



Article Pyrrolidine-Derived Phenanthroline Diamides: An Influence of Fluorine Atoms on the Coordination of Lu(III) and Some Other f-Elements and Their Solvent Extraction

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Abstract: Three pyrrolidine-derived phenanthroline diamides were studied as ligands for lutetium trinitrate. The structural features of the complexes have been studied using various spectral methods and X-ray. The presence of halogen atoms in the structure of phenanthroline ligands has a significant impact on both the coordination number of lutetium and the number of solvate water molecules in the internal coordination sphere. The stability constants of complexes with La(NO₃)₃, Nd(NO₃)₃, Eu(NO₃)₃, and Lu(NO₃)₃ were measured to demonstrate higher efficiency of fluorinated ligands. NMR titration was performed for this ligand, and it was found that complexation with lutetium leads to an approximately 13 ppm shift of the corresponding signal in the ¹⁹F NMR spectrum. The possibility of formation of a polymeric oxo-complex of this ligand with lutetium nitrate was demonstrated. Experiments on the liquid–liquid extraction of Am(III) and Ln(III) nitrates were carried out to demonstrate advantageous features of chlorinated and fluorinated pyrrolidine diamides.

Keywords: phenanthroline; ligand; complex; lanthanide; lutetium; coordination number; XRD; UV-vis titration; NMR

1. Introduction

Lutetium is the heaviest and the smallest element of all the lanthanides [1,2]. Natural lutetium exists in two isotopic forms—in the form of a stable isotope ¹⁷⁵Lu and a radioactive isotope ¹⁷⁶Lu, which is used for radioisotope dating [3]. ¹⁷⁷Lu is one of the most attractive isotopes in clinical nuclear medicine for the diagnosis and therapy of cancer [4].

A regular decrease in the ionic radii is observed in the lanthanide row. This effect, called "lanthanide contraction", has been well studied and documented [5–9]. A variety of ligands have been shown to form complexes with lanthanides and the importance of lanthanide contraction on the structure of the formed complexes has been demonstrated [10–12]. Recently, we observed the effect of lanthanide contraction on tetrabutyl 1,10-phenanthroline-2,9-diamide [13], which acts as an N,N,O,O-tetradentate ligand. We revealed that in the La, Nd, and Eu complexes, metal ions are located below the plane of the phenanthroline core and the coordination number of the metal in the complexes with the ligand is 10. In the lutetium complex, the Lu³⁺ ion is located almost in the plane of the nucleus. As a result, the coordination number in the complex with lutetium decreases to nine and one of the nitrates became a monodentate. We have obtained a complex of lutetium nitrate with similar ligand-containing chlorine atoms at positions four and seven of the phenanthroline core. In this case, the coordination number of lutetium was also



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). equal to nine. However, one of the nitrate groups was replaced with a more compact water molecule. The complex has been built on the principle of a tight ion pair having one nitrate group in the external coordination sphere [14].

Pyrrolidine-derived diamides are more compact ligands in comparison with tetrabutyl ligands. As a result, valuable properties of these ligands during the extraction separation of f-elements have been demonstrated [14–17]. Both the selectivity and extraction ability of the ligands under study decrease with the expansion of alicycle in the amide function despite an increase in solubility. These unusual properties can be explained by the molecular dynamics of such compounds [18–22].

It was shown in [17] that the presence of chlorine atoms in positions four and seven of the phenanthroline core and the variation of the structure of amide substituents may strongly affect the extraction properties of the ligands toward separation of lanthanides. At the same time, the replacement of chlorine atoms with fluorine allows us to expect increased resistance of ligands toward radiolysis in comparison with the chlorine-containing ligands. Recently, we reported on the effective synthesis of fluorinated phenanthrolinediamides [23]. A detailed comparison of the coordination properties of pyrrolidine-derived phenanthroline diamides is of significant interest. This study is devoted to a comparison of three phenanthroline-derived ligands L1–L3 toward formation of lutetium complexes.

2. Results and Discussion

2.1. Structure of Ligands and Complexes

The ligands **L1–L3** have significant differences in their electronic properties (Figure 1). Calculated electrostatic potential maps (ESP maps) of ligands **L1–L3** permit the visualization of differences in electron distribution, which can be explained by the electron withdrawing influence of chlorine and fluorine.



Figure 1. ESP maps of ligands L1–L3 in two projections.

