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Pentadentate Ligands for the 1:1 Coordination of Lanthanide(III) Salts

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Dedicated to Professor Dr. H.-J. Gais on the occasion of his 65th birthday

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Three hydrazone type ligands, namely **2**-H, **3**, and **4**, which were designed to form 1:1 complexes with lanthanoid(III) ions, are presented. Although the tetradentate ligand $\mathbf{2}^-$ leads to an interesting complex [(**2**)(**2**-H)YCl_2] with yttrium(III), a more general principle for the coordination of the metal ions by hydrazone-type ligands can be found with ligand **3**, where 1:1 complexes are obtained with an effective coordination of the metal salts by the ligand. The stable dimer [{(**3**)Nd(CF_3SO_3)}$_2$(μ-CF_3SO_3)$_3$]CF_3SO_3 was characterized by X-ray structure determination. Depending on the size of the metal ion, additional co-ligands can also be bound to the metal centers. This is observed in the molecular structures of [(**3**)Pr(NO_3)$_2$(MeOH)$_2$](NO_3), [(**3**)$NdCl_2$(MeOH)(EtOH)]Cl, [(**3**)$ErCl_2$(MeOH)]Cl, and [(**3**)$LuCl_2$]Cl. The solid-state molecular structures of **4** and **4**·HCl show the helicating ability of this ligand upon metal coordination. The corresponding lanthanide complexes of **4** are characterized by standard techniques such as NMR and CD spectroscopy and mass spectrometry.

Introduction

Lanthanide chemistry has become more and more important in recent years due to the special properties of these metal ions. Their use in lighting devices, their magnetic properties, their unique redox chemistry, and their application in catalysis and diagnostics make them an attractive target of current research,[1] with the main focus being on solid-phase materials and organometallic chemistry.[2] Coordination chemistry is mainly based on the development of new imaging agents and sensors.[3] However, this field offers an easy entry to prepare stable, well-defined molecular species and to introduce special properties with the ligand.

Coordination compounds of the lanthanides are frequently used as catalysts, as impressively demonstrated by the work of Shibasaki,[4] Kobayashi,[5] and others,[6] although often the catalytically active complexes are not isolated but are only generated in solution.

Herein we present a general study of the preparation of a series of lanthanide(III) complexes with pentadentate ligands in order to obtain Lewis acidic compounds. The introduction of chirality at the ligands offers the opportunity to prepare enantiomerically pure complexes with ligands wrapping around the metal in a helical fashion.[7]

Results and Discussion

Studies with 8-Hydroxyquinoline Derivatives

We recently described the formation and molecular structures of a series of lanthanide(III) complexes with the semicarbazone ligand **1**-H.[8,9] In order to get enantiomerically pure coordination compounds the semicarbazone moiety is now substituted by the SAMP hydrazone to give ligand **2**-H, which can be prepared in a simple condensation reaction of SAMP[10] with 8-hydroxyquinoline 2-carbaldehyde in 94% yield (Scheme 1).[11]

Compound **2**-H is a tetradentate ligand like **1**-H with the difference that the strongly donating carbonyl unit is substituted by a more weakly donating ether moiety and that the chelating N,O unit in the side chain is elongated by one atom. In addition, the chiral information at the hydrazone leads to a helical twisting in **2**-H, while **1**-H usually adopts a planar conformation.

Treatment of **2**-H with a series of lanthanide(III) salts under different conditions did not lead to well-defined complexes, and only the reaction of **2**-H with YCl_3 in methanol in the presence of potassium carbonate gave a red powder, which exhibits in its ^1H NMR spectrum two different sets

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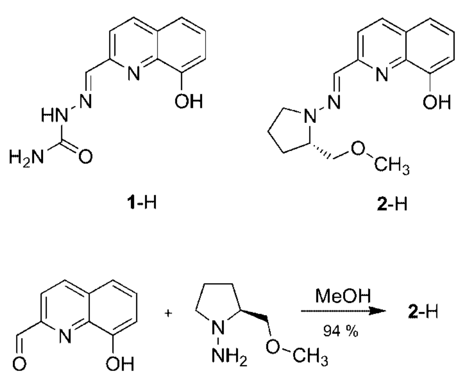


Scheme 1. Semicarbazone ligands **1**-H and **2**-H.

of signals for two unsymmetrically bound $\mathbf{2}^-$ ligands. The ESI mass spectrum reveals the peak of $[(\mathbf{2})_2Y]^+$ at *m/z* 657.

X-ray quality crystals were obtained from a $CH_3CN/CHCl_3$ solution of the complex. The X-ray diffraction analysis shows that the two ligands are coordinated in different ways, with one binding in a tetradentate and the other a monodentate fashion. The latter binds to the metal through the phenolate oxygen atom and is additionally fixed by hydrogen bonding of the protonated quinoline to the phenolate of the tetracoordinate ligand. This bridging hydrogen atom can be observed by ^1H NMR spectroscopy at $\delta = 15.80$ ppm in $CDCl_3$ solution. In addition, two chloride atoms bind to yttrium(III) in mutually *trans* position. The molecular structure of $[(\mathbf{2})(\mathbf{2}\text{-H})YCl_2]$ is shown in Figure 1.

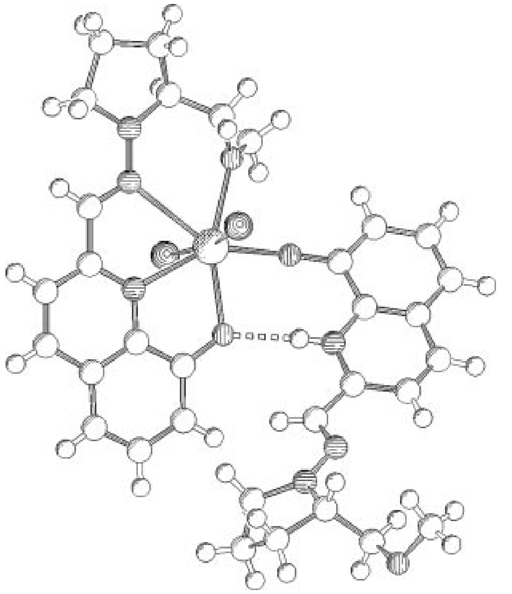


Figure 1. Molecular structure of $[(\mathbf{2})(\mathbf{2}\text{-H})YCl_2]$ as found in the crystal.

Based on those preliminary results, which show that ligand **2**-H is not ideal for the effective coordination of lanthanide(III) ions, the new pentadentate ligands **3** and **4** were developed.[12] Compound **4** (Figure 2) is a helicating ligand[13] with the potential to wrap around a single lanthanide(III) center to form a single-stranded helix.[14]

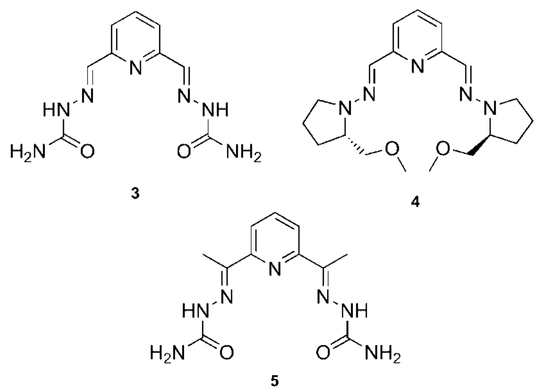


Figure 2. Pentadentate ligands **3**–**5**.

While we were investigating the coordination chemistry of ligands **3** and **4**, a publication by Palenik on the lanthanide(III) coordination chemistry of the related ligand **5** appeared concerning various lanthanide(III) coordination compounds $[(\mathbf{5})LnX_n]$. As expected, **5** provides a planar pentacoordinate platform.[15a]

Preparation of Ligands 3 and 4 and the Solid-State Structures of 4 and 4·HCl

Ligands **3** and **4** were synthesized by a simple imine-type condensation of the easy to prepare 2,6-pyridinedicarbaldehyde with either semicarbazide hydrochloride or SAMP [(*S*)-1-amino-2-(methoxymethyl)pyrrolidine] in methanol. Ligand **3** was obtained in 72% yield as its bis-HCl adduct, while **4** was isolated as the unprotonated species in 78% yield. Both compounds were characterized by standard procedures.

We were able to obtain X-ray quality crystals of the chiral compound **4** as well as of its mono-HCl adduct **4**·HCl (Figure 3). In both compounds the external imine bonds show an *s-trans* conformation at the pyridine nitrogen. The methoxymethyl substituents at the pyrrolidine units are located at the "back side" of the molecules. One of the substituents is placed above the plane of the molecule while the other is pointing downwards, which means that the symmetry of the molecule is close to C_2.

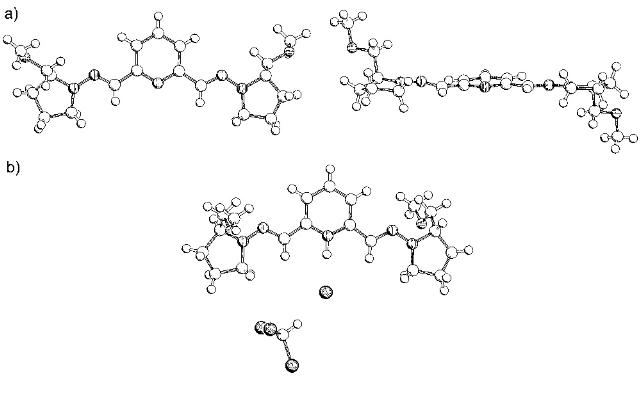


Figure 3. Molecular structures of compounds **4**; a) top and side view, b) **4**·HCl.

The conformations of **4** in its free as well as in its protonated form are very similar. However, the additional proton of **4**·HCl is located at the pyridine nitrogen atom with the chloride atom in close contact with this positively charged unit. In addition, one molecule of chloroform co-crystallizes with its hydrogen atom pointing towards the halide anion.

In order to form coordination compounds ligand **4** has to undergo a conformational change of the $C_{pyridine}$–C_{imine} bonds involving a 180° rotation. This provides a pocket that is ideal for metal binding in a tri- or pentadentate fashion.

