Unequivocal Synthetic Pathway to Heterodinuclear (4f,4f′) Complexes: Magnetic Study of Relevant (Ln^{III}, Gd^{III}) and (Gd^{III}, Ln^{III}) Complexes

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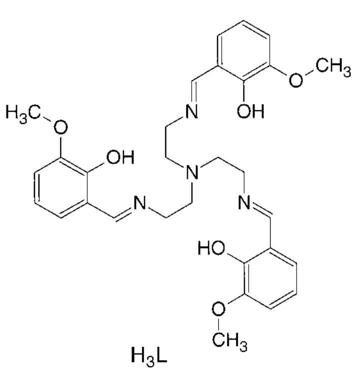
Abstract: The tripodal ligand tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]amine (LH_3) is capable of coordinating to two different lanthanide ions to give complexes formulated as $[LLnLn'(NO_3)_3]\cdot xH_2O$. The stepwise synthetic procedure consists of introducing first a Ln^{III} ion in the inner N_4O_3 coordination site. The isolated neutral complex LLn is then allowed to react with a second and different Ln′ ion that occupies the outer O_6 site, thus yielding a $[LLnLn'(NO_3)_3]\cdot xH_2O$ complex. A FAB^+ study has confirmed the existence of (Ln, Ln′) entities as genuine, when the Ln′ ion in the outer site has a larger ionic radius than the Ln ion in the inner site. The qualitative magnetic study of the (Gd, Ln) and (Ln, Gd) complexes, based on the comparison of the magnetic properties of (Gd, Ln) (or (Ln, Gd)) pairs and (Y, Ln) (or (Ln, La)) pairs, is very informative. Indeed, these former complexes are governed by the thermal population of the Ln^{III} Stark levels and the Ln–Gd interaction, while the latter are influenced by the thermal population of the Ln^{III} Stark levels. We have been able to show that a ferromagnetic interaction exists at low temperature in the (Gd, Nd), (Gd, Ce), and (Yb, Gd) complexes. In contrast, an antiferromagnetic interaction occurs in the (Dy, Gd) and (Er, Gd) complexes. Although we cannot give a quantitative value to these interactions, we can affirm that their magnitudes are weak since they are only perceptible at very low temperature.

Keywords: lanthanides · magnetic properties · N ligands · tripodal ligands

Introduction

Recently, we proposed an empirical analysis describing the nature (antiferro- or ferromagnetic) of the interaction within (Cu^{II},Ln^{III}) pairs.[1] A similar approach was reported shortly thereafter by Kahn and co-workers.[2] The two studies have led to some divergences that have been attributed to the different nature of the considered complexes. Indeed, we have shown[3] that for a given pair (e.g. Cu^{II},Gd^{III}) slight structural modifications may induce significant changes in the magnetic properties. A more quantitative evaluation of the magnetic behavior of (Cu^{II},Ln^{III}) pairs is in progress and the results available so far[4] support our empirical analysis. This result prompted us to extend the approach to heterodimetallic (4f,4f′) complexes.

As part of previous studies we prepared and structurally determined a heterometallic (4f,4f′) species,[5] one of only a few examples of heterodimetallic 4f–4f′ complexes to have been structurally characterized;[5–9] the first one was a triple-decker sandwich complex with porphyrin and phthalocyanine ligands,[6] the most recent one a triple-stranded helicate.[9] Our heterometallic (4f,4f′) complex was obtained by using the tripodal ligand H_3L, which possesses two well-differentiated coordination sites: an inner mixed N_4O_3 coordination site and a fully oxygenated outer O_6 coordination site. In the structurally determined complex, the lanthanide ions were Yb^{3+} and La^{3+}; the Yb^{3+} ion residing in the inner site and the La^{3+} ion in the outer one. The powder sample from the preparation proved to be an ionic species formulated as $[LYbLa(NO_3)_2]NO_3$;[10] however, the crystalline form, ob-



H_3L

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tained after many attempts, displayed a somewhat different formulation comprising two cationic $[LYbLa(NO_3)_2]^+$ entities and a $[La(NO_3)_5]^{2-}$ ion. Owing to its strict dinuclearity, the $[LYbLa(NO_3)_2]NO_3$ complex is more appropriate for a magnetic investigation than the $[LYbLa(NO_3)_2]_2[La(NO_3)_5(H_2O)]$ complex, which countains two Ln metal ions in three different coordination sites. The magnetic properties of five heterometallic pairs ((Gd, Ce), (Gd, Nd), (Dy, Gd), (Er, Gd), and (Yb, Gd))[10] have been studied and compared to those of related reference complexes containing only one active center ((Y, Ce), (Y, Nd), (Dy, La), (Er, La), and (Yb, La)).