Another possible way to view the electronic distribution in the ligands L1–L3 is to use Merz-Kollman (ESP) charges [24]. For example, a difference in the corresponding charges on the nitrogen and oxygen atoms was observed for ligands L1–L3 according to the calculated data (Table 1). The differences in the charges on nitrogen and oxygen atoms are due to the fact that the ligand structures are asymmetric. Ligands of this type exist in twisted conformations (Figure 1, a single potential scale from -0.02 to +0.02 conventional units). All quantum chemical calculations were performed by DFT with functional—B3LYP and basis—6-31G (d,p), using the Gaussian 16 program [25] method. The calculated ESP charges in carbonyl oxygen and phenanthroline nitrogen atoms in ligands **L1** and **L3** look very similar; small differences in the values of the corresponding charges are observed only for the ligand **L2** (Table 1).

Table 1. ESP charges of N_{Phen} and O_{amide} atoms of ligands L1–L3.

Ligand	ESP Charges		
	N _{Phen}	O _{amide}	
L1	-0.339/-0.367	-0.500/-0.502	
L2	-0.263/-0.307	-0.488/-0.489	
L3	-0.366/-0.405	-0.501/-0.502	

It is quite remarkable that the negative charges on the nitrogen atoms of the phenanthroline core are the highest in the L3 ligand, while the charges on the oxygen atoms in L3 are somewhat lower than in L1, but higher than in L2. As is well known, fluorine is a strong σ -electron acceptor, but at the same time a good π -donor. The effect of direct polar conjugation manifests itself most clearly on nitrogen atoms in *para*-positions with respect to fluorine atoms, which is reflected in the stability constants of complexes with lanthanide cations (see below).

As follows from the X-ray diffraction data (Figure 2), the carboxyl groups in all three L1–L3 [15,17,23] ligands are on the same side of the phenanthroline core. The length of the C = O bonds varies from 1.220(3) Å in the ligand L2 to 1.246(2) Å in the ligand L1. Some geometric parameters are given in Table 2.



Figure 2. General view of ligands **L1** (**a**), **L2** (**b**), and **L3** (**c**) in two projections. The non-hydrogen atoms are shown as thermal ellipsoids at a 50% probability level [16,17].

Table 2.	Some geometric	parameters o	f ligands L1	-L3	16,17].
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Ligand/Bond Length, Å	C = O(1)	C = O(2)	C-N(Amide)	C-N(Amide)	OCCN(°)	OCCN(°)
L1	1.241(2)	1.241(2)	1.347(2)	1.348(2)	139.48(16)	160.72(16)
	[1.246(2)]	[1.245(2)]	[1.337(2)]	[1.344(2)]	[150.64(18)]	[173.73(18)]
L2	1.220(3)	1.223(3)	1.328(3)	1.332(3)	128.6(3)	141.1(3)
L3	1.232(4)	1.235(4)	1.330(4)	1.324(4)	124.6(3)	152.6(3)

The values for the second symmetry-independent molecule are given in brackets.

Next, we synthesized complex compounds of ligands L1–L3 with lutetium nitrate (see the Materials and Methods section and Supplementary Materials Figures S1–S6). In each of the cases, we were able to investigate the structure of the obtained complex compounds by

combining various spectral methods (NMR and IR) and by XRD analysis (Figure 3). Table 3 shows the IR data of ligands L1–L3 and their complexes with $Lu(NO_3)_3$. It can be seen from the data that moving from L1 to L3 results in the shift difference of C=O increasing to 20 cm⁻¹.



Figure 3. General view of the complexes $L1 \bullet Lu(NO_3)_3$ (a), $L2 \bullet Lu(NO_3)_3$ (b), and $L3 \bullet Lu(NO_3)_3$ (c) in two projections. Hydrogen atoms, except those of coordinated water molecules as well as the lattice solvent in $L3 \bullet Lu(NO_3)_3$, are omitted for clarity, and the non-hydrogen atoms are shown as thermal ellipsoids at a 50% probability level.

	IR (CO), cm^{-1}		IR (CO), cm^{-1}	Δ (CO), cm $^{-1}$
L1	1613	$L1 \bullet Lu(NO_3)_3$	1602	11
L2	1622	$L2 \bullet Lu(NO_3)_3$	1609	13
L3	1628	$L3 \bullet Lu(NO_3)_3$	1608	20

Table 3. IR data of ligands L1–L3 and their complexes with Lu(NO₃)₃.

Single crystals were obtained by slow isothermal recrystallization of these complexes from the MeCN/CHCl₃ solvent system. The resulting crystals of $L2\bullet Lu(NO_3)_3$ and $L3\bullet Lu(NO_3)_3$ also contained a lattice acetonitrile molecule. In the complexes with the ligands L1 and L2, the coordination number of the metal ion was nine (Figure 3).