Coordination Chemistry of Ligand 3 with Lanthanide(III) Ions

Complexes of ligand **3** with lanthanides were prepared by addition of lanthanide(III) salts to a suspension of **3** in either methanol or acetonitrile. Characterization of the complexes was done by mass spectrometry and, where possible, by elemental analysis. Coordination compounds of the diamagnetic meta ions yttrium(III), lanthanum(III), and lutetium(III) were also characterized by NMR spectroscopy (Table 1).

Table 1 lists some results of mass spectrometric investigations of the coordination compounds of ligand **3** with lanthanides. In all cases 1:1 complexes between the ligands and the metals are observed, although with neodymium(III) triflate a dimeric 2:2 species is found in addition to the monomer. In some cases displacement of the anion by hydroxide or methoxide from the solvent matrix occurs.

Representative portions of the ^{1}H NMR spectra of complexes of **3** with diamagnetic lanthanum(III) and lutetium(III) ions in [D$_4$]MeOH are depicted in Figure 4. Unfortunately, the free ligand **3** is not soluble in this solvent therefore the spectrum of the ligand was recorded in [D$_6$]DMSO.

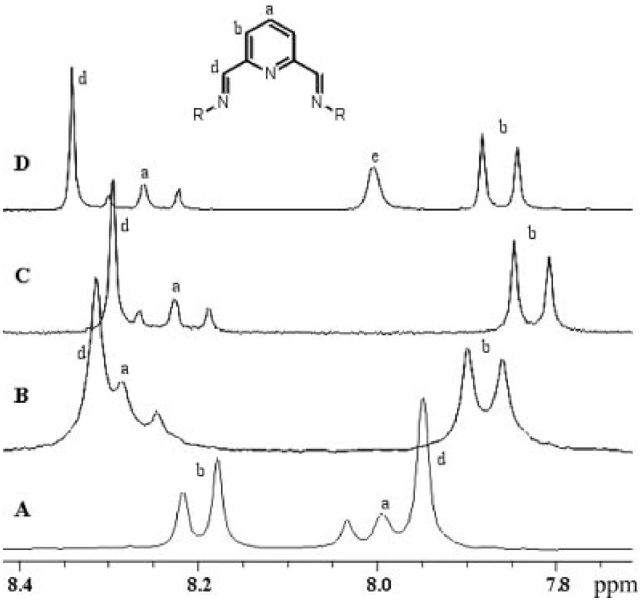


Figure 4. Portions of the ^{1}H NMR spectra of **3** in [D$_6$]DMSO (A) and [(**3**)La][CF$_3$SO$_3$]$_3$ (B), [(**3**)La][Cl]$_3$ (C), and [(**3**)Lu][NO$_3$]$_3$ (D) in [D$_4$]MeOH. The assignment of ligand signals is presented in the inset (e = NH$_{hydrazone}$).

Due to the different solvents the spectra of the ligand and the complexes cannot be compared directly. However, a remarkable shift difference can be detected for the hydrazone CH=N proton. Thus, in the ligand (in [D$_6$]DMSO) its resonance is observed at δ = 7.95 ppm while in the complexes (in CD$_3$OD) shifts of δ = 8.32 [La(CF$_3$SO$_3$)], 8.30 (LaCl), and 8.38 ppm [Lu(NO$_3$)] are found. In addition, significant low-field shifts are observed for the proton in the 4-position and high-field shifts for the protons in the 3- and 5-positions of the pyridine ring of **3**. The shift differences between coordinated and free ligands are due to the conformational changes that occur in **3** upon coordination to the metal, and the differences in the NMR spectra of complexes with different anions indicate that at least some of the anions are still coordinated to the metals in solution.

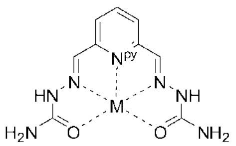
We were able to obtain X-ray quality crystals of several coordination compounds of ligand **3** with different lanthanide salts and the complexes of the larger lanthanides Pr^{III} and Nd^{III} as well as of the smaller lanthanides Er^{III} and Lu^{III} were structurally characterized (Table 2).

Table 1. Representative results of mass spectrometric investigations of the lanthanide(III) complexes of ligand **3** (anion: triflate, chloride, nitrate).

Ln	[(**3**)Ln(F$_3$CSO$_3$)$_3$]	[(**3**)LnCl$_3$]	[(**3**)Ln(NO$_3$)$_3$]
Y	–[d]	407 [(**3**)YCl$_2$]$^+$ 400 [(**3**)Y(OCH$_3$)$_2$]$^+$ [c]	462 [(**3**)Y(NO$_3$)$_2$]$^+$ [c]
La	686 [(**3**)La(F$_3$CSO$_3$)$_2$]$^+$ [a]	458 [(**3**)LaCl$_2$]$^+$ [c]	209.5 [(**3**)La(CH$_3$O)]$^{2+}$ [c]
Pr	688 [(**3**)Pr(F$_3$CSO$_3$)$_2$]$^+$ [b]	–[d]	451.5 [(**3**)Pr(NO$_3$) – H]$^{2+}$ [c]
Nd	1531 [(**3**)$_2$Nd$_2$(F$_3$CSO$_3$)$_5$]$^+$ 691 [(**3**)Nd(F$_3$CSO$_3$)$_2$]$^+$ [c]	269.5 [(**3**)NdCl(CH$_3$OH)$_3$(H$_2$O)]$^{2+}$ 254 [(**3**)NdCl(CH$_3$OH)$_2$(H$_2$O)]$^{2+}$ [c]	–[d]
Sm	699 [(**3**)Sm(F$_3$CSO$_3$)$_2$]$^+$ [b]	–[d]	209.5 [(**3**)Sm(OH)]$^{2+}$ [b]
Er	715 [(**3**)Er(F$_3$CSO$_3$)$_2$]$^+$ [c]	451 [(**3**)ErCl – H]$^+$ [b]	–[d]
Lu	722 [(**3**)Lu(F$_3$CSO$_3$)$_2$]$^+$ [a]	458 [(**3**)LuCl – H]$^+$ [b]	229.5 [(**3**)Lu(H$_2$O)(OH)]$^{2+}$ [c]

[a] MALDI-TOF. [b] LDI-TOF. [c] ESI. [d] Not prepared.

Table 2. Selected bond lengths [Å] and angles [°] of lanthanide(III) complexes of ligand **3** with different co-ligands (anions: triflate, chloride; methanol). OTf = triflate.



	[(**3**)Pr$(NO_3)_2$ $(MeOH)_2$]$^+$	[{(**3**)Nd(CF_3SO_3)}$_2$ (μ-$CF_3SO_3)_3$]$^+$			[(**3**)NdCl_2 (MeOH)(EtOH)]$^+$	[(**3**)ErCl_2 (MeOH)]$^+$
N^{py}–M	2.740	2.619	2.633	2.785	2.500	2.426
N–M	2.712/2.684	2.623/2.621	2.628/2.624	2.704/2.708	2.481/2.480	2.414
O–M	2.531/2.549	2.403/2.407	2.412/2.387	2.474/2.413	2.336/2.283	2.264
Cl–M				2.774/2.779	2.657/2.628	2.560
O^{OTf}–M	2.625/2.637				2.430	
O^{OTf}–M (bridging)		2.549/2.502 2.474	2.462/2.459/2.484			
O^{OTf}–M (terminal)		2.411	2.437			
N^{py}–M–N	58.54/58.96	60.58/60.30	59.65/60.25	57.68/57.98	63.32/63.41	64.54
N–M–O	59.52/59.98	61.80/61.35	61.58/61.67	59.54/60.10	63.98/6439	66.58
Cl–M–Cl				143.33	150.91	177.14
N^{py}–M–O$^{ROR'}$	141.31/142.37			141.24 (MeOH) 145.73 (Et_2O)	141.18	
O^{MeOH}–M–O$^{ROR'}$	75.64			72.88		

[(3)Pr$(NO_3)_2(CH_3OH)_2$]$NO_3\cdot CH_3OH$

X-ray quality crystals of the complex of **3** with praseodymium(III) nitrate were obtained from methanol solution. Two different views of the molecular structure of the cation [(**3**)Pr$(NO_3)_2(CH_3OH)_2$]$^+$ are presented in Figure 5 and selected bond lengths and angles are listed in Table 2. Compound **3** acts as a pentadentate ligand that coordinates to the praseodymium ion through the pyridine and two "imine" nitrogen atoms of the semicarbazone as well as through the two carbonyl oxygen atoms. The coordinated ligand is not planar but possesses a slight helical twisting. In addition, two bidentate nitrate anions binding to the metal above and below the plane of the "(**3**)Pr" platform. The third nitrate anion does not coordinate to the metal center. This leaves additional sites in the front of the complex, where two molecules of methanol are coordinated to the metal. The coordination number for Pr^{III} is therefore eleven. The coordination of two nitrate anions to the metal center presents a remarkable difference to the structures obtained by Palenik et al. for their complexes of ligand **5**,[15b] where only one nitrate as well as numerous water molecules bind to the metals.

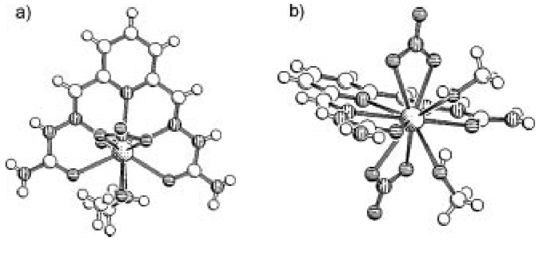


Figure 5. Top (a) and side view (b) of the cation [(**3**)Pr$(NO_3)_2$-$(CH_3OH)_2$]$^+$ as observed in the solid state.

[{(3)Nd(CF_3SO_3)}$_2$(μ-$CF_3SO_3)_3$]$CF_3SO_3\cdot 2CH_3CN\cdot$ $(CH_3CH_2)_2O$

Crystals of neodymium(III) triflate were obtained from acetonitrile/diethyl ether solution. The molecular structure of the cation [{(**3**)Nd(CF_3SO_3)}$_2$(μ-$CF_3SO_3)_3$]$^+$ in the crystal is depicted in Figure 6 and representative bond length and angles are listed in Table 2.

