Use of 155Gd, 151Eu, 166Er Mössbauer spectroscopy to characterize heterodinuclear Ln–Ln' complexes

Jean- Pierre Costes, Franck Nicodème, Takanari Ayabe, Masuo Takeda, Masashi Takahashi

Use of ^{155}Gd, ^{151}Eu, ^{166}Er Mössbauer Spectroscopy to characterize heterodinuclear Ln-Ln' complexes

Jean-Pierre Costes,[a*] Franck Nicodème,[a] Takanari Ayabe[b], Masuo Takeda[b], Masashi Takahashi[b*]

[a)] LCC-CNRS, Université de Toulouse, CNRS, Toulouse, France

[b)] Department of Chemistry, Faculty of Science, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan

Abstract

Use of ^{155}Gd Mössbauer spectroscopy allows a straightforward characterization of heterodinuclear Ln-Ln' complexes ($LLnLn'(NO_3)_3 \cdot (H_2O)_2$) with a tripodal ligand L, possessing two different N_4O_3 and O_3O_3 coordination sites. Thanks to the isomer shift value, the location of the Gd^{III} ion is confirmed; the Gd atom in the Gd–Ln' series (Ln' = Ce, Nd, Eu) occupies the inner N_4O_3 site with a eight-coordination (N_4O_3 + O), but on the other hand the Gd atom in the Ln–Gd series (Ln = Dy, Er, Yb) resides in the outer O_3O_3 site with a ten-coordination (O_3O_3 + O_2 +O_2). The smaller isomer shift values for the former indicate that coordination of the basic nitrogen atoms enhances the 6s orbital population. With the help of ^{151}Eu Mössbauer spectroscopy, we demonstrate that the Gd–Eu entity is a genuine heterodinuclear complex, in which the Gd^{III} ion is located in the inner site and the Eu^{III} ion in the outer oxygenated site. This result highlights the feasibility of our synthetic process described earlier to introduce in a heterodinuclear complex two consecutive ions of the periodic table. And the slow paramagnetic relaxation observed in the ^{166}Er Mössbauer spectrum of the Er–Gd complex confirms presence of a magnetic interaction in the genuine Er–Gd complex.

Introduction. The synthesis of heteronuclear lanthanide complexes still remains a challenge in coordination chemistry[1-11]. This is mainly due to the fact that these Ln^{III} ions possess an open shell made of 4f electrons which is screened by the filled 5s and 5p shells. So these ions are partially perturbed by the ligand field coming from the first coordination sphere of the ligands able to link to these different ions. The main consequence is that their chemical and physical properties do not greatly differ from those of the free ions in their most stable +III oxidation state. An important characteristic of these Ln^{III} ions comes from the decrease of their ionic radii with the increase of their atomic number. This lanthanide contraction, recently revisited [12], introduces an increase of the Lewis acidity on going from the larger La^{III} ion to the smaller Lu^{III} ion. We have previously used this property to suggest a synthetic pathway based on the use of a tripodal ligand possessing two different coordination sites able to coordinate two different Ln^{III} ions [3a]. Indeed, thanks to the positive fast-atom bombardment (FAB^+) mass spectrometry, we have shown that it was possible to isolate pure $Ln^{III}Ln'^{III}$ complexes by a stepwise process if the Ln^{III} ion introduced in the inner N_4O_3 coordination site has a greater Lewis acidity than the one introduced in the outer O_3O_3 site. But we were not able at that stage to obtain crystals in order to give structural determinations of such complexes. In a following work [3b], we could present structural determinations of complexes resulting from the different steps needed to success in isolating pure heterodinuclear Ln complexes. In a recent paper [6e] G. Aromi and coworkers have developed a one-pot ligand-based strategy in order to prepare heterodinuclear systems by use of a non-symmetric 6-(3-oxo-3-(2-hydroxyphenyl)propionyl)-pyridine-2-carboxylic acid ligand . The prepared $Ln^{III}Pr^{III}$ series allows the authors to show that the selectivity of their synthetic pathway, both in solution and in the solid state, is proportional to the difference between the ionic radius of Pr^{III} ion and that of its Ln^{III} partner (Δr). In the solid state, when the two Ln^{III} ions have a size difference of $\Delta r > 0.06$ Å, the synthetic pathway can selectively place each Ln^{III} inside the expected corresponding cavity. We want to show here, with help of different techniques, FAB^+ mass spectrometry, ^{155}Gd Mössbauer, SQUID data, that we can isolate pure heterodinuclear complexes and that it is also possible to obtain information on their magnetic properties. Indeed Mössbauer spectra of rare earth elements such as ^{151}Eu, ^{155}Gd and ^{166}Er provide local information on a magnetic material through hyperfine magnetic fields and electric field gradients [13], and have been applied to the magnetism of intermetallic compounds, alloys and oxides [14]. They are also useful to characterize the homo- and heterodinuclear Ln complexes having weak magnetic interactions.