In L1•Lu(NO₃)₃, the coordination environment of the metal ion includes the ligand L1 and two nitrate anions acting as bidentate ligands (Table 4) while the third nitrate group is displaced by the water molecule. The O-H ... O hydrogen bond (O ... O 2.683(5) Å, OHO 170.2(2)°) holds the latter species together to produce a centrosymmetric dimer from the neighboring complex molecules (Figure 3). No stacking interactions occur despite the presence of the extended aromatic phenanthroline core in the ligand L1; apart from the above hydrogen bonds, only weak van der Waals interactions operate in the crystal of this complex.

In L2•Lu(NO₃)₃, two nitrate anions occur in the outer sphere so that the metal ion coordinates one nitrate anion in a similar bidentate manner and three water molecules (Figure 3). The latter three molecules are involved in hydrogen bonding with the outer-sphere nitrate anions (O . . . O 2.72(2)–3.264(6) Å, OHO 126.3(3)–175.7(3)°) and the lattice acetonitrile molecule (O . . . N 2.853(6) Å, OHN 177.5(3)°) to produce corrugated double tapes along the crystallographic axis *a* (Figure 4). These tapes are packed into the 3D

framework by Cl... Cl halogen bonds [26], as judged by the Cl... Cl distance of 3.251(2) Å and the C-Cl... Cl angle of $166.97(13)^{\circ}$, and stacking interactions between the parallel phenanthroline cores (the interplane angle is 0° and the intercentroid and shift distances are 4.6063(18) and 3.065(3) Å, respectively).

	$L1 \bullet Lu(NO_3)_3$	$L2 \bullet Lu(NO_3)_3$	$L3 \bullet Lu(NO_3)_3$		
	Bond Length, Å				
R _{M-O(1)}	2.304(3)	2.311(2)	2.324(5)		
R _{M-O(2)}	2.267(3)	2.321(3)	2.313(5)		
R _{M-N(1)}	2.416(3)	2.472(3)	2.500(6)		
R _{M-N(2)}	2.404(3)	2.483(3)	2.531(6)		
R _{M-ONO2(2)}	2.363(3)-2.471(4)	2.405(3), 2.478(3)	2.406(7)-2.490(6)		
R _{M-OH2}	2.281(3)	2.260(2)-2.392(3)	-		
Out-of-plane	0.090(4)	0.438(2)	0.027(7)		
Torsions (°)					
N _{phen} -C-C=O	1.8(6), 11.5(6)	4.6(4), 6.0(4)	24.4(11), 17.4(12)		
C _{amide1} -N _{amide} -C=O ^{a)}	173.2(5), 177.3(5)	173.6(3), 167.3(5) [173.4(12)]	172.0(8), 174.0(10)		
C _{amide2} -N _{amide} -C=O ^{a)}	0.6(7), 2.7(5)	1.8(5), 6.2(6) [16.8(8)]	8.5(13), 1.4(14)		

Table 4. Some geometric parameters of the complexes L•Lu(NO₃)₃.

^{a)} The values for the minor component of the disordered moiety are given in brackets.



Figure 4. Fragments of the crystal packing illustrating the formation of a hydrogen-bonded dimer in $L1 \bullet Lu(NO_3)_3$ (a), a hydrogen-bonded tape in $L2 \bullet Lu(NO_3)_3$ (b), and a dimer formed by stacking interactions in $L3 \bullet Lu(NO_3)_3$ (c). Red dotted lines represent hydrogen bonds and the phenanthroline cores involved in stacking interactions are highlighted in pink.

The coordination environment of the metal ion in $L3 \bullet Lu(NO_3)_3$ is formed only by the ligand L3 and three nitrate anions that all act as bidentate ligands. As a result, the coordination number reaches 10 (Figure 3). This type of coordination of the lutetium ion has already been observed in complexes with some organic ligands [27–29], however, it is still quite rare. For 1,10-phenanthroline-2,9-diamides, this is the first time that such a coordination number has been observed. As there are no convenient proton donors, such as the coordinated water molecules in L1•Lu(NO₃)₃ and L2•Lu(NO₃)₃, the crystal packing of L3•Lu(NO₃)₃ is dominated by parallel-displaced stacking interactions between the phenanthroline cores (the interplane angle is 0° and the intercentroid and shift distances are 4.217(5) and 2.507(8) Å, respectively) that produce centrosymmetric dimers (Figure 4).

In the complexes $L1 \bullet Lu(NO_3)_3$ and $L3 \bullet Lu(NO_3)_3$, the metal ion is located almost in the plane of the phenanthroline core of the ligand; the distance between the plane and the

metal ion for these two complexes is 0.090(4) and 0.027(7) Å, respectively. In the complex L2•Lu(NO₃)₃, however, the metal ion moves away from the phenanthroline plane by 0.438(2) Å (Table 4). The Lu-N bond lengths increase in the row of substituents H–Cl–F in the four and seven positions of the ligands.