Results and Discussion

Synthesis and characterization: The ligand H_3L contains two different coordination sites, which owing to their natures (N_4O_3 versus O_6) are expected to display different reactivities, and thus allows insertion of two lanthanides ions by a controlled stepwise process. The neutral mononuclear complexes LLn have been described previously[11] but a slight modification of their preparation gives samples devoid of any trace of $CsNO_3$ as supplementary salt. In our first paper in this series,[11] we focused on the synthesis of mononuclear lanthanide complexes of a tripodal ligand having only one N_4O_3 coordination site. Deprotonation of the ligand by cesium hydroxide prior to addition of $Ln(NO_3)_3 \cdot 6H_2O$ was necessary to avoid ligand hydrolysis. $CsNO_3$ salts, which formed as a by-product of the reaction, were removed by washing the resulting precipitate with water. In the present case, the tripodal ligand H_3L, which contains two coordination sites, can coordinate cesium in the outer O_6 site such that washing with water does not eliminate cesium in every case. The improved synthesis of the mononuclear LLn complexes is based on use of $LnCl_3 \cdot 6H_2O$ instead of $Ln(NO_3)_3 \cdot 6H_2O$. One advantage is that the CsCl by-product is more easily eliminated (than $CsNO_3$) by washing with water, thus leaving the LLn complexes devoid of any supplementary salt. Addition of a slight excess (1.1/1 ratio) of a second lanthanide ion $Ln'(NO_3)_3 \cdot 6H_2O$ to a methanolic suspension of the mononuclear species LLn yields a precipitate whose analysis reveals a composition $LLnLn'(NO_3)_3$. We use a slight excess of the lanthanide ion added to the mononuclear LLn complex to avoid contamination of the final product by the sparingly soluble monomeric LLn entity; the excess of the methanol-soluble lanthanide ion is eliminated by filtration. Indeed this process does not give a pure complex when the starting material is $LLnCs(NO_3)$ because the free $CsNO_3$ salt liberated during the exchange reaction is insoluble in methanol and precipitates with the desired product.

Although chemical analysis affords a first indication of the composition of the isolated products, it is insufficient for a complete characterization since it gives no information about possible scrambling of the lanthanide ions. To investigate such a possibility we performed FAB^+ mass spectrometry experiments in DMF as solvent and *meta*-nitrobenzyl alcohol as matrix. For the entire set of investigated complexes, the most important signal in each spectrum is attributable to the related $[LLnLn'(NO_3)_2]^+$ ion. The signal patterns observed in the mass spectra are characteristic of the lanthanide-containing species (particularly in light of the isotope patterns of most of the Ln^{3+} ions) and afford unambiguous assignments. Besides the characterization of a number of binuclear complexes, the FAB^+ spectra provide interesting information about the limits of the synthetic process. This is exemplified by the lanthanum – gadolinium complexes. The spectrum of the species resulting from the reaction of LGd with $La(NO_3)_3$ shows a single signal centered at *m*/*z* 966 amu that displays an isotopic pattern characteristic of the $[LGdLa(NO_3)_2]^+$ ion. The spectrum corresponding to the precipitate issued from the addition of $Gd(NO_3)_3$ to the LLa precursor displays two signals centered at *m*/*z* 966 and 985 amu with relative intensities of 100% and 52%, respectively. The most intense signal corresponds to what is expected for $[LLaGd(NO_3)_2]^+$, while the second signal corresponds to $[LGdGd(NO_3)_2]^+$, showing that some La^{3+} ions in the N_4O_3 site have been replaced by Gd^{3+} ions coming from the O_6 site or, less likely, from the reaction mixture since a slight excess of the ion introduced in the outer site is used in each reaction. We never observed the signal corresponding to the $[LLaLa(NO_3)_2]^+$ ion. This means that the replaced La^{3+} ion goes directly into the solution, without being trapped in the O_6 site, and that the exchange between ions complexed into the O_6 outer site and uncomplexed ions is not facile. Furthermore, as the Gd^{3+}/La^{3+} ratio for the free ions is very large, a possible (La, La) recombination, yielding the $[LLaLa(NO_3)_2]^+$ ion is unlikely. Similar results have been obtained with the (La, Eu) and (Dy, Yb) samples. It should be noted that under the experimental conditions used to perform the preparative reaction, there is no indication of the presence of homodinuclear complexes. Accordingly, we conclude that scrambling does not occur if the lanthanide ion with the smaller ionic radius is located in the inner N_4O_3 coordination site of the complex. It has been pointed out that the Lewis acidity of the lanthanide ions increases on going from lanthanum to lutecium.[12] Thus, scrambling exchange in our dinuclear complexes could also be explained by a better affinity of the smaller Ln ion of the (Ln, Ln′) pair for the inner and smaller N_4O_3 coordination site because of its larger Lewis acidity. This rationale suggests that out of the 196 possible (Ln, Ln′) species theoretically conceivable,[13] 91 may be synthesized and isolated. If we add 14 homodinuclear pairs for which scrambling has no meaning, 105 dinuclear complexes would be attainable with our method. Understandably, we have not checked all these different permutations but have limited our study to the following examples: (Yb,Gd), (Yb, La), (Er, Gd), (Er, La), (Dy, Gd), (Dy, La), (Gd, Nd), (Y, Nd), (Gd, Ce), (Y, Ce) which have been characterized by chemical analysis and mass spectrometry. The choice was made based on the requirements of the magnetic study (see below).