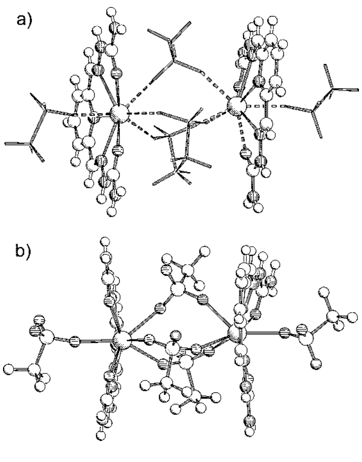


Figure 6. Two different views of the cation [{(**3**)Nd(CF_3SO_3)}$_2$(μ-$CF_3SO_3)_3$]$^+$ as observed in the solid state. The triflate anions in a) are indicated by lines.

The cation $[\{(\mathbf{3})Nd(CF_3SO_3)\}_2(\mu\text{-}CF_3SO_3)_3]^+$ adopts a dimeric structure with two "(**3**)Nd(OTf)" moieties connected by three bridging triflate anions. The bridging triflates each coordinate through two different oxygen atoms to the different metals, while the terminal triflates act only as monodentate ligands. The two ligands **3** are orientated in an *anti* fashion within a planar arrangement. However, the steric bulk of the three bridging anions forces the metal ions out of the plane of the pentacoordinate ligands. The remaining triflate anion does not interact with the metal center but is incorporated within the crystal lattice. This dimer possesses an unusual stability as positive-ion ESI mass spectrometry showed its presence even in methanol solution. The corresponding peak of the dimer $[(\mathbf{3})_2Nd_2(F_3CSO_3)_5]^+$ is detected at *m*/*z* 1531 along with the monomer $[(\mathbf{3})Nd(F_3CSO_3)_2]^+$ at *m*/*z* 691.

[(3)NdCl$_2$(CH$_3$OH){(CH$_3$CH$_2$)$_2$O}]Cl

The complex of neodymium(III) chloride with **3** was crystallized from methanol/ethanol solution. Figure 7 presents the solid-state structure of $[(\mathbf{3})NdCl_2(CH_3OH)\{(CH_3CH_2)_2O\}]^+$.

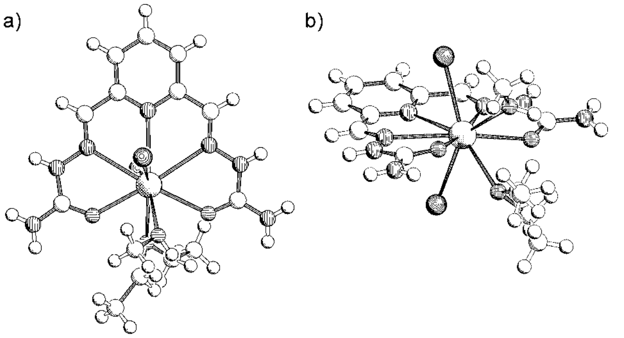


Figure 7. Two different views of the cation $[(\mathbf{3})NdCl_2(CH_3OH)\{(CH_3CH_2)_2O\}]^+$ as observed in the solid state.

Ligand **3** coordinates to the metal center in an almost planar fashion with the chloride atoms sitting above and below the plane of the ligand. In addition, one methanol molecule and one molecule of diethyl ether coordinate at the front of the complex. Due to the high coordination number and the steric bulk of the co-ligands, the Nd–N bonds are longer than those in the dimer $[\{(\mathbf{3})Nd(CF_3SO_3)\}_2(\mu\text{-}CF_3SO_3)_3]^+$ (see Table 2).

[(3)ErCl$_2$(CH$_3$OH)]Cl

Crystals of the erbium complex of ligand **3** were obtained from methanol. Figure 8 (a) shows a top view of the structure of the cation $[(\mathbf{3})ErCl_2(CH_3OH)]^+$ where the almost planar coordination of the ligand is clear. However, the side view (Figure 8 b) reveals a slight helical twisting. This is caused by an asymmetric coordination of further ligands; one chloride anion from the top and chloride and methanol from the bottom. The steric bulk of the methanol forces the ligand to deviate from planarity and additionally leads to a nonplanar Cl–Er–Cl arrangement with an angle of 150.92°. In the crystal, the third chloride ion is found close to the NH units of the semicarbazones.

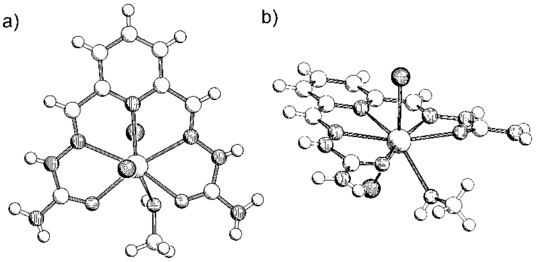


Figure 8. Two different views of the cation $[(\mathbf{3})ErCl_2(CH_3OH)]^+$ as observed in the solid state.

[(3)LuCl$_2$]Cl

X-ray quality crystals of $[(\mathbf{3})LuCl_2]Cl$ were obtained by diffusion of diethyl ether into a solution of the complex in acetonitrile/methanol. The solid-state structure of the cation $[(\mathbf{3})LuCl_2]^+$ is shown in Figure 9.

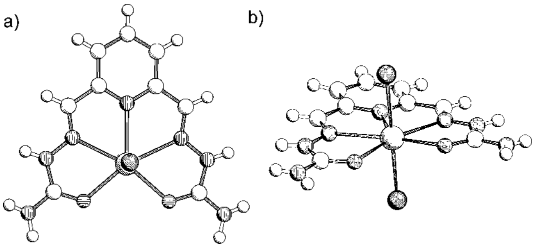


Figure 9. Two different views of the cation $[(\mathbf{3})LuCl_2]^+$ as observed in the solid state.

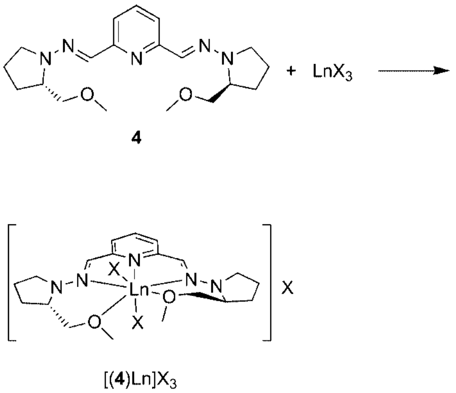
In principle it is related to the corresponding cation $[(\mathbf{3})ErCl_2(CH_3OH)]^+$ described above. Due to the smaller size of lutetium(III) than erbium(III), however, a lower coordination number of seven is adopted, which means that no methanol is bound to the metal in the lutetium complex. This results in some structural differences between $[(\mathbf{3})LuCl_2]^+$ and $[(\mathbf{3})ErCl_2(CH_3OH)]^+$. Thus, the chloride atoms are now bound in a more symmetric fashion leading to a nearly planar Cl–Lu–Cl arrangement of 177.14°. Consequently, the ligand adopts a close to planar geometry with no significant helical distortion.

The results of the above X-ray structural investigations show that ligand **3** acts as a pentadentate ligand for the complexation of lanthanide(III) ions. Due to the different sizes of the different metal ions, varying numbers of coligands are bound to the metal centers. In order to adjust to the different metals, the ligand has to adopt a more open (for larger ions) or a more closed (for smaller ions) tweezer-type arrangement. This is demonstrated by a decrease of the distance between the two terminal NH_2 groups of **3** depending on the size of the metals. This N–N distance is 8.998 Å for Pr, 8.783 Å for the Nd monomer, 8.134/8.230 Å for the Nd dimer, 7.983 Å for Er, and 7.842 Å for Lu.

Following the series of structures with chloride anions, it is clear that the $[(\mathbf{3})MCl_2]^+$ cation is only observed for the small lutetium(III) ion, whereas for the larger erbium(III) ion the metal center is not coordinatively saturated and an additional solvent molecule is bound in the front of the complex. The still larger neodymium(III) ion even provides space for two such solvent molecules, which means that the complexes of the larger cations would be the best candidates to test their ability to act as Lewis acid catalysts.

Coordination Chemistry of the Chiral Ligand 4 with Lanthanide(III) Ions

Coordination compounds of lanthanides with the chiral ligand **4** were synthesized in analogy to the preparation of complexes with the semicarbazone ligand **3**. Thus, the corresponding lanthanide(III) salt in methanol or acetonitrile was added to a solution of the ligand **4** in methanol or acetonitrile. The mixture was stirred for 16–72 h and the solvent was then removed in vacuo to yield orange-yellow to red compounds (Scheme 2).



Scheme 2. Formation of lanthanide(III) complexes of ligand **4**. The coordination at the metal is proposed based on the described results obtained with ligand **3** and the NMR spectroscopic and mass spectrometric observations. Ln = La, Pr, Nd, Sm, Er, Yb, Lu, and Y; X = Cl, NO_3, and triflate.

We could not obtain X-ray quality crystals of the complexes with ligand **4**, although we were able to characterize them by NMR spectroscopy, mass spectrometry, and, in several cases, by elemental analysis. The ^{1}H NMR spectrum of ligand **4** (A) is compared with the corresponding spectra of representative complexes in Figure 10. The spectra of the diamagnetic lutetium (B) and the paramagnetic ytterbium complex (C) are shown, the latter of which reveals a nicely resolved NMR spectrum with some line broadening due to the presence of the paramagnetic metal ion.

Similarly to the coordination compounds with ligand **3**, complexes of **4** exhibit a low-field shift for the proton in the 4-position of the pyridine and a high-field shift for those in the 3- and 5-positions relative to the signals of free ligand (in [D$_3$]acetonitrile). However, in contrast to complexes of **3**, the signal for the CH=N "imine" proton is observed at higher field. This is probably due to the different nature of the two hydrazone-type substituents of **3** and **4**, which leads to different electronic influences on the CH=N proton upon metal coordination. In addition, ligand **4** adopts a helical conformation upon complexation while **3** is more or less planar.