2.2. UV-Vis Titration

Stability constants for L3 with four representatives of lanthanides La(III), Nd(III), Eu(III), and Lu(III) were determined using UV-vis spectrophotometry titration. The absorption band of L3 in the range from 240 to 360 nm is very sensitive to its coordination environment.

Thus, these spectral changes can be used to determine stability constants (log β). Figure 5 shows an example of the absorption spectrum obtained by spectrophotometric titration of the ligand L3 with lanthanum trinitrate in a solution of dry acetonitrile (Figure 5a), the molar absorptions of free ligand L3 and Eu(III) complexes calculated from spectral deconvolution (Figure 5b), and the titration curve at maximum absorption (Figure 5c). Similar data for Nd(III), Eu(III), and Lu(III) are shown in Supplementary Materials Figure S7. All spectra have similar trends of change. With an increase in the number of metal ions added, the peak of the ligand L3 (~260 nm) gradually decreases, and a new peak corresponding to the metal-ligand complex appears in the 280 nm region. The obtained titration curves were analyzed using the Hypspec2014 program [30]. For all studied lanthanide ions, it was found that the titration data best correspond to the formation of L3:metal complexes 1:1 and 2:1 stoichiometry, which was previously also observed for L1 and L2 ligands [16,17]. The obtained stability constants of complexes of L3 with lanthanide ions (log β) are shown in Table 5. The L3 ligand has a greater affinity for light lanthanides since a decrease in log $\beta 1$ is observed during the transition from La to Lu. It is worth noting that the stability constants for the L3 ligand with La^{3+} , Nd^{3+} , and Eu^{3+} are approximately 0.5 greater than the stability constants for the L1 and L2 ligands, while the log β 1 values for complexes with Lu³⁺ are similar for all three ligands (log β 1 = 5.98 \pm 0.02 for L1 and 6.06 ± 0.02 for L2). The reason for this has been discussed above.



Figure 5. Spectrophotometric titration of **L3** (ca. $10^{-5} \text{ mol } L^{-1}$) with La³⁺ ions (ca. $5 \times 10^{-4} \text{ mol } L^{-1}$) in CH₃CN solution (T = 25.0 ± 0.1 °C, I = 0 M, V₀ = 2.0 mL): (a) absorption spectra, (b) the molar absorptivities of free ligand **L3** and La(III) complexes calculated from spectral deconvolution, and (c) titration curve at maximum absorption (282 nm).

2.3. NMR Titration

Next, we studied the complexation of L3 with lutetium trinitrate at 25 °C using ¹H and ¹⁹F NMR titration in deuterated acetonitrile (Figure 6). The gradual addition of a solution of lutetium pentahydrate Lu(H₂O)₅(NO₃)₃ in CD₃CN to a solution of L3 in the same solvent led to a downfield shift of phenanthroline H^{5,6} and H^{3,8} signals as well as signals of the α -CH₂ groups of the pyrrolidine moieties. Adding two equimoles of lutetium trinitrate caused the H^{5,6} and H^{3,8} signals to shift by 0.18 and 0.46 ppm, respectively, and the signals of the α -CH₂ groups to shift by 0.17 and 0.22 ppm. An especially significant shift was observed in the ¹⁹F NMR. For example, the starting ligand had a signal with a shift of

-112.22 ppm, which decreased to -99.25 ppm and -98.95 ppm after the addition of one or two equimoles of lutetium trinitrate, respectively. At the same time, the spectrum continued to change slightly even with the addition of lutetium nitrate to the solution of the 1:1 stoichiometry complex. In the case of stoichiometry, clear signals are observed in both the ¹H and ¹⁹F NMR spectra when the metal:ligand ratio is 2:1, which may indicate that in the case of 1:1 stoichiometry, the ligand molecules may not be equivalent [31].

Ligand	Metal Ion	log β1	log β2
	La ³⁺	5.90 ± 0.02	11.64 ± 0.04
T 1	Nd ³⁺	5.96 ± 0.02	11.78 ± 0.04
LI	Eu ³⁺	5.92 ± 0.02	11.62 ± 0.04
	Lu ³⁺	5.98 ± 0.03	11.78 ± 0.04
	La ³⁺	5.82 ± 0.02	11.63 ± 0.05
10	Nd ³⁺	5.85 ± 0.02	11.64 ± 0.05
L2	Eu ³⁺	5.90 ± 0.02	11.66 ± 0.05
	Lu ³⁺	6.06 ± 0.02	11.63 ± 0.04
	La ³⁺	6.53 ± 0.02	11.81 ± 0.06
I O	Nd ³⁺	6.50 ± 0.01	11.70 ± 0.03
L3	Eu ³⁺	6.39 ± 0.02	11.62 ± 0.04
	Lu ³⁺	6.02 ± 0.02	12.04 ± 0.04
(a)			
(b)			
		n	home
(c)			
			Ma
(d)			8
	······		Mu
(e)			
-95 -100 -105	-110 9.0 8.5	8.0 4.0 3.5	3.0 2.5 2.0 1.5

Table 5. Stability constants (log β) for L1, L2, and L3 complexes with Ln(III) nitrates.