In addition, these complexes give rise to very similar infrared spectra in the 400 – 4000 cm^{-1} range. In comparison with the IR spectrum of the structurally characterized $[LYLa(NO_3)_2]_2[La(NO_3)_5(H_2O)]$ complex, the main difference in the IR spectra of the complexes reported herein comes from the presence of an absorption characteristic of ionic nitrates[14] at 1384 cm^{-1}, while bands attributable to bidentate nitrates are observed in every case at 1467(±5) and 1300(±3) cm^{-1}. The bands attributable to the deprotonated ligand (ν_{CC}, ν_{CN}, ν_{CO}) occur at the same positions (1626(±1), 1467(±5), and 1227(±5) cm^{-1}), some of them being masked by the bands for η^2-coordinated nitrates. These data support the view that apart from the number of coordinated nitrates, the structure of these new complexes is similar to that of the cationic $[LYLa(NO_3)_2]^+$ unit, the Ln and Ln′ ions being bridged through three phenolato oxygen atoms. Infrared spectroscopy, however, is unable to differentiate between, for example, a (Gd,La) sample, which is a genuine complex, and a (La,Gd) sample, which is a mixture of (La,Gd) and (Gd,Gd) complexes. The spectra of the mononuclear LLn complexes show slightly different patterns, due to absence of nitrate groups, but they are very similar on going from the lanthanum to the ytterbium complex.

Magnetic properties: The difficulty in studying the magnetic properties of species containing lanthanide ions arises from the fact that most of the Ln^{3+} ions possess an orbital momentum; the exceptions are La^{3+} and Lu^{3+} that are diamagnetic, and Gd^{3+} that displays spin-only magnetism in accordance with a $^8S_{7/2}$ ground state.

The 4f^n configuration of a Ln^{3+} ion is split into $^{2S+1}L_J$ states by the interelectronic repulsion and the spin–orbit coupling. Further splitting into Stark components is caused by the crystal-field perturbation; the number of components depends on the symmetry site of the ion.[15] At room temperature, all the Stark levels arising from the ground state are populated but, as the temperature decreases, a progressive depopulation of these levels occurs. Even for a mononuclear Ln^{3+} complex, the temperature dependence causes the magnetic susceptibility to deviate from the Curie law. In a polynuclear complex the thermal variation of $\chi_M T$ depends on the populations of the Stark levels and on the exchange (Ln, Ln′) coupling constant. In addition, these exchange constants are expected to be weak; for instance, the (Gd, Gd) interactions in different di- or trinuclear complexes vary from -0.05 cm^{-1} to -0.15 cm^{-1}.[5, 11, 16–21] Finally, it appears that it would be difficult to determine the nature of the (Ln, Ln′) interaction if the two Ln^{3+} centers have an orbital momentum.