Experimental Section

Materials. The tripodal LH_3 ligand was prepared according to literature procedure [15]. The mononuclear LGd, LLu [16] and dinuclear LGdLn'$(NO_3)_3\cdot(H_2O)_2$ (Ln' = Ce, Nd, Gd) and LLnGd$(NO_3)_3\cdot(H_2O)_2$ (Ln = Dy, Er, Yb) were prepared as previously described [2a,2b]. $Eu(NO_3)_3\cdot 6H_2O$ (Aldrich) was used as purchased. High-grade solvents (methanol, isopropanol, diethyl ether) were used for the syntheses of complexes.

LGdEu$(NO_3)_3\cdot(H_2O)_2$. A mixture of LGd (0,70 g, 1 mmol) and of $Eu(NO_3)_3.6H_2O$ (0.47 g, 1.05 mmol) in methanol (20 mL) was stirred for four hours at room temperature. The resulting light yellow precipitate was filtered off, washed with isopropanol and diethyl oxide. Yield 1.03 g (96 %). Anal. Calcd for $C_{30}H_{37}EuGdN_7O_{17}$ (1076.9): C 33.46, H 3.46, N 9.10. Found: C 33.38, H 3.15, N 8.80. MS (FAB^+, 3-nitrobenzyl alcohol matrix): *m/z* (%) 978 (100), $[LGdEu(NO_3)_2]^+$.

LLuEu$(NO_3)_3\cdot(H_2O)_2$(iPrOH). A mixture of LLu (0,72 g, 1 mmol) and of $Eu(NO_3)_3.6H_2O$ (0.47 g, 1.05 mmol) in methanol (20 mL) was stirred for four hours at room temperature. The resulting light yellow precipitate was filtered off, washed with isopropanol and diethyl oxide. Yield 0.99 g (86 %). Anal. Calcd for $C_{33}H_{45}EuLuN_7O_{18}$ (1154.7): C 34.33, H 3.93, N 8.49. Found: C 33.81, H 3.50, N 8.29. MS (FAB^+, 3-nitrobenzyl alcohol matrix): *m/z* (%) 997 (100), $[LLuEu(NO_3)_2]^+$.

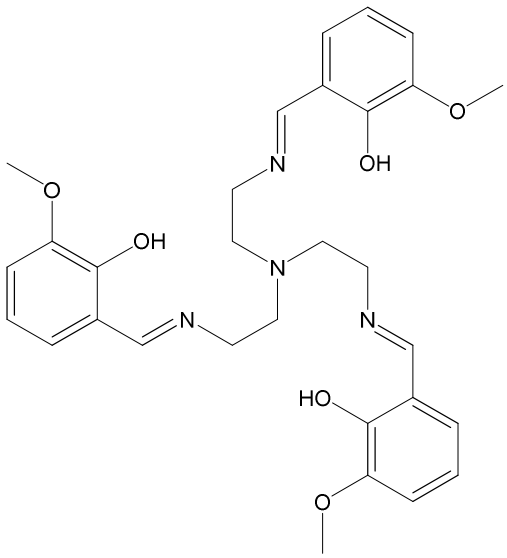
LTbEu$(NO_3)_3\cdot(H_2O)_2$. A mixture of LTb (0,70 g, 1 mmol) and of $Eu(NO_3)_3.6H_2O$ (0.47 g, 1.05 mmol) in methanol (20 mL) was stirred for four hours at room temperature. The resulting light yellow precipitate was filtered off, washed with isopropanol and diethyl oxide. Yield 0.85 g (79%). Anal. Calcd for $C_{30}H_{37}EuN_7O_{17}Tb$ (1078.6): C 33.41, H 3.46, N 9.09. Found: C 33.25, H 3.19, N 8.77. MS (FAB^+, 3-nitrobenzyl alcohol matrix): *m/z* (%) 981 (100), $[LTbEu(NO_3)_2]^+$.