Figure 6. ¹⁹F (left) and ¹H (right) spectra of NMR titration in CD₃CN at 25 °C. From top to bottom (a) before adding Lu³⁺, (b) L3: Lu³⁺ = 1:0.5, (c) L3: Lu³⁺ = 1:1, (d) L3: Lu³⁺ = 1:1.5, and (e) L3: Lu³⁺ = 1:2.

Having identified the structural differences in the studied lutetium complexes, the question of whether the ligands **L2** and **L3** are able to produce complexes with a metal:ligand ratio of 1:2 arose. We attempted to synthesize such a complex by reacting two ligand equivalents with lutetium nitrate. With the **L2** ligand, we again obtained a complex with a metal:ligand raio of 1:1. With the ligand **L3**, a poly-nuclear oxo-complex (**L3**)₃Lu₃O₂(NO₃)₅ in which the monomers are interconnected via the Lu-O bond, was obtained (Figure 7). In this complex, there are two symmetry-independent metal ions, the one in the center—Lu(2)—with a coordination number of eight and the two at the periphery—Lu(1)—with a coordination number of nine. The coordinated in a bidentate manner and two oxygen atoms in the axial positions (Table 6). The latter coordinate involves another nitrate anion

instead of one of the oxygen atoms. The central metal ion is located almost in the plane of the phenanthroline core of the ligand L3 (the distance from the plane and the metal ion is only 0.053(15) Å), while the metal ion at the periphery is shifted by 0.207(4) Å from this plane away from the central metal ion (Table 6).



Figure 7. General view of the oxo-complex $(L3)_3Lu_3O_2(NO_3)_5$ with hydrogen atoms omitted for clarity and other atoms shown as thermal ellipsoids at a 50% probability level. Phenanthroline cores involved in stacking interaction are highlighted by pink.

	Lu(1)	Lu(2)
	Bond length, Å	
R _{M-O(1)} , R _{M-O(2)}	2.311(4), 2.320(4)	2.34(2) [2.24(2)]
$R_{M-N(1)}, R_{M-N(2)}$	2.463(4), 2.420(4)	2.431(7) [2.400(11)]
R _{M-ONO2(2)}	2.390(18) - 2.474(4)	2.375(3)
R _{M-O}	2.129(2)	2.116(2)
Out-of-plane shift	0.207(4)	0.053(15)
	Bond angles (°)	
Lu-O-Lu	170.	99(14)
O-Lu-O	-	154.79(14)
	Torsions (°)	
N _{phen} -C-C=O	12.1(6), 13.3(6)	9.6(18) [10(2)]
C _{amide} -N _{amide} -C=O	2.7(7)-3(4)	1(2) [2(2)]

Table 6. Some geometric parameters of the oxo-complex $(L3)_3Lu_3O_2(NO_3)_5^{a}$.

^{a)} The values for the minor component of the disordered moiety are given in brackets.

In addition to the above coordinate bonds, the complex $(L3)_3Lu_3O_2(NO_3)_5$ is stabilized by intramolecular parallel-displaced stacking interactions between the phenanthroline cores; the appropriate interplane angles are 5.27(14) and 6.0(2)°, the intercentroid distances are 4.476(4) and 3.662(5) Å, and the shift distances are 2.663(4) and 2.974(6) Å. Therefore, only weak van der Waals interactions pack the complex molecules into the 3D framework.

2.4. Extraction of Am(III) and Eu(III)

For ligands **L2** and **L3**, the distribution ratio and separation factors of the Am(III)/Eu(III) pair were determined during extraction from nitric acid solutions with 0.01 M ligand solutions in 3-nitrobenzotrifluoride (F3) (Figure 8, Table 7). Ligand **L1** did not participate in extraction experiments since this ligand has a negative log P = -0.08 and, as we have shown earlier, the distribution coefficients of Am(III) and Eu(III) during extraction with this ligand decrease with increasing phase contact time, which may be due to the fact that the

complexes transition to the aqueous phase. The introduction of electron σ -acceptor fluorine atoms, which are stronger than chlorine atoms, leads to a greater decrease in the electron density on phenanthroline nitrogen atoms. As a result, the distribution ratios of Am(III) and Eu(III) are 5–10 times smaller in the case of extraction with L3 compared with L2.