To circumvent this difficulty, we have restricted our study to dinuclear complexes containing a Gd^{3+} ion and a Ln^{3+} ion possessing an orbital momentum. The magnetic data obtained for these complexes were submitted to an empirical analysis similar to that previously applied to heterodinuclear (Cu^{2+}, Ln^{3+}) complexes.[1] It is based on comparing the thermal dependence of $\chi_M T$ for the (Gd, Ln) and (Ln, Gd) complexes with those of the related (Y, Ln) and (Ln, La) complexes. These latter species allow the evaluation of the local effects originating in the Stark levels on depopulation of a Ln^{3+} ion located in the inner or outer coordination site. According to the previous structural determination, we suppose that the dinuclear entities are well separated from each other and that the observed magnetic interaction corresponds to the intramolecular one. As for the Gd^{3+} ion, its contribution to $\chi_M T$ is expected to be constant and equal to 7.9 cm^{3}mol^{-1}K, independent of the nature (N_4O_3 or O_6) of the complexation site. Indeed the gadolinium ion, with its $^8S_{7/2}$ ground state and its seven uncoupled electrons obeys the Curie law in the temperature range in which the exchange interaction is not active.[15] Finally if the (Gd, Ln) interaction is negligible, the difference between the (Gd, Ln) and (Y, Ln) or (Ln, La) $\chi_M T$ curves would be constant and equal to 7.9 cm^{3}mol^{-1}K. As the temperature decreases, the $\chi_M T$ difference would decrease or increase depending on the antiferro- or ferromagnetic nature of the interaction.

We have considered the (Yb, Gd), (Dy, Gd), (Er, Gd), (Gd, Nd), and (Gd, Ce) complexes and the related references (Yb, La), (Dy, La), (Er, La), (Y, Nd), and (Y, Ce). Two types of magnetic behavior are observed. The first one corresponds to the (Dy, Gd) and (Er, Gd) complexes. It is illustrated in Figure 1, which shows the thermal dependence of $\chi_M T$ for (Dy, Gd) (Figure 1 A) and (Dy, La) (Figure 1 B). In both instances $\chi_M T$ decreases continuously on lowering temperature. For (Dy, La) $\chi_M T$ at 300 K is equal to 13.9 cm^{3}mol^{-1}K, which is the value expected for Dy^{3+} ($^6H_{15}$) in the free-ion approximation. Evidently, La^{3+} does not contribute to the molecular paramagnetism. As the temperature decreases $\chi_M T$ decreases to reach a value of 7.8 cm^{3}mol^{-1}K at 2 K. This is in accordance with a progressive depopulation of the highest Stark levels. A similar evolution is observed in the case of the (Dy, Gd) complex, $\chi_M T$ varying from 21.9 cm^{3}mol^{-1}K at 300 K to 13.7 cm^{3}mol^{-1}K at 2 K. However, it should be emphasized that the value of 21.9 cm^{3}mol^{-1}K is equal to the sum of the contributions attributable to Dy^{3+} (13.9 cm^{3}mol^{-1}K) and Gd^{3+} (7.9 cm^{3}mol^{-1}K), while the experimental value at 2 K (13.7 cm^{3}mol^{-1}K) is lower than estimated from the contributions of the individual ions (15.4 cm^{3}mol^{-1}K) and probably

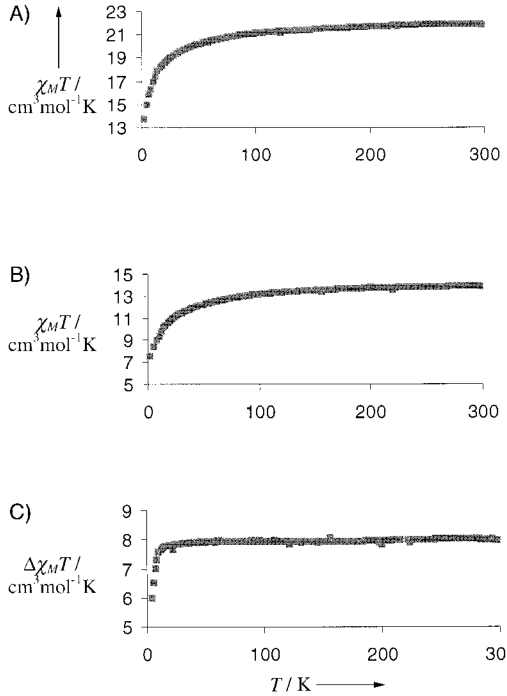

Figure 1. Thermal dependence of $\chi_M T$ for the (Dy, Gd) (A) and (Dy, La) (B) complexes along with the $\Delta\chi_M T$ difference (C) between the (Dy, Gd) and (Dy, La) complexes.