A strong influence of the anions on the NMR spectra is found for these complexes, as shown in Figure 11 for the ^{1}H NMR spectrum of the lutetium(III) complexes of **4** in [D$_3$]acetonitrile. The "imine" proton only shifts to higher field if anions are present that coordinate in a bidentate fashion [triflate (A) or nitrate (C)]. In the presence of chloride a shift of this ligand signal to lower field occurs upon complexation to lutetium (B). The differences in the chemical shifts of the imine, 3- and 5-pyridine protons, and of the proton in the 4-position show that the anions are still coordinated to the lutetium in solution.

As representative examples of the mass spectrometric investigations, the molar peaks, including the isotopic patterns, of the cations $[(\mathbf{4})ErX_2]^+$ (X = triflate, chloride, nitrate) are presented in Figure 12. The depicted spectra were obtained by using the positive-ion LDI-TOF technique. The observed patterns correspond to the calculated ones. Similar spectra are observed for most of the prepared coor-

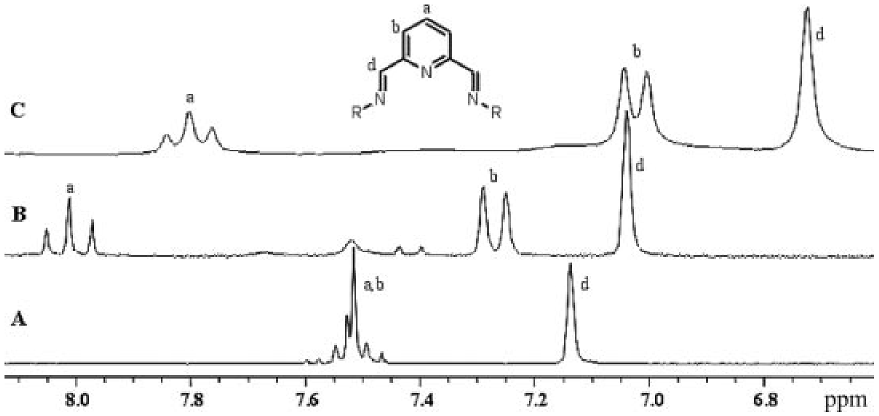


Figure 10. Portions of the ^{1}H NMR spectra of **4** (A), $[(\mathbf{4})Lu][F_3CSO_3]_3$ (B), and $[(\mathbf{4})Yb][F_3CSO_3]_3$ (C) in [D$_3$]acetonitrile. The assignment of the protons to the pyridine and the imine moiety is indicated.

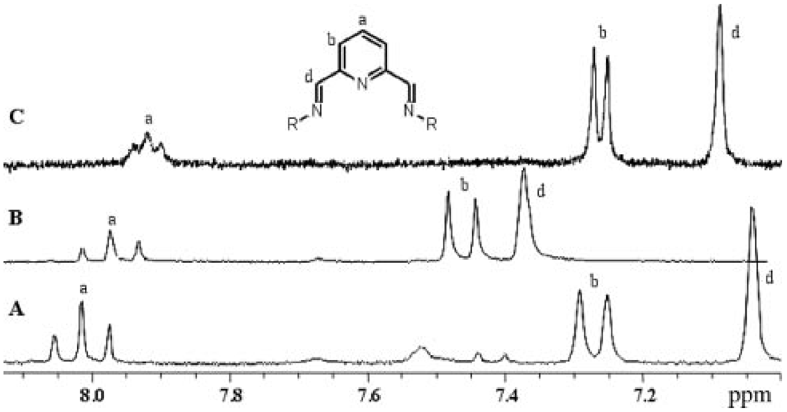


Figure 11. Portions of the ^{1}H NMR spectra of [(**4**)Lu][F_3CSO_3]$_3$ (A), [(**4**)Lu][Cl]$_3$ (B), and [(**4**)Lu][NO_3]$_3$ (C) in [D$_3$]acetonitrile. The assignment of the protons to the pyridine and imine moieties is indicated.

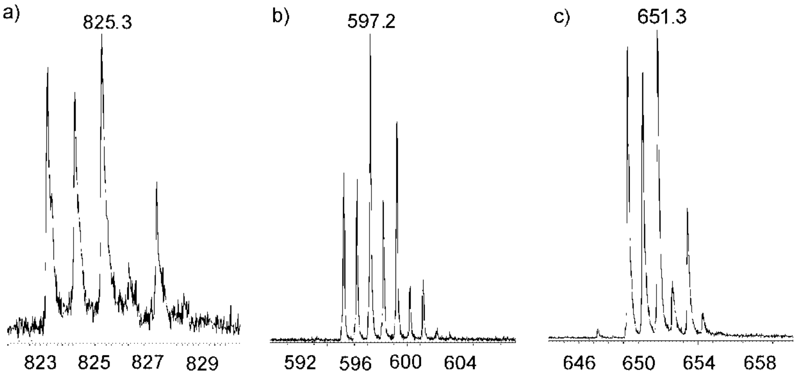


Figure 12. Part of the positive-ion LDI-TOF mass spectra of the cationic complexes [(**4**)Er(F_3CSO_3)$_2$]$^+$ (a), [(**4**)Er(Cl)$_2$]$^+$ (b), and [(**4**)Er(NO_3)$_2$]$^+$ (c). The observed isotopic patterns correspond to the calculated ones.

dination compounds (see Table 3), which shows that stable 1:1 complexes are formed between ligand **4** and lanthanide(III) ions.

Table 3. Representative results of mass spectrometric investigations of the lanthanide(III) complexes of ligand **4** (anions: triflate, chloride, nitrate). Measurements were performed with either the positive-ion ESI or LDI-TOF technique. n.d. = not determined.

Ln	[(**4**)Ln(F_3CSO_3)$_3$]	[(**4**)LnCl$_3$]	[(**4**)Ln(NO_3)$_3$]
Y	–[a]	n.d.	572 [(**4**)Y(NO_3)$_2$]$^+$
La	796 [(**4**)La(F_3CSO_3)$_2$]$^+$	568 [(**4**)LaCl$_2$]$^+$	–[a]
Pr	798 [(**4**)Pr(F_3CSO_3)$_2$]$^+$	–[a]	–[a]
Nd	801 [(**4**)Nd(F_3CSO_3)$_2$]$^+$	n.d.	–[a]
Sm	809 [(**4**)Sm(F_3CSO_3)$_2$]$^+$	583 [(**4**)SmCl$_2$]$^+$	635 [(**4**)Sm(NO_3)$_2$]$^+$
Er	825 [(**4**)Er(F_3CSO_3)$_2$]$^+$	597 [(**4**)ErCl$_2$]$^+$	651 [(**4**)Er(NO_3)$_2$]$^+$
Yb	831 [(**4**)Yb(F_3CSO_3)$_2$]$^+$	–[a]	–[a]
Lu	832 [(**4**)Lu(F_3CSO_3)$_2$]$^+$	604 [(4)LuCl$_2$]$^+$	658 [(**4**)Lu(NO_3)$_2$]$^+$

[a] Not prepared.

We also performed CD spectroscopic studies with ligand **4** and selected complexes of this ligand with lanthanides. The spectra of the complexes in dichloromethane reveal essentially the same features and therefore only the spectrum of [(**4**)Er(Cl)$_3$] is described as a representative example. Very similar UV spectra are observed for ligand **4** and [(**4**)Er-

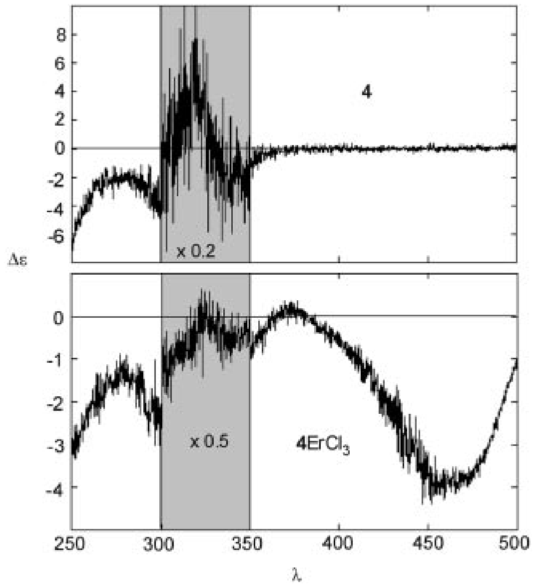


Figure 13. CD spectra of **4** (top) and [(**4**)Er(Cl)$_3$] (bottom) in dichloromethane. Note that measurement of the spectrum between 300 and 350 nm (grey) was problematic due to the high optical density of the sample in this region. The measurements in this region therefore had to be performed at lower concentrations.

$(Cl)_3]$, both of which show an intense transition at 320 nm. CD spectra proved difficult to record in the region of this band due to the high optical density of the sample (Figure 13).

The most intriguing difference between the CD spectra of **4** and $[(\mathbf{4})ErCl_3]$ is the presence of a strong band with a negative Cotton effect at 400–500 nm. This becomes dominant in the CD spectrum due to the chirality that is induced around the metal center.

Conclusions

We have presented a structural work on the coordination chemistry of the pentadentate bis-semicarbazone pyridine ligand **3**. The ligand provides a planar coordination platform and effectively binds lanthanide(III) salts (chlorides, nitrates, or triflates). Small lanthanide(III) ions preferably form cationic complexes $[(\mathbf{3})LnX_2]^+$. One or more additional co-ligands, which are often are not the remaining third counteranions but solvent molecules, bind to the metal center in the case of the bigger ions. This latter finding gives some hint as to how complexes related to those of ligand **4** should be designed to obtain effective Lewis acid catalysts: (i) a pentadentate ligand must exhibit poorer donor ability than **3** in order to enhance Lewis acidity, (ii) the "side arms" of the ligand have to be more labile coordinating units, and (iii) chirality should be introduced.

Following those three requirements we prepared the helicating ligand **4** and showed that it can form 1:1 complexes with lanthanide(III) salts. Further studies will be directed towards the use of complexes of **4** with lanthanides as Lewis acid catalysts.