6

Figure 8. The dependence of the distribution ratio Am(III) and Eu(III) on the concentration of nitric acid in the equilibrium aqueous phase during extraction with 0.01 M ligand solutions in F3 (a). Distribution ratios of lanthanides(III) and Am(III) for extraction by (b) 0.01 mol L⁻¹ L2 and L3 from 5 mol L⁻¹ HNO₃ and (c) 0.05 mol L⁻¹ L3 from 3 and 5 mol L⁻¹ HNO₃.

C(HNO ₃), M	L2	L3
1	1.4	3.3
2	5.9	8.7
3	12.1	14.8
4	12.7	12.3
5	16.7	14.1

18.0

13.9

Table 7. The values of the Am/Eu pair separation factors during extraction with 0.01 M ligand solutions in F3 from nitric acid solutions.

However, the introduction of electron σ -acceptor atoms (both chlorine and fluorine) into the positions four and seven of the phenanthroline fragment leads to a decrease in the Brønsted basicity of diamides for ligands **L2** and **L3**. As a result, an increase in the distribution coefficients of Am(III) and Eu(III) is observed over the entire studied range of nitric acid concentrations (1–6 mol·L⁻¹). Unsubstituted diamides usually have an extraction maximum at a nitric acid concentration of 3–4 mol·L⁻¹. A higher acid content leads to ligand protonation and a decrease in the distribution coefficients [17,32].

The extraction of lanthanides(III) (except for Pm(III)) was also studied. Figure 8b shows the distribution coefficients of the lanthanides(III) in the extraction of 0.01 M L2 and L3 from 5 M HNO₃. The distribution coefficients of lanthanides(III) also take smaller values in the case of extraction with diamide with more σ -electron-withdrawing fluorine atoms, like what is seen with L3. Since the distribution coefficients of lanthanides(III) and americium(III) in the extraction of L3 under these conditions take values less than one, we also studied the extraction of lanthanides(III) with 0.05 M solutions of L3 in F3 from 3 and 5 M HNO₃. During extraction from 5 M HNO₃, the distribution coefficients of lanthanides(III) was greater than one, which made it possible to separate it from lanthanides(III). It should be noted that in all cases, Am(III) was extracted better than lanthanides(III). The dependence of the distribution coefficients D on the cation atomic number Z when moving along the lanthanide series has a V-shaped character, which has already been observed for ligands of this type. The reasons for the appearance of such dependencies were considered by us earlier [14].

3. Materials and Methods

Chemical reagents such as $Lu(NO_3)_3 \cdot xH_2O$ and other inorganic/organic reagents and solvents were of analytical grade. Lutetium trinitrate hydrate $Lu(NO_3)_3 \cdot xH_2O$ was purchased from Sigma-Aldrich, Co. (St. Louis, MO, USA) and used without further purification. The water content x in lutetium nitrate was determined as x = 5. Deuterated solvent CD₃CN for NMR spectra registration was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA) and used without further purification. Acetonitrile, chloroform, and diethyl ether which were used for the synthesis of complexes were purified according to known procedures. C₆F₆ was purchased from Sigma-Aldrich, Co. (St. Louis, MO, USA) and used without further purification. Analytical grade 3-nitrobenzotrifluoride (F3) was purchased from Rhodia (France).

NMR spectra were recorded using standard 5 mm sample tubes on an Agilent 400-MR spectrometer (Agilent Technologies, Santa Clara, CA, USA) with operating frequencies of 400.1 MHz (¹H) and 376 MHz (¹⁹F). IR spectra in the solid state were recorded on a Nicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) using an internal reflectance attachment with a diamond optical element and an attenuated total reflection (ATR) with a 45° angle of incidence. The resolution was 4 cm⁻¹ and the number of scans was 32. HRMS ESI mass spectra were recorded on the MicroTof Bruker Daltonics and Orbitrap Elite instruments.

All quantum chemical calculations were performed by the Gaussian 16 program [25] DFT method with B3LYP functional and basis 6-31G (d,p).

3.1. Synthesis and Analytical Data

Syntheses of ligands L1, L2 and L3 were reported earlier [15,17,23].

General procedure for preparation of the complexes with $Lu(NO_3)_3$.

A solution of lutetium nitrate (0.1 mmol) in acetonitrile (1 mL) was added dropwise to a solution of 1,10-phenanthroline-2,9-dicarboxamide (0.1 mmol) in chloroform (1 mL). After, the reaction mixture was concentrated in a vacuum to 1/10 of its initial volume and then treated with diethyl ether (2 mL). The resulting complex was filtered and washed with ether and dried in air.