indicates an antiferromagnetic interaction between the two lanthanide ions. Indeed, the $\Delta\chi_M T$ difference between the two complexes (Dy, Gd) and (Dy, La) becomes significative only below 15 K (Figure 1 C). The difference is approximately constant in the 30–300 K range, with a value of 7.9 ± 0.1 cm^{3}mol^{-1}K, which corresponds to the $\chi_M T$ value of an isolated gadolinium(III) ion. This behavior supports the view that for a given lanthanide ion, here Dy^{3+}, a similar crystal field is operative in both complexes, giving rise to an identical distribution of the Stark levels. Below 15 K, the rapid decrease of $\Delta\chi_M T$ is attributable to an antiferromagnetic intramolecular interaction. Indeed, in agreement with the characterizations described above and the previously published structural data,[5] this behavior cannot originate from intermolecular interactions. As this interaction is only observable at low temperature, we can confirm that its magnitude is weak.

The behavior of the (Er, La) and (Er, Gd) complexes is very similar. The former complex has a $\chi_M T$ value of 9.1 cm^{3}mol^{-1}K at 45 K, which decreases to 6.2 cm^{3}mol^{-1}K at 2 K, while for the latter complex the variation is from 17.1 cm^{3}mol^{-1}K at 300 K to 11.4 cm^{3}mol^{-1}K at 2 K. The value at 300 K is merely equal to the sum of the individual contributions, while the value at 2 K is lower than expected (14.1 cm^{3}mol^{-1}K).

The situation is very different for the (Gd, Nd), (Gd, Ce), and (Yb, Gd) pairs, which show behavior fundamentally distinct from that of their related reference complexes (Y, Nd), (Y, Ce), and (Yb, La), respectively. For the latter complexes, the usual decrease in the value of $\chi_M T$ is observed on lowering the temperature, while for the former species in which Gd^{3+} is associated with a magnetically active Ln^{3+} ion the $\chi_M T$ versus T curves display a minimum. These features are illustrated in Figure 2 for the (Yb, Gd) (Figure 2 A) and (Yb, La) (Figure 2 B) complexes. In the present case the minimum is reached at $T_{min} = 12$ K (10 K for (Gd, Nd) and 4 K for (Gd, Ce)). Lowering the temperature below T_{min} causes the $\chi_M T$ values to increase sharply. This overall behavior indicates the occurrence of two conflicting effects. On the one hand there is the Stark effect which tends to lower the local contributions of the lanthanide ions (it may be evaluated from the (Ln, La) curves) and on the other hand there is the ferromagnetic interaction within the (Ln, Gd) pair which would increase the molecular magnetism. The coupling interaction predominates at low temperature, below 12 K for (Yb, Gd), 10 K for (Gd, Nd), and 4 K for (Gd, Ce), as shown in Figure 2 C by the difference $\Delta\chi_M T$.

A literature survey affords few elements for comparison. Indeed the magnetic study of (4f, 4f′) interactions based on structurally characterized species is essentially limited to homopolynuclear gadolinium(III) complexes. Until recently the Gd–Gd interaction has always been found to be antiferromagnetic with a magnitude varying from 0.045 to 0.21 cm^{-1}.[5, 11, 16–21] However, we have recently reported the structures and magnetic properties of two complexes $[L_6Ln_2] \cdot x H_2O$ (L = salicylic acid; Ln = Gd^{3+}, Er^{3+}) that display a ferromagnetic ground state.[22] The Gd–Gd interaction like the Cu–Gd one may be either antiferro- or ferromagnetic and thus it is not completely unexpected to observe both types of behavior in the (Gd, Ln) complexes. To our knowledge, the exchange phenomenon in the presence of orbital degeneracy is a problem for which no general solution is available. Thus, at present we are unable to give a general explanation for our results, even at a qualitative level.