Experimental Section

General: NMR spectra were recorded with a Bruker AC 200, AMX 400, or a Varian Inova 400 or Mercury 300 spectrometer. FT-IR spectra were recorded by the diffuse reflection technique (KBr) with a Bruker Vector 22 or Perkin–Elmer PE-1760 FT spectrometer. Mass spectra were recorded with a Finnigan MAT MS 90, LCQ Deca XP Plus, Bruker Reflex IV, or Micromass Quattro LC-Z mass spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer or a Vario EL III CHNS. Melting points: Büchi B-540 (uncorrected). Lanthanide chlorides, triflates, and nitrates were prepared as described before.[16]

X-ray Crystallography: Data sets were collected with Nonius KappaCCD and Bruker APEX CCD diffractometers, both equipped with rotating anode generators. Programs used: data collection: COLLECT (Nonius B.V., 1998) and SMART (Bruker AXS, 2000); data reduction: Denzo-SMN[17] and SAINT (BrukerAXS, 2000); absorption correction: SORTAV,[18] Denzo,[19] and SADABS (Bruker AXS, 2000); structure solution: SHELXS-97;[20] structure refinement: SHELXL-97 (G. M. Sheldrick, University of Göttingen, 1997); graphics: SCHAKAL (E. Keller, University of Freiburg, 1997).

CCDC-631745 to -631752 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2-H: A mixture of 8-hydroxyquinoline-2-carbaldehyde (1 equiv., 0.052 g, 0.3 mmol) and SAMP (1.1 equiv., 0.043 g, 0.33 mmol) in methanol was stirred overnight at room temp. The solvent was then distilled off and the crude residue was washed with diethyl ether and dried in vacuo. The product was obtained in 94% yield (0.08 g, 0.28 mmol) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.98 (m, 2 H), 7.33 (d, J = 7.4 Hz, 1 H), 7.30 (d, J = 7.4 Hz, 1 H), 7.23 (dd, J = 8.2, 1.5 Hz, 1 H), 7.11 (dd, J = 7.4, 1.5 Hz, 1 H), 3.83 (m, 1 H), 3.68 (dd, J = 9.4, 3.7 Hz, 1 H), 3.55 (dd, J = 9.4, 6.7 Hz, 1 H), 3.46 (m, 1 H), 3.40 (s, 3 H), 3.21 (m, 1 H), 2.00 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 154.62 (C), 151.80 (C), 137.70 (C), 135.49 (CH), 130.89 (CH), 127.27 (C), 126.40 (CH), 117.97 (CH), 117.74 (CH), 109.98 (CH), 74.33 (CH_2), 62.89 (CH), 59.34 (CH_3), 48.36 (CH_2), 26.99 (CH_2), 22.29 (CH_2) ppm. Positive-ion ESI MS: m/z 286.2 $[M + H]^+$.

$[(\mathbf{2})(\mathbf{2}\text{-H})YCl_2]$: The ligand **2**-H (2 equiv., 0.04 g, 0.14 mmol) and YCl_3 (1 equiv., 0.021 g, 0.07 mmol) were stirred overnight in MeOH (10 mL) in the presence of K_2CO_3 as a base (1.9 equiv., 0.01 g, 0.072 mmol) at room temp. The solvent was then removed and the residue dried in vacuo. Extraction with CH_2Cl_2 gave a red powder in quantitative yield (0.053 g, 0.07 mmol). ^1H NMR (300 MHz, $CDCl_3$): δ = 15.80 (br., 1 H), 8.18 (d, J = 8.4 Hz, 1 H), 8.09 (d, J = 8.4 Hz, 1 H), 7.55 (m, 1 H), 7.63 (d, J = 7.9 Hz, 1 H), 7.4–7.2 (m, 6 H), 6.92 (d, J = 8.2 Hz, 1 H), 6.69 (d, J = 7.4 Hz, 1 H), 5.23 (d, J = 9.1 Hz, 1 H), 4.94 (d, J = 6.2 Hz, 1 H), 4.06 (m, 1 H), 3.99 (s, 2 H), 3.85 (m, 2 H), 3.70 (s, 3 H), 3.56 (m, 3 H), 3.41 (s, 3 H), 2.31 (m, 1 H), 2.03 (m, 6 H), 1.71 (m, 2 H), 1.61 (m, 2 H) ppm. Positive-ion ESI MS: m/z 657.4 $[M - HCl - Cl]^+$. IR (KBr): $\tilde{\nu}$ = 3851, 3745, 3406, 2929, 2873, 2361, 2338, 1629, 1586, 1527, 1456, 1389, 1323, 1235, 1099, 848, 744, 677, 598 cm^{-1}. $C_{32}H_{37}Cl_2N_6O_4Y \cdot H_2O \cdot CH_3OH$: calcd. C 50.84, H 5.56, N 10.78; found C 51.06, H 5.45, N 11.01.

X-ray quality crystals of $[(\mathbf{2})(\mathbf{2}\text{-H})YCl_2]$ were obtained by slow evaporation of a concentrated $CH_3CN/CHCl_3$ solution. X-ray crystal structure analysis for $[(\mathbf{2})(\mathbf{2}\text{-H})YCl_2]$: formula $C_{32}H_{37}Cl_2N_6O_4Y$, M = 729.49, orange crystal $0.10 \times 0.06 \times 0.05$ mm^3, a = 15.660(1), b = 12.582(1), c = 17.051(1) Å, β = 104.64(1)°, V = 3250.6(4) $Å^3$, ρ_{calc} = 1.491 $g\,cm^{-3}$, μ = 2.005 mm^{-1}, empirical absorption correction ($0.825 \leq T \leq 0.906$), Z = 4, monoclinic, space group $P2_1$ (no. 4), λ = 0.71073 Å, T = 198 K, ω and ϕ scans, 12952 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.54 $Å^{-1}$, 7864 independent (R_{int} = 0.081) and 5566 observed reflections $[I \geq 2\sigma(I)]$, 815 refined parameters, R = 0.066, wR_2 = 0.113, Flack parameter –0.004(11), max. residual electron density 0.43 (–0.45) $e\,Å^{-3}$. The hydrogen atom at nitrogen was found from difference Fourier calculations. The others were calculated and refined as riding on their parent atoms. Due to crystal size the analysis is of limited accuracy.

2,2′-[Pyridine-2,6-diylbis(methan-1-yl-1-ylidene)]bis(hydrazinecarboxamide) (3): Semicarbazone hydrochloride (670 mg, 6.0 mmol) was dissolved in 40 mL of methanol and pyridine-2,5-dicarbaldehyde (400 mg, 2.9 mmol) in 15 mL of methanol was added. The yellow precipitate that formed over 70 h was collected, washed with cold methanol, and dried in vacuo to give a yellow solid. Yield: 666 mg (2.1 mmol, 72%). M.p. 214.8 °C (dec.). ^1H NMR (400 MHz, $[D_6]DMSO$): δ = 10.88 (s, 2 H), 8.23 (d, J = 7.9 Hz, 2 H, b), 8.04 (t, J = 7.9 Hz, 1 H), 7.99 (s, 2 H), 6.76 (br. s, 2 H) ppm. ^{13}C NMR (50 MHz, $[D_6]DMSO$): δ = 156.2, 151.2, 139.3, 136.1, 120.1 ppm. IR (KBr): $\tilde{\nu}$ = 3779, 3705, 3632, 3411, 2974, 2381, 2275, 1815, 1717, 1587, 1513, 1430, 1343, 1294, 1229, 1178, 1074, 933, 817, 725, 634, 559, 486 cm^{-1}. MS (pos. MALDI-TOF, DHB): m/z 272.0 (26) $[M + Na]^+$, 250.0 (100) $[M + H]^+$. $C_9H_{11}N_7O_2 \cdot 2HCl \cdot H_2O$: calcd. C 31.78, H 4.44, N 28.82; found C 31.70, H 4.60, N 27.96.

(2*S*,2′*S*)-*N*,*N*′-[Pyridine-2,6-diylbis(methan-1-yl-1-ylidene)]bis[2-(methoxymethyl)pyrrolidin-1-amine] (4): Pyridine-2,6-dicarbaldehyde (1.00 g, 7.4 mmol) in 10 mL of methanol was slowly added to a solution of SAMP (2.00 g, 15.4 mmol) in 4 mL of methanol and, after stirring overnight, the solvent was removed in vacuo. The crude product was recrystallized from hot pentane by cooling to 6 °C. Yield: 2.07 g (5.8 mmol, 78 %) of a colorless solid. M.p. 77.8 °C. ^{1}H NMR (400 MHz, CD_3CN): δ = 7.54 (t, *J* = 6.0 Hz, 1 H), 7.51 (d, *J* = 6.0 Hz, 2 H), 7.14 (s, 2 H), 3.69 (quint, *J* = 4.0 Hz, 2 H), 3.60 (dd, *J* = 7.6, 4.0 Hz, 2 H), 3.47 (dd, *J* = 9.6, 6.9 Hz, 2 H), 3.41 (dt, *J* = 6.9, 4.0 Hz, 2 H), 3.33 (s, 6 H), 3.13 (dt, *J* = 9.6, 7.6 Hz, 2 H), 2.08–1.77 (m, 8 H) ppm. ^{13}C NMR (100 MHz, CD_3CN): δ = 156.9, 137.1, 132.2, 116.2, 75.3, 63.9, 59.4, 49.4, 27.8, 23.0 ppm. IR (KBr): $\tilde{\nu}$ = 3851, 3745, 3678, 3621, 2361, 1836, 1649, 1547, 1459, 1107, 669 cm^{-1}. MS (EI-DIP, 70 eV): *m*/*z* (%) 359.1 (66) [M$^+$], 314.1 (45), 246 (100), 219 (59), 201 (47). $C_{19}H_{29}N_5O_2$: calcd. C 63.48, H 8.13, N 19.48; found C 63.21, H 8.00, N 19.08.