N²,N⁹-bis(pyrrolidine)-N²,N⁹-diethyl-1,10-phenanthroline-2,9-dicarboxamide lutetium trinitrate **L1**•Lu(NO₃)₃. Yield 88.7% (65.2 mg). White powder. T_{decomp.} > 340 °C; ¹H NMR (CD₃CN) δ 8.93 (d, *J* = 8.6 Hz, 2H, Phen), 8.59 (d, *J* = 8.6 Hz, 2H, Phen), 8.29 (s, 2H, Phen), 4.19 (t, *J* = 6.9 Hz, 4H, Pyrr), 3.89 (t, *J* = 6.9 Hz, 4H, Pyrr), 2.21–2.14 (m, 4H, Pyrr) 2.08–2.01 (m, 4H, Pyrr); IR (ν, cm⁻¹) 3149, 3069, 2975, 2878 (C-H stretching vibrations), 1602 (C=O); HRMS (ESI-TOF) (m/z) [M + H⁺] calculated for $[C_{22}H_{22}LuN_6O_8]^+$ 673.0902, found 673.0886.

N²,N⁹-bis(pyrrolidine)-4,7-dichloro-N²,N⁹-diethyl-1,10-phenanthroline-2,9-dicarboxamide lutetium trinitrate **L2**•Lu(NO₃)₃. Yield 88.1% (70.5 mg). Yellow powder. T_{decomp.} 240 °C; ¹H NMR (CD₃CN) δ 8.62 (s, 2H, Phen), 8.58 (s, 2H, Phen), 4.18 (t, *J* = 6.9 Hz, 4H, Pyrr), 3.88 (t, *J* = 6.9 Hz, 4H, Pyrr), 2.20–2.13 (m, 4H, Pyrr), 2.07–2.00 (m, 4H, Pyrr); IR (ν, cm⁻¹) 3120, 3083, 2987, 2883 (C-H stretching vibrations), 1609 (C=O); HRMS (ESI-TOF) (*m*/*z*) [M + H⁺] calculated for $[C_{22}H_{20}Cl_2LuN_6O_8]^+$ 741.0122, found 741.0122.

N²,N⁹-bis(pyrrolidine)-4,7-difluoro-N²,N⁹-diethyl-1,10-phenanthroline-2,9-dicarboxamide lutetium trinitrate **L3**•Lu(NO₃)₃. Yield 96.8% (74.6 mg). White powder. T_{decomp.} 250 °C; ¹H NMR (CD₃CN) δ 8.40 (s, 2H, Phen), 8.33 (d, *J* = 9.8 Hz, 2H, Phen), 4.16 (t, *J* = 6.9 Hz, 4H, Pyrr), 3.87 (t, *J* = 6.9 Hz, 4H, Pyrr), 2.21–2.12 (m, 4H, Pyrr), 2.07–1.99 (m, 4H, Pyrr); ¹⁹F NMR (376 MHz, Acetonitrile-*d*₃) δ –99.52 (d, *J* = 9.8 Hz), –103.28; IR (ν , cm⁻¹) 3115, 3087, 2979, 2881 (C-H stretching vibrations), 1608 (C=O); HRMS (ESI-TOF) (*m*/*z*) [M + H⁺] caclulated for [C₂₂H₂₀F₂LuN₆O₈]⁺ 709.0713, found 709.0705.

Oxo-complex $(L3)_3Lu_3O_2(NO_3)_5$ was obtained in accordance with the general procedure starting from 0.2 mmol of L3 and 0.1 mmol of lutetium nitrate. The treatment of the residue with ether yielded 112.8 mg of yellowish powder. This material was used for growing single crystals.

3.2. UV-Vis Titration Experiment

UV-VIS spectra were recorded at a temperature of 25.0 ± 0.1 °C in the wavelength region of 200-500 nm (0.5 nm interval) on a Shimadzu UV 1800 spectrophotometer controlled by LabSolutions version 1.2.35 UV-Vis software with a thermostatic attachment (Shimadzu TCC-100) using quartz cuvettes with an optical path length of 10 mm. A stock solution of the ligand was prepared (ca. 10^{-4} mol L⁻¹) by dissolving the respective ligand in CH₃CN; a working ligand solution (ca. 10^{-5} mol L⁻¹) was then prepared from the initial solution. A working titrant solution $(10^{-3} \text{ mol L}^{-1})$ was prepared by dissolving the respective lanthanide(III) nitrate hydrate Ln(NO₃)₃·xH₂O compound (Ln = La, Nd, Eu, Lu; x = 6 in the case of La, Nd, Eu and x = 5 in the case of Lu) in CH₃CN. Acetonitrile (CH₃CN; 99.95%, HPLC grade, Panreac AppliChem) was dried over molecular sieves (zeolite KA, 3 Å, balls, diameter 1.6–2.5 mm, production HKC Corp., Hong Kong) prior to use. The titration was carried out by adding 2 µL aliquots of the working metal cation solution to 2 mL of the working ligand solution in the titration cell. The titration continued until no obvious change was observed in the spectra. The stability constants of the Ln(III) complexes were calculated using the HypSpec2014 program.