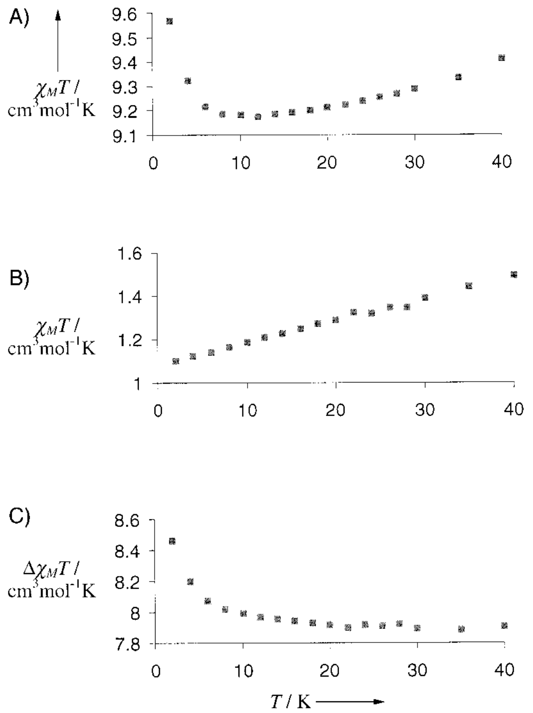

Figure 2. Thermal dependence of $\chi_M T$ for the (Yb, Gd) (A) and (Yb, La) (B) complexes along with the $\Delta\chi_M T$ difference (C) between the (Yb, Gd) and (Yb, La) complexes.

Conclusion

The first interesting aspect of this work is the description of a synthetic pathway that allows an easy access to a large number of heterodinuclear (4f, 4f′) complexes. The key point in our stepwise strategy is the preparation of the mononuclear LLn species in which the Ln ion is complexed in the inner N_4O_3 coordination site. Then to synthesize genuine heterodinuclear species starting from these mononuclear entities, the lanthanide(III) ion introduced requires a larger ionic radius or a lower Lewis acidity than that of mononuclear precursor. If we do not obey these rules we always isolate a mixture of two complexes instead of a pure heterodinuclear entity. The second, more important, aspect of this work is the unequivocal experimental proof showing that ferromagnetic interactions can exist between pairs of lanthanide ions, such as Yb–Gd, Gd–Nd, and Gd–Ce. Such magnetic behavior provides additional support corroborating the existence of the heterodinuclear complexes.

Experimental Section

Materials and methods: All starting materials were purchased from Aldrich and were used without further purification. Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse (C, H, N). Magnetic susceptibility data were collected on powdered samples of the different compounds by using a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument. All data were corrected for diamagnetism of the ligand estimated from Pascal's constants[23] (-331×10^{-6} emu mol^{-1} for the deprotonated tripodal ligand). Positive-ion FAB mass spectra were recorded on a Nermag R10–10 spectrometer by using DMF as solvent and *meta*-nitrobenzyl alcohol as matrix.

Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]amine (H_3L): This ligand was obtained as previously described.[24]

The preparation of the mononuclear species has been improved since the first description.[11] As these syntheses are analogous for each mononuclear species and also analogous for each of the heterodinuclear complexes, only the experimental procedure for one of each is given, together with the analytical data of the entire set of complexes studied.

Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]aminato(3 –)dysprosium(III) ([Ldy]): $DyCl_3 \cdot 6H_2O$ (0.38 g, 1 mmol) was added to a mixture of LH_3 (0.54 g, 1 mmol) and $CsOH \cdot H_2O$ (0.50 g, 3 mmol) in absolute ethanol (20 mL). After the mixture had been heated gently for 10 min and stirred vigorously, the yellow precipitate which appeared was filtered off after cooling, and washed with water, ethanol, and diethyl ether. Yield: 0.66 g (86 %); elemental analysis calcd (%) for $C_{30}H_{33}DyN_4O_6$ (708.1): C 50.9, H 4.7, N, 7.9; found: C 50.5, H 4.4, N 7.7; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 710 (100), $[LDy + 1]^+$; IR (KBr disk): $\tilde{\nu} = 1627$ s, 1469 s, 1444 s, 1406 m, 1326 m, 1242 s, 1219 s, 1083 m, 858 m, 749 m cm^{-1},.

[LEr]: Yield 88 %; elemental analysis calcd (%) for $C_{30}H_{33}ErN_4O_6$ (712.9): C 50.5, H 4.7, N, 7.8; found: C 50.0, H 4.4, N 7.5; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 714 (100), $[LEr + 1]^+$; IR (KBr disk): $\tilde{\nu} = 1627$ s, 1470 s, 1447 s, 1407 m, 1242 s, 1220 s, 1083 m, 859 m, 749 m cm^{-1}.