X-ray Crystal Structure Analysis for 4: $C_{19}H_{27}N_5O_2$, *M* = 357.46, colorless crystal 0.49 × 0.28 × 0.17 mm^3, *a* = 7.8706(15), *b* = 12.524(2), *c* = 20.475(4) Å, *V* = 2018.2(7) Å^3, ρ_{calc} = 1.176 g cm^{-3}, μ = 0.079 mm^{-1}, empirical absorption correction ($0.962 \leq T \leq 0.987$), *Z* = 4, orthorhombic, space group $P2_12_12_1$ (no. 19), λ = 0.71073 Å, *T* = 233 K, ω and ϕ scans, 16268 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.60 Å^{-1}, 3549 independent (R_{int} = 0.038) and 2835 observed reflections [$I \geq 2\sigma(I)$], 237 refined parameters, *R* = 0.065, wR_2 = 0.185, Flack parameter 3(3), max. residual electron density 0.38 (–0.20) e Å^{-3}; hydrogen atoms were calculated and refined as riding.

X-ray Crystal Structure Analysis for 4·HCl·CHCl$_3$: $C_{20}H_{31}Cl_4N_5O_2$, *M* = 515.30, colorless crystal 0.22 × 0.20 × 0.15 mm^3, *a* = 5.601(1), *b* = 17.230(1), *c* = 13.217(4) Å, β = 93.41(1)°, *V* = 1273.3(3) Å^3, ρ_{calc} = 1.344 g cm^{-3}, μ = 0.491 mm^{-1}, empirical absorption correction ($0.902 \leq T \leq 0.930$), *Z* = 4, monoclinic, space group $P2_1$ (no. 4), λ = 0.71073 Å, *T* = 198 K, ω and ϕ scans, 10536 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 5622 independent (R_{int} = 0.051) and 4225 observed reflections [$I \geq 2\sigma(I)$], 286 refined parameters, *R* = 0.045, wR_2 = 0.109, Flack parameter 0.02(5), max. residual electron density 0.38 (–0.20) e Å^{-3}. The hydrogen atom at nitrogen was observed in the difference Fourier calculations; the others were calculated and refined as riding.

General Procedure for the Preparation of Metal Complexes: A solution of the lanthanoid(III) salt (approx. 0.1 mmol) in methanol or acetonitrile was added to the ligand (**3** or **4**) in either methanol, acetonitrile, or nitromethane and the mixture was stirred overnight. The solvent was then removed in vacuo and the residue dried in vacuo. In the case of complexations with ligand **3** in acetonitrile, the mixture was filtered prior to work up.

[(3)YCl$_3$]: The reaction was performed in methanol. Yield: 70.7 mg (0.12 mmol, quant.), colorless solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.30 (t, *J* = 8.0 Hz, 1 H), 8.27 (s, 2 H), 7.88 (d, *J* = 8.0 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3381, 3220, 1670, 1543, 1388, 1175 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 407.9 (18) [(**3**)YCl$_2$]$^+$, 399.7 (100) [(**3**)Y(CH_3O)$_2$]$^+$. $C_9H_{11}Cl_3N_7O_2Y·7H_2O$: calcd. C 18.94, H 4.42, N 17.18; found C 18.49, H 3.82, N 16.63.

[(3)Y(NO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 75.4 mg (0.12 mmol, quant.), pale-yellow solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.31 (t, *J* = 7.9 Hz, 1 H), 8.29 (s, 2 H), 7.90 (d, *J* = 7.9 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3422, 1670, 1559, 1386, 1167 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 462.0 (10) [(**3**) Y(NO$_3$)$_2$]$^+$, 209.5 (79) [(**3**)Y(CH_3OH)(OH)]$^{2+}$, 200.5 (100) [(**3**) Y(CH_3O)]$^{2+}$, 193.5 (95) [(**3**)Y(OH)]$^{2+}$. $C_9H_{11}N_{10}O_{11}Y·CH_3OH·4H_2O$: calcd. C 19.12, H 3.69, N 22.29; found C 18.89, H 3.65, N 21.23.

[(3)La(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 59.5 mg (0.07 mmol, 59 %) colorless solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.32 (s, 2 H), 8.28 (t, *J* = 7.9 Hz, 1 H), 7.87 (d, *J* = 7.9 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3422, 1684, 1559, 1409, 1255, 1168, 1037, 643 cm^{-1}. MS (pos. MALDI-TOF, DCTB): *m*/*z* 686.0 (100) [(**3**)La(CF_3SO_3)$_2$]$^+$, 536.1 (58) [(**3**)La(CF_3SO_3) – H]$^+$.

[(3)La(Cl)$_3$]: This complex was prepared in methanol. Yield: 46.4 mg (0.09 mmol, 78 %), colorless solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.30 (s, 2 H), 8.23 (t, *J* = 7.7 Hz, 1 H), 7.83 (d, *J* = 7.7 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3448, 1670, 1559, 1406, 1168 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 457.7 (75) [(**3**)La(Cl)$_2$]$^+$, 421.9 (80) [(**3**)La(Cl) – H]$^+$, 417.8 (100) [(**3**)La(MeO) – H]$^+$.

[(3)La(NO$_3$)$_3$]: This reaction was performed in acetonitrile. Yield: 68.9 mg (0.12 mmol, quant.), colorless solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.34 (s, 2 H), 8.26 (t, *J* = 7.7 Hz, 1 H), 8.00 (br. s, 2 H), 7.86 (d, *J* = 7.7 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3394, 1676, 1551, 1396, 1166 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 218.5 (89) [(**3**)-La(CH_3OH)(OH)]$^{2+}$, 209.5 (100) [(**3**)La(CH_3O)]$^{2+}$.

[(3)Pr(CF$_3$SO$_3$)$_3$]: This complex was prepared in methanol. Yield: 66.7 mg (0.08 mmol, 66 %), colorless solid. IR (KBr): $\tilde{\nu}$ = 3432, 3318, 3226, 1684, 1625, 1559, 1255, 1169, 1029, 633 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 688 [(**3**)Pr(CF_3SO_3)$_2$]$^+$.

[(3)Pr(NO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 32.4 mg (0.05 mmol, 43 %), pale-yellow solid. IR (KBr): $\tilde{\nu}$ = 3453, 3373, 1672, 1559, 1464, 1385, 1320, 1171, 1041 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 451.5 (65) [**3**Pr(NO$_3$) – H]$^{2+}$. $C_9H_{11}N_{10}O_{11}Pr·5H_2O$: calcd. C 16.23, H 3.18, N 21.02; found C 15.86, H 2.58, N 20.40.

X-ray Crystal Structure Analysis for [(3)Pr(NO$_3$)$_3$]·MeOH: $C_{12}H_{23}N_{10}O_{14}Pr$, *M* = 672.31, yellow crystal 0.30 × 0.30 × 0.15 mm^3, *a* = 8.175(1), *b* = 11.971(1), *c* = 13.054(4) Å, α = 90.35(1)°, β = 103.78(1)°, γ = 101.02(1)°, *V* = 1216.1(2) Å^3, ρ_{calc} = 1.836 g cm^{-3}, μ = 2.089 mm^{-1}, empirical absorption correction ($0.573 \leq T \leq 0.745$), *Z* = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, *T* = 223 K, ω and ϕ scans, 13426 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 5743 independent (R_{int} = 0.041) and 5311 observed reflections [$I \geq 2\sigma(I)$], 358 refined parameters, *R* = 0.031, wR_2 = 0.084, max. residual electron density 0.38 (–0.20) e Å^{-3}. The hydrogen atoms at nitrogens were obtained from the difference Fourier calculations; the others were calculated and refined as riding.

[(3)Nd(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 88.2 mg (0.10 mmol, 88 %), colorless solid. IR (KBr): $\tilde{\nu}$ = 3448, 1654, 1559, 1406, 1256, 1169, 682, 639 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 1530.9 (8) [{(**3**)Pr}$_2$(CF_3SO_3)$_5$]$^+$, 691.0 (84) [(**3**)-Pr(CF_3SO_3)$_2$]$^+$, 539.1 (69).

X-ray Crystal Structure Analysis for [{(3)Nd(CF$_3$SO$_3$)}$_2$(μ-CF$_3$SO$_3$)$_3$]CF$_3$SO$_3$·2CH$_3$CN·Et$_2$O: $C_{32.4}H_{37}N_{17}Nd_2O_{22.6}PS_6$, *M* = 1849.03, colorless crystal 0.16 × 0.12 × 0.10 mm^3, *a* = 18.296(3), *b* = 19.739(4), *c* = 18.033(3) Å, β = 90.275(4)°, *V* = 6512(2) Å^3, ρ_{calc} = 1.886 g cm^{-3}, μ = 1.903 mm^{-1}, empirical absorption correction ($0.751 \leq T \leq 0.833$), *Z* = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, *T* = 153 K, ω and ϕ scans, 62688 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.65 Å^{-1}, 14981 independent (R_{int} = 0.070) and 11053 observed reflections [$I \geq 2\sigma(I)$], 358 refined parameters, *R* = 0.052, wR_2 = 0.120, max. residual electron density 1.51 (–1.09) e Å^{-3}. The hydrogen atoms at nitrogens were obtained from the difference Fourier calculations; the others were calculated and refined as riding.

[(3)Nd(Cl)$_3$]: This complex was prepared in methanol. Yield: 68.6 mg (0.12 mmol, quant.), pale-yellow solid. IR (KBr): $\tilde{\nu}$ = 3448, 1654, 1636, 1559, 1400, 1341, 1168 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 269.5 (22) $[(\mathbf{3})NdCl(CH_3OH)_3(H_2O)]^{2+}$, 253.9 (100) $[(\mathbf{3})NdCl(CH_3OH)_2(H_2O)]^{2+}$. $C_9H_{11}Cl_3N_7ONd_2{\cdot}4H_2O$: calcd. C 18.90, H 3.35, N 17.14; found C 19.35, H 3.41, N 17.30.

