

To assess the ability of *dpat* to be used for Ln_{III} extraction experiments, given its ability to hydrogen-bond and engage in weak anion-π interactions in solution, 0.01 M aqueous La_{III} was acidified to pH 4 with 0.1 M HCl and this solution treated with *dpat* in toluene. The results of this experiment are summarized in Table 1. To perform these experiments, we held the amount of La_{III}

in the aqueous phase constant, and varied the relative amounts of *dpat* in the organic phase. We observed that the ligand shows moderate extraction ability with extraction ratios up to ~14% for the 4:1 stoichiometry. After the extraction process, the pH of the aqueous solution is ~6, which might point to the protonation of the ligand as it binds the La^{III} and extracts it to the organic phase. This extraction ability is smaller than we observed for the analogous experiment with nitrate salts,[95] which might be a consequence of the weaker secondary interactions between the *dpat* and the chloride salts. These result in partial encapsulation in the case of the chloride complex anions, and complete encapsulation of the Ln-nitrato complex anions.

Table 1. Extraction of La^{III} in aqueous solution in the presence of 0.1 M HCl as a function of the relative amounts of *dpat* in the organic phase to the amount of $LaCl_3$ in the aqueous phase.

L:M ratio	Initial average pH	Final average pH	Initial Concentration of $LaCl_3$ (M)	Final Concentration of $LaCl_3$ (M)	Percentage of La^{III} extracted
1:1	4.01	6.27 ± 0.12	0.01331 ± 0.0031	0.01277 ± 0.00031	4.1%
2:1	4.01	6.36 ± 0.16	0.01331 ± 0.0031	0.01223 ± 0.00048	8.1%
3:1	4.01	6.34 ± 0.07	0.01331 ± 0.0031	0.01187 ± 0.00018	10.8%
4:1	4.01	6.31 ± 0.09	0.01331 ± 0.0031	0.01139 ± 0.00027	14.4%

CONCLUSION

In summary, we have isolated the first two examples of chloro-Ln^{III} complexes partially encapsulated by an organic ligand, *dpat*. These complexes show an unprecedented combination of secondary anion-π , π-π and hydrogen-bonding interactions involving the ligand triazine ring, pyridine rings and the central metal-bearing unit, as shown through single crystal X-ray diffraction. MS, NMR, and aqueous phase extractions indicate that while there is interaction between the LnIII ion and the ligand, that it is most likely not direct coordination. Planned experiments, such as EXAFS and variable temperature NMR, will shed more light on the modes of coordination in solution.

With this work, we have shown how secondary interactions, namely weak anion-π, π-π and more importantly hydrogen bonding, so richly displayed in this 1,3,5-triazine-based ligand bearing dipicolylamine pendant arms, and the interplay of these interactions, lead to the formation of the outer-sphere complexes. Knowledge and control of these secondary interactions open the avenue for the design of new ligand systems with improved capabilities for the extraction of LnIII ions 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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SYNOPSIS

Partial encapsulation of chloro-lanthanide complexes by a tri-protonated dipicolylamine-based 1,3,5-triazine ligand is supported by anion-π interactions, π-π stacking and hydrogen-bonding interactions