$[LYb] \cdot H_2O$: Yield 90 %; elemental analysis calcd (%) for $C_{30}H_{35}N_4O_7Yb$ (736.7): C 48.9, H 4.8, N, 7.6; found: C 48.5, H 4.5, N 7.5; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 720 (100), $[LYb + 1]^+$; IR (KBr disk): $\tilde{\nu} = 3413$ br, 1627 s, 1471 s, 1448 s, 1407 m, 1242 s, 1221 s, 1083 m, 860 m, 748 m cm^{-1}.

[LGd]: Yield 81 %; elemental analysis calcd (%) for $C_{30}H_{33}GdN_4O_6$ (702.8): C 51.3, H 4.7, N, 8.0; found: C 51.0, H 4.5, N 8.0; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 704 (100), $[LGd + 1]^+$; IR (KBr disk): $\tilde{\nu} = 1627$ s, 1469 s, 1444 s, 1406 m, 1326 m, 1241 s, 1219 s, 1083 m, 858 m, 749 m cm^{-1}.

$[LLa] \cdot H_2O$: Yield 81 %; elemental analysis calcd (%) for $C_{30}H_{35}LaN_4O_7$ (702.8): C 51.3, H 5.0, N, 8.0; found: C 51.0, H 4.7, N 7.8; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 685 (100), $[LLa + 1]^+$; IR (KBr disk): $\tilde{\nu} = 3436$ br, 1627 s, 1469 s, 1444 s, 1406 m, 1326 m, 1241 s, 1219 s, 1083 m, 858 m, 749 m cm^{-1}.

[LY]: Yield 85 %; elemental analysis calcd (%) for $C_{30}H_{33}N_4O_6Y$ (634.5): C 56.8, H 5.2, N 8.8; found C 56.5, H 5.0, N 8.6; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 635 (100), $[LY + 1]^+$; IR (KBr disk): $\tilde{\nu} = 1627$ s, 1470 s, 1447 s, 1407 m, 1242 s, 1220 s, 1083 m, 859 m, 749 m cm^{-1}.

Tris[4-(2-hydroxy-3-methoxyphenyl)-3-aza-3-buten]aminato(3 –)gadolinium(III) · neodymium(III) nitrate · $2H_2O$: A mixture of [LGd] (0.36 g, 0.5 mmol) and of $Nd(NO_3)_3 \cdot 6H_2O$ (0.25 g, 0.56 mmol) in methanol (20 mL) was stirred until a light yellow precipitate appeared. The precipitate was filtered off, and washed with methanol and diethyl ether. Yield 0.47 g (88 %); elemental analysis calcd (%) for $C_{30}H_{37}GdN_7NdO_{17}$ (1069.1): C 33.7, H 3.5, N 9.2; found: C 33.8, H 3.2, N 8.9; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 971 (100), $[LGdNd(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3400$ br, 1626 s, 1559 m, 1446 s, 1384 s, 1299 s, 1228 s, 1074 m, 958 m, 856 m, 737 m cm^{-1}.

$[LGdCe(NO_3)_3] \cdot 2H_2O$: Yield 75 %; elemental analysis calcd (%) for $C_{30}H_{37}CeGdN_7O_{17}$ (1065.0): C 33.8, H 3.5, N 9.2; found: C 33.8, H 3.4, N 8.9; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 967 (100), $[LGdCe(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3400$ br, 1627 s, 1558 m, 1464 s, 1384 s, 1298 s, 1227 s, 1075 m, 958 m, 851 m, 740 m cm^{-1}.

$[LGdLa(NO_3)_3] \cdot 2H_2O$: Yield 50 %; elemental analysis calcd (%) for $C_{30}H_{37}GdLaN_7O_{17}$ (1063.8): C 33.9, H 3.5, N 9.2; found: C 33.8, H 3.4, N 8.9; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 966 (100), $[LGdCe(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3400$ br, 1626 s, 1559 m, 1466 s, 1439 s, 1384 s, 1298 s, 1228 s, 1074 m, 958 m, 855 m, 737 m cm^{-1}.

$[LLaGd(NO_3)_3] \cdot 2H_2O$: Yield 75 %; elemental analysis calcd (%) for $C_{30}H_{37}GdLaN_7O_{17}$ (1063.8): C 33.9, H 3.5, N 9.2; found: C 33.5, H 3.4, N 8.8; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 966 (100), $[LGdCe(NO_3)_2]^+$, 985 (52), $[LGdGd(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3435$ br, 1626 s, 1559 m, 1466 s, 1439 s, 1384 s, 1299 s, 1228 s, 1074 m, 957 m, 852 m, 737 m cm^{-1}.