X-ray Crystal Structure Analysis for [(3)NdCl$_2$(CH$_3$OH)(Et$_2$O)]Cl: $C_{14}H_{27}N_7O_5Cl_3Nd$, M = 624.02, colorless crystal $0.20\times0.10\times0.02$ mm^3, a = 7.7520(16), b = 27.659(6), c = 10.055(2) Å, β = 95.335(4)°, V = 2146.6(8) Å^3, ρ_{calc} = 1.931 g cm^{-3}, μ = 2.835 mm^{-1}, empirical absorption correction ($0.601 \leq T \leq 0.946$), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 153 K, ω and ϕ scans, 16991 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 3769 independent (R_{int} = 0.057) and 3043 observed reflections [$I \geq 2\sigma(I)$], 255 refined parameters, R = 0.046, wR_2 = 0.105, max. residual electron density 1.53 (–1.12) e Å^{-3}. The hydrogen atoms at nitrogens were obtained from the difference Fourier calculations; the others were calculated and refined as riding.

[(3)Sm(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 76.7 mg (0.09 mmol, 75%), colorless solid. IR (KBr): $\tilde{\nu}$ = 3463, 1685, 1654, 1559, 1395, 1256, 1229, 1171, 637 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 699 $[(\mathbf{3})Sm(CF_3SO_3)_2]^+$. $C_{12}H_{11}F_9N_7O_{11}S_3Sm{\cdot}CH_3OH{\cdot}9H_2O$: calcd. C 15.00, H 3.20, N 9.42; found C 14.70, H 3.05, N 9.43.

[(3)Sm(NO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 32.7 mg (0.05 mmol, 39%), pale-yellow solid. IR (KBr): $\tilde{\nu}$ = 3453, 3365, 1675, 1559, 1491, 1405, 1385, 1301, 1165 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 209 $[(\mathbf{3})Sm(OH)]^{2+}$. $C_9H_{11}N_{10}O_{11}Sm{\cdot}CH_3CN{\cdot}3H_2O$: calcd. C 19.41, H 2.96, N 22.63; found C 19.51, H 2.53, N 22.10.

[(3)Er(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 65.5 mg (0.08 mmol, 63%), colorless solid. IR (KBr): $\tilde{\nu}$ = 3449, 1701, 1654, 1256, 1174, 1031, 641 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* 714.9 (12) $[(\mathbf{3})Er(CF_3SO_3)_2]^+$, 223.1 (100) $[(\mathbf{3})Er(CH_3O)]^{2+}$. $C_{12}H_{11}ErF_9N_7O_{11}S_3{\cdot}8H_2O$: calcd. C 14.30, H 2.70, N 9.73; found C 14.53, H 2.84, N 9.31.

[(3)Er(Cl)$_3$]: This complex was prepared in methanol. Yield: 60.1 mg (0.09 mmol, 78%), colorless solid. IR (KBr): $\tilde{\nu}$ = 3448, 1664, 1637, 1396, 1174 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 451 $[(\mathbf{3})ErCl - H]^+$.

X-ray Crystal Structure Analysis for [(3)ErCl$_2$(CH$_3$OH)]Cl: $C_{10}H_{15}N_7O_3Cl_3Er$, M = 554.90, pale-yellow crystal $0.20\times0.15\times0.10$ mm^3, a = 12.004(1), b = 13.769(1), c = 21.713(1) Å, V = 3588.8(4) Å^3, ρ_{calc} = 2.054 g cm^{-3}, μ = 5.148 mm^{-1}, empirical absorption correction ($0.426 \leq T \leq 0.627$), Z = 8, orthorhombic, space group $Pbca$ (no. 61), λ = 0.71073 Å, T = 223 K, ω and ϕ scans, 21485 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.67 Å^{-1}, 4329 independent (R_{int} = 0.033) and 3535 observed reflections [$I \geq 2\sigma(I)$], 239 refined parameters, R = 0.028, wR_2 = 0.072, max. residual electron density 1.35 (–1.28) e Å^{-3}. The hydrogen atoms at nitrogens were obtained from the difference Fourier calculations; the others were calculated and refined as riding.

[(3)Lu(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 104.5 mg (0.12 mmol, quant.), colorless solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.36 (t, J = 7.9 Hz, 1 H), 8.31 (s, 2 H), 7.95 (d, J = 7.9 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3443, 1656, 1540, 1399, 1276, 1252, 1174, 1034, 646 cm^{-1}. MS (pos. MALDI-TOF, DCTB): *m*/*z* $[(\mathbf{3})Lu(CF_3SO_3)_2]^+$.

[(3)Lu(Cl)$_3$]: This complex was prepared in methanol. Yield: 68.3 mg (0.11 mmol, 93%), pale-yellow solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.40 (s, 2 H), 8.35 (t, J = 7.8 Hz, 1 H), 7.95 (d, J = 7.8 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3448, 3170, 1670, 1648, 1600, 1541, 1396, 1177 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 458 $[(\mathbf{3})LuCl - H]^+$. $C_9H_{11}Cl_3LuN_7O_2{\cdot}5H_2O$: calcd. C 17.42, H 3.41, N 15.80; found C 17.73, H 3.38, N 15.26.

X-ray Crystal Structure Analysis for [(3)LuCl$_2$]Cl: $C_{18}H_{22}Cl_6Lu_2N_{14}O_4$, M = 1061.14, pale-yellow crystal $0.18\times0.09\times0.07$ mm^3, a = 11.126(3), b = 10.348(3), c = 13.655(3) Å, β = 101.281(4)°, V = 1541.7(6) Å^3, ρ_{calc} = 2.286 g cm^{-3}, μ = 6.939 mm^{-1}, empirical absorption correction ($0.368 \leq T \leq 0.642$), Z = 2, monoclinic, space group $C2/c$ (no. 15), λ = 0.71073 Å, T = 153 K, ω and ϕ scans, 8687 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.71 Å^{-1}, 2263 independent (R_{int} = 0.040) and 2133 observed reflections [$I \geq 2\sigma(I)$], 111 refined parameters, R = 0.030, wR_2 = 0.064, max. residual electron density 1.47 (–1.42) e Å^{-3}. The hydrogen atoms at nitrogens were obtained from the difference Fourier calculations; the others were calculated and refined as riding.

[(3)Lu(NO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 96.0 mg (0.12 mmol, quant.), colorless solid. ^{1}H NMR (200 MHz, CD_3OD): δ = 8.38 (s, 2 H), 8.33 (t, J = 7.8 Hz, 1 H), 7.94 (d, J = 7.8 Hz, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 3406, 1670, 1546, 1384, 1172 cm^{-1}. MS (pos. ESI, CH_3OH): *m*/*z* (%) 236.5 (70) $[(\mathbf{3})Lu(CH_3OH)(OH)]^{2+}$, 229.5 (100) $[(\mathbf{3})Lu(H_2O)(OH)]^{2+}$. $C_9H_{11}LuN_{10}O_{11}{\cdot}2CH_3CN{\cdot}6H_2O$: calcd. C 19.51, H 3.65, N 21.00; found C 19.53, H 3.51, N 20.55.

[(4)Y(Cl)$_3$]: This complex was prepared in methanol. Yield: 72.9 mg (0.11 mmol, quant.), yellow solid. ^{1}H NMR (200 MHz, CD_3OH): δ = 8.06 (t, J = 7.9 Hz, 1 H), 7.52 (d, J = 7.9 Hz, 2 H), 7.20 (s, 2 H), 4.02 (br. m, 2 H), 3.70 (d, J = 5.2 Hz, 4 H), 3.60–3.30 (m, 4 H), 3.42 (s, 6 H), 2.31–1.95 (m, 8 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.9, 141.5, 112.0, 114.7, 74.1, 63.5, 59.6, 48.9, 27.1, 22.3 ppm. IR (KBr): $\tilde{\nu}$ = 3448, 1617, 1540, 1341, 1276, 1154, 669 cm^{-1}. $C_{19}H_{29}Cl_3N_5O_2Y{\cdot}6H_2O$: calcd. C 34.43, H 6.23, N 10.57; found C 34.38, H 6.41, N 10.33.

[(4)Y(NO$_3$)$_3$]: This complex was prepared in methanol. Yield: 78.7 mg (0.11 mmol, quant.), orange/green solid. ^{1}H NMR (200 MHz, CD_3CN): δ = 8.00 (t, J = 8.1 Hz, 1 H), 7.27 (d, J = 8.1 Hz, 2 H), 7.03 (s, 2 H), 3.94 (br. m, 2 H), 3.62 (d, J = 5.1 Hz, 4 H), 3.52–3.26 (m, 4 H), 3.32 (s, 6 H), 2.23–1.85 (m, 8 H) ppm. ^{13}C NMR (50 MHz, CD_3CN): δ = 148.7, 146.3, 119.1, 118.0, 74.2, 64.6, 59.5, 49.9, 27.5, 22.8 ppm. MS (pos. ESI, CH_3CN): *m*/*z* (%) 572.3 (15) $[(\mathbf{3})Y(NO_3)_2]^+$. MS (pos. LDI-TOF): *m*/*z* 572 $[(\mathbf{3})Y(NO_3)_2]^+$. $C_{19}H_{29}N_8O_{11}Y{\cdot}2CH_3OH{\cdot}H_2O$: calcd. C 34.20, H 5.31, N 15.95; found C 34.60, H 5.11, N 16.05.

[(4)La(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 56.7 mg (0.06 mmol, 54%), orange solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.78 (t, J = 7.9 Hz, 1 H), 7.52 (d, J = 7.9 Hz, 2 H), 7.19 (s, 2 H), 3.68–3.20 (m, 16 H), 2.27–1.88 (m, 8 H) ppm. IR (KBr): $\tilde{\nu}$ = 3445, 1617, 1560, 1275, 1255, 1161, 1032, 756, 639 cm^{-1}. MS (pos. ESI, CH_3CN): *m*/*z* (%) 796.1 (4) $[(\mathbf{4})La(CF_3SO_3)_2]^+$, 360.3 (100) $[(\mathbf{4})LaH(CF_3SO_3)_3]^+$.