3.3. NMR Titration Experiment

For the NMR titration experiments, the stock solutions of L3 and Lu(NO₃)₃ were obtained by dissolving weighed amounts of ligand L3 and Lu(NO₃)₃·5H₂O in CD₃CN, respectively. The initial aliquot solution of L3 was divided equally into five NMR tubes equally and a certain amount of Lu(NO₃)₃ solution was added to four of them to obtain a series of samples with molar ligand:metal ratios of 1:0, 1:0.5, 1:1, 1:1.5, and 1:2. The total concentrations of metals and ligands were 0.0585 mol L⁻¹ and 0.0244 mol L⁻¹, respectively. After the addition, ¹H and ¹⁹F NMR spectra were recorded on an Agilent 400-MR instrument with a frequency of 400.1 MHz (¹H) and 376 MHz (¹⁹F). C₆F₆ in CD₃CN was used as a reference for the ¹⁹F-NMR spectra.

3.4. X-ray Crystallography

X-ray diffraction data for the ligand L3 and for the complexes L•Lu(NO₃)₃ were collected at 295 K using a STOE STADIVARI diffractometer with a Pilatus 100K detector using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) for L2•Lu(NO₃)₃ and the Cu K α radiation (λ = 1.54186 Å) from the fine-focus Cu GeniX 3D radiation source for the others. The data for $(L3)_3Lu_3O_2(NO_3)_5$ were collected at 100 K with a Bruker Quest D8 CMOS diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ A). The structures of the ligand L3 and of the complexes $L \circ Lu(NO_3)_3$ were solved and refined with the program SHELX [33], while the ShelXT [34] structure solution program using intrinsic phasing and refined with the XL [33] refinement package using least-squares minimization against F^2 was used for (L3)₃Lu₃O₂(NO₃)₅. The non-hydrogen atoms were refined by using the anisotropic full matrix least-squares procedure. Hydrogen atoms of coordinated water molecules were located from different Fourier syntheses while the positions of others were calculated, and all of them were refined in isotropic approximation within the riding model. Crystal data and structure refinement parameters for the ligand L3 and the complexes $L \bullet Lu(NO_3)_3$ and $(L3)_3 Lu_3O_2(NO_3)_5$ are given in Table S1 (see the Supplementary Materials).

CCDC 2221666 (for L3), 2221667 (for L1•Lu(NO₃)₃), 2191901 (for L2•Lu(NO₃)₃), 2221670 (for L3•Lu(NO₃)₃), and 2232270 (for (L3)₃Lu₃O₂(NO₃)₅) contain the supplementary crystallographic data for this paper.

4. Conclusions

In summary, we revealed important structural features of complexes of lutetium trinitrate with pyrrolidine-derived phenanthroline diamides L1–L3. Depending on the presence and type of halide atoms in positions four and seven of the phenanthroline core, the coordination number of lutetium can be equal to either nine (complexes of L1 and

L2), which is typical for lutetium complex compounds, or 10 (fluorine-containing ligand **L3**), which is very rare. The measurement of bond lengths in the structures of complexes studied by the XRD analysis shows that in the case of **L3**, the bonds of the lutetium atom with the coordination centers are longer than similar bonds in the complexes of the other two ligands. Also, in the case of the lutetium trinitrate complex with **L3**, the smallest out-of-plane distance of the metal from the phenanthroline plane is observed. Apparently, this makes the coordination of three bidentate nitrate groups possible. It is also noteworthy that in the case of a complex with the **L2** ligand, only one of three nitrate groups is located in the internal coordination sphere, while the other two nitrate groups are displaced by three compact water molecules.

Using UV-Vis and NMR titration techniques, we elucidated the coordination chemistry of ligands in acetonitrile solutions and obtained the values of stability constants. The log β 2 values for lanthanide complexes of L3 turned out to be much higher than those of the corresponding complexes of ligands L1 and L2. Counting on greater stability of the L3:lanthanide = 2:1 complexes, we tried to obtain complexes of such stoichiometry with lutetium trinitrate in an individual form. As a result, the oxo-complex was isolated using XRD analysis. It is very likely that in this case, one ligand molecule works as a base by binding the nitrate anion.

In addition, we performed preliminary liquid–liquid extraction tests. The results obtained indicate a lower extraction efficiency of the ligand L3 compared to its chlorinecontaining analog L2, but the selectivity in the separation of the Am(III)/Eu(III) remains high. This is probably the result of the lower lipophilicity of the L3 ligand, which affects the formation of water-soluble complexes with lanthanide nitrates.

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