$[LDyGd(NO_3)_3] \cdot 2H_2O$: Yield 69 %; elemental analysis calcd (%) for $C_{30}H_{37}DyGdN_7O_{17}$ (1087.4): C 33.1, H 3.4, N 9.0; found: C 32.9, H 3.4, N 8.9; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 989 (100), $[LDyGd(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu}$3400 br, 1626 s, 1559 m, 1470 s, 1440 s, 1384 s, 1300 s, 1230 s, 1073 m, 960 m, 852 m, 738 m cm^{-1}.

$[LDyLa(NO_3)_3] \cdot 4H_2O$: Yield 76 %; elemental analysis calcd (%) for $C_{30}H_{41}DyLaN_7O_{19}$ (1105.1): C 32.6, H 3.7, N 8.9; found: C 32.3, H 3.4, N 8.8; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 972 (100), $[LDyLa(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3430$ br, 1626 s, 1558 m, 1465 s, 1444 s, 1384 s, 1300 s, 1222 s, 1071 m, 960 m, 850 m, 735 m cm^{-1}.

$[LErGd(NO_3)_3] \cdot 2H_2O$: Yield 88 %; elemental analysis calcd (%) for $C_{30}H_{37}ErGdN_7O_{17}$ (1092.2): C 33.0, H 3.4, N 9.0; found: C 33.1, H 3.1, N 8.8; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 993 (100), $[LErGd(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3369$ br, 1626 s, 1562 m, 1471 s, 1441 s, 1384 s, 1303 s, 1230 s, 1074 m, 960 m, 854 m, 739 m cm^{-1}.

$[LErLa(NO_3)_3] \cdot 4H_2O$: Yield 76 %; elemental analysis calcd (%) for $C_{30}H_{41}ErLaN_7O_{19}$ (1109.8): C 32.5, H 3.7, N 8.8; found C 32.3, H 3.4, N 8.5; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 976 (100), $[LErLa(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3427$ br, 1626 s, 1561 m, 1468 s, 1444 s, 1384 s, 1300 s, 1223 s, 1072 m, 960 m, 850 m, 745 m cm^{-1}.

$[LYbGd(NO_3)_3] \cdot 2H_2O$: Yield 73 %; elemental analysis calcd (%) for $C_{30}H_{37}GdN_7O_{17}Yb$ (1097.9): C 32.8, H 3.4, N 8.9; found C 32.5, H 3.1, N 8.7; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 1001 (100), $[LYbGd(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3369$ br, 1627 s, 1562 m, 1472 s, 1440 s, 1384 s, 1303 s, 1232 s, 1075m, 961 m, 854 m, 740 m cm^{-1}.

$[LYbLa(NO_3)_3] \cdot 2H_2O$: Yield 70 %; elemental analysis calcd (%) for $C_{30}H_{37}LaN_7O_{17}Yb$ (1079.6): C 33.4, H 3.4, N 9.1; found: C 34.0, H 3.1, N 8.9; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 982 (100), $[LYbLa(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3436$ br, 1626 s, 1549 m, 1471 s, 1449 s, 1384 s, 1301 s, 1223 s, 1073 m , 962 m, 858 m, 739 m cm^{-1}.

$[LYCe(NO_3)_3] \cdot 2H_2O$: Yield 60 %; elemental analysis calcd (%) for $C_{30}H_{37}CeN_7O_{17}Y$ (996.7): C 36.2, H 3.7, N 9.8; found: C 35.9, H 3.4, N 9.5; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix): *m/z* (%): 898 (100), $[LYCe(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3408$ br, 1626 s, 1559 m, 1466 s, 1440 s, 1384 s, 1301 s, 1230 s, 1074 m, 958 m, 853 m, 737 m cm^{-1}.

$[LYNd(NO_3)_3] \cdot 2H_2O$: Yield 65 %; elemental analysis calcd (%) for $C_{30}H_{37}N_7NdO_{17}Y$ (996.7): C 36.0, H 3.8, N 9.8; found: C 35.7, H 3.5, N 9.6; MS (FAB$^+$, 3-nitrobenzyl alcohol matrix) : *m/z* (%): 902 (100), $[LYNd(NO_3)_2]^+$; IR (KBr disk): $\tilde{\nu} = 3408$ br, 1626 s, 1560 m, 1467 s, 1440 s, 1384 s, 1301 s, 1230 s, 1074 m, 958 m, 853 m, 737 m cm^{-1}.

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