[(4)La(Cl)$_3$]: This complex was prepared in methanol. Yield: 73.4 mg (0.11 mmol, 99%), orange solid. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.81 (s, 2 H), 7.79–7.49 (m, 3 H), b), 3.90 (br. m, 2 H), 3.70 (d, J = 5.2 Hz, 4 H), 3.67–3.31 (m, 4 H), 3.37 (s, 6 H), 2.21–1.88 (m, 8 H) ppm. IR (KBr): $\tilde{\nu}$ = 3400, 2929, 1610, 1539, 1274, 1152, 1116, 728 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 568 $[(\mathbf{4})La(Cl)_2]^+$. $C_{19}H_{29}Cl_3LaN_5O_2{\cdot}4H_2O$: calcd. C 33.72, H 5.51, N 10.35; found C 34.18, H 5.50, N 10.33.

[(4)Pr(CF$_3$SO$_3$)$_3$]: This complex was prepared in methanol. Yield: 104.2 mg (0.11 mmol, quant.), orange solid. IR (KBr): ṽ = 2933, 2883, 1617, 1540, 1450, 1350, 1276, 1198, 1162, 1032, 839, 757, 640 cm^{-1}. MS (pos. ESI, CH$_3$CN): *m*/*z* (%) 798.1 (6) [(**4**)Pr(CF$_3$SO$_3$)$_2$]$^+$, 360.3 (100) [(**4**)PrH(CF$_3$SO$_3$)$_3$]$^+$.

[(4)Nd(CF$_3$SO$_3$)$_3$]: This complex was prepared in methanol. Yield: 104.5 mg (0.11 mmol, quant.), orange solid. IR (KBr): ṽ = 3448, 1663, 1559, 1256, 1235, 1169, 1031, 754, 639 cm^{-1}. MS (pos. ESI, CH$_3$CN): *m*/*z* (%) 801.1 (4) [(**4**)Nd(CF$_3$SO$_3$)$_2$]$^+$.

[(4)Nd(Cl)$_3$]: This complex was prepared in methanol. Yield: 54.5 mg (0.08 mmol, 73%), orange-red solid. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.81 (s, 2 H), 7.87–7.51 (m, 3 H), b), 3.90 (br. m, 2 H), 3.70–3.25 (m, 8 H), 3.36 (s, 6 H), 2.21–1.86 (m, 8 H) ppm. IR (KBr): ṽ = 3448, 2885, 1635, 1608, 1544, 1453, 1360, 1325, 1281, 1155, 1117, 749 cm^{-1}. $C_{19}H_{29}Cl_3N_5NdO_2\cdot CH_3OH\cdot 2H_2O$: calcd. C 35.42, H 5.50, N 10.33; found C 35.98, H 5.68, N 10.91.

[(4)Sm(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 105.4 mg (0.11 mmol, quant.), orange solid. IR (KBr): ṽ = 2936, 2894, 1617, 1535, 1445, 1415, 1344, 1273, 1256, 1162, 1032, 749, 640 cm^{-1}. MS (pos. ESI, CH$_3$CN): *m*/*z* (%) 809.1 (2) [(**4**)Sm(CF$_3$SO$_3$)$_2$]$^+$.

[(4)Sm(Cl)$_3$]: This complex was prepared in methanol. Yield: 70.0 mg (0.11 mmol, quant.), orange solid. IR (KBr): ṽ = 3448, 1617, 1540, 1340, 1288, 1271, 1155 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 583 [(**4**)SmCl$_2$]$^+$. $C_{19}H_{29}Cl_3N_5O_2Sm\cdot H_2O$: calcd. C 33.16, H 5.42, N 10.18; found C 33.15, H 5.14, N 10.05.

[(4)Sm(NO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 66.9 mg (0.10 mmol, 87%), orange solid. ^{1}H NMR (200 MHz, CD$_3$CN): δ = 8.01 (t, *J* = 7.8 Hz, 1 H), 7.27 (d, *J* = 7.8 Hz, 2 H), 7.04 (s, 2 H), 3.94 (br. m, 2 H), 3.62 (d, *J* = 4.8 Hz, 4 H), 3.47–3.26 (m, 4 H), 3.32 (s, 6 H), 2.23–1.84 (m, 8 H) ppm. IR (KBr): ṽ = 3443, 1617, 1540, 1384, 1288, 1271, 1155 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 635 [(**4**)Sm(NO$_3$)$_2$]$^+$.

[(4)Er(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 107.2 mg (0.11 mmol, quant.), orange solid. IR (KBr): ṽ = 3446, 1617, 1559, 1273, 1261, 1160, 1033, 755, 640 cm^{-1}. MS (pos. ESI, CH3CN): *m*/*z* (%) 825.1 (3) [(**4**)Er(CF$_3$SO$_3$)$_2$]$^+$. MS (pos. LDI-TOF): *m*/*z* 825 [(**4**)Er(CF$_3$SO$_3$)$_2$]$^+$).

[(4)Er(Cl)$_3$]: This complex was prepared in methanol. Yield: 79.0 mg (0.11 mmol, quant.), orange solid. ^{1}H NMR (200 MHz, CD$_3$OD): δ = 8.07 (t, *J* = 7.9 Hz, 1 H), 7.52 (d, *J* = 7.9 Hz, 2 H), 7.20 (s, 2 H), 4.00 (br. m, 2 H), 3.67 (d, *J* = 4.7 Hz, 4 H), 3.60–3.20 (m, 4 H), 3.40 (s, 6 H), 2.32–1.89 (m, 8 H) ppm. IR (KBr): ṽ = 3443, 1617, 1534, 1340, 1288, 1156 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 597 [(**4**)ErCl$_2$]$^+$. $C_{19}H_{29}Cl_3ErN_5O_2\cdot CH_3OH\cdot 3H_2O$: calcd. C 33.40, H 5.47, N 9.74; found C 33.48, H 5.58, N 10.21.

[(4)Er(NO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 75.7 mg (0.10 mmol, 94%), yellow solid. ^{1}H NMR (200 MHz, CD$_3$OD): δ = 7.74 (br. t, *J* = 7.6 Hz, 1 H), 7.54 (br. d, *J* = 7.6 Hz, 2 H), 7.16 (br. s, 2 H), 3.92–3.13 (br. m, 10 H), 3.40 (br. s, 6 H), 2.24–1.86 (br. m, 8 H) ppm. IR (KBr): ṽ = 3443, 1617, 1540, 1384, 1288, 1270, 1155 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 651 [(**4**)Er(NO$_3$)$_2$]$^+$. $C_{19}H_{29}ErN_8O_{11}\cdot H_2O$: calcd. C 29.08, H 4.75, N 14.28; found C 29.59, H 4.18, N 15.21.

[(4)Yb(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 107.8 mg (0.11 mmol, quant.), orange solid. ^{1}H NMR (200 MHz, CD$_3$CN): δ = 7.80 (t, *J* = 7.9 Hz, 1 H), 7.02 (d, *J* = 7.9 Hz, 2 H), 6.72 (s, 2 H), 3.69 (br. m, 2 H), 3.38 (br. d, *J* = 5.1 Hz, 4 H), 3.13 (br. s, 6 H), 2.88 (m, 4 H), 2.05–1.62 (m, 8 H) ppm. ^{13}C NMR (50 MHz, CD$_3$CN): δ = 147.1, 144.7, 121.7, 117.4, 116.2, 72.5, 62.9, 57.9, 46.3, 25.9, 21.2 ppm. IR (KBr): ṽ = 3446, 1624, 1540, 1275, 1261, 1162, 1032, 756, 641 cm^{-1}. MS (pos. ESI, CH$_3$CN): *m*/*z* (%) 831.1 (1) [(**4**)Yb(CF$_3$SO$_3$)$_2$]$^+$ ppm. MS (pos. LDI-TOF): *m*/*z* 831 [(**4**)Yb(CF$_3$SO$_3$)$_2$]$^+$.

[(4)Lu(CF$_3$SO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 106.9 mg (0.11 mmol, quant.), orange solid. ^{1}H NMR (200 MHz, CD$_3$CN): δ = 8.02 (t, *J* = 7.9 Hz, 1 H), 7.27 (d, *J* = 7.9 Hz, 2 H), 7.04 (s, 2 H), 4.08–3.22 (m, 16 H), 2.25–1.84 (m, 8 H) ppm. IR (KBr): ṽ = 3447, 2993, 2881, 1617, 1544, 1450, 1347, 1276, 1198, 1161, 1032, 756, 640 cm^{-1}. MS (pos. ESI, CH3CN): *m*/*z* (%) 832.1 (4) [(**4**)Lu(CF$_3$SO$_3$)$_2$]$^+$.

[(4)Lu(Cl)$_3$]: This complex was prepared in methanol/acetonitrile. Yield: 76.2 mg (0.11 mmol, quant.), orange solid. ^{1}H NMR (200 MHz, CD$_3$CN): δ = 7.96 (t, *J* = 8.1 Hz, 1 H), 7.44 (d, *J* = 8.1 Hz, 2 H), 7.35 (s, 2 H), 3.92 (br. m, 2 H), 3.61 (d, *J* = 4.8 Hz, 4 H), 3.49–3.23 (m, 4 H), 3.32 (s, 6 H), 2.21–1.82 (m, 8 H) ppm. IR (KBr): ṽ = 3448, 1617, 1540, 1340, 1287, 1154 cm^{-1}. MS (pos. LDI-TOF): *m*/*z* 604 [(**4**)LuCl$_2$]$^+$. $C_{19}H_{29}Cl_3LuN_5O_2\cdot 3H_2O$: calcd. C 32.84, H 5.08, N 10.08; found C 32.77, H 5.15, N 9.99.

[(4)Lu(NO$_3$)$_3$]: This complex was prepared in acetonitrile. Yield: 77.7 mg (0.10 mmol, 94%), yellow solid. ^{1}H NMR (200 MHz, CD$_3$CN): δ = 7.92 (br. t, *J* = 8.0 Hz, 1 H), 7.26 (d, *J* = 7.6 Hz, 2 H), 7.09 (s, 2 H), 3.92 (br. m, 2 H), 3.60 (br. d, *J* = 4.7 Hz, 4 H), 3.42 (dt, *J* = 8.0, 6.7 Hz, 4 H), 3.34 (s, 6 H), 2.36–1.75 (hidden under solvent peak, 8 H) ppm. MS (pos. LDI-TOF): *m*/*z* 658 [(**4**)Lu(NO$_3$)$_2$]$^+$.

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