Physical measurements. 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 with use of a SQUID-based sample magnetometer on a QUANTUM Design Model MPMS instrument under an applied field of 0.1 T. All data were corrected for diamagnetism of the samples estimated from Pascal's constants [17]. ^{155}Gd Mössbauer spectra of 86.5 keV transition were measured at 12 K using a ^{155}Eu/ $^{154}SmPd_3$ source (about 231 MBq) prepared by us on a WissEl 1200 Mössbauer system [18], and ^{151}Eu spectra of 21.55 keV at 77 K on a WissEl 500 Mössbauer system with use of a $^{151}Sm/SmF_3$ source (3.7 GBq). ^{166}Er Mössbauer spectrum was recorded on the same instrument as that of ^{155}Gd using a $^{166}Ho/Y_{0.6}Ho_{0.4}H_2$ source (1.5 GBq) [19]. The ^{155}Gd and ^{151}Eu

Mössbauer spectra were fitted assuming the sum-of-Lorentzian approximation. The ^{166}Er spectrum was analyzed using a Nowik-Wickman relaxation model [20].

Results and Discussion

Complexes. The different homo- and hetero-dinuclear Ln–Ln' complexes were prepared in a stepwise process with use of a tripodal ligand that is schematized hereunder (Scheme 1). This ligand possesses ten coordinating atoms, four nitrogen and six oxygen atoms, which give an inner N_4O_3 and an outer O_3O_3 coordination sites. The three central phenol functions belonging to the two sites are able to deprotonate. There are only few structural determinations of Ln complexes made with this ligand, such as $[LYb(OCMe_2)La(NO_3)_2][La(NO_3)_5]$ [2a], $[LEu(OH_2)Na(ClO_4)]$ [3b] or $[LDy(H_2O)Dy(ovan)(H_2O)]$ $(NO_3)_2(H_2O)_2$ complexes [3b]. According



Scheme 1. The tripodal LH_3 ligand used in the preparation of different heterodinuclear Ln–Ln' complexes.

to the previously described experimental process [3], mixing $Ln(NO_3)_3$, xH_2O with the LH_3 ligand yields a first complex in which the Ln ion enters into the O_3O_3 site. The three phenol functions are deprotonated but the three liberated protons are picked by the three nitrogen imine functions, the isolated complex corresponding to the $[(LH_3)Ln(NO_3)_3]$ formulation. Deprotonation of this entity induces migration of the Ln ion into the N_4O_3 inner site and formation of a neutral LLn complex. Reacting this neutral compound with another $Ln'(NO_3)_3{\cdot}6H_2O$ salt allows isolation of a $LLnLn'(NO_3)_3(H_2O)_2$ complex, the Ln^{III} ion

appearing first in the compound name being located in the inner N_4O_3 site while the following Ln^{III} ion is in the outer O_3O_3 site.

Unfortunately crystallization of these complexes is not an easy task, so that they have been characterized by their positive fast-atom bombardment $(FAB)^+$ mass spectra in 3-nitrobenzyl alcohol matrices [3a]. Due to the rich isotopic family of Ln ions, it has been easy to know if the isolated complexes were pure Ln-Ln' samples or mixtures of Ln–Ln, Ln–Ln' and Ln'–Ln' complexes. As the Ln^{III} ions have very similar chemical properties, it is difficult to prepare complexes assembling two different Ln^{III} ions. Our previous study has shown that pure heterodinuclear Ln-Ln' complexes are isolated if the Ln ion present in the inner N_4O_3 coordination site is a better Lewis acid than the one introduced in the outer O_3O_3 site [3a]. If that rule is not respected, the resulting heterodinuclear complex is polluted by a large amount, around 15-20 %, of the homodinuclear complex involving the better Lewis acid Ln^{III} ion. In other words, the Ln^{III} ion with the lowest ionic radius must be introduced first. In the case of the $LGdEu(NO_3)_3{\cdot}(H_2O)_2$ complex, the signal corresponding to the $LGdEu(NO_3)_2]^+$ cation appears at *m/z* equal to 978 u. In that particular case, it is difficult to know if the signals corresponding to the $LGdGd(NO_3)_2]^+$ and $LEuEu(NO_3)_2]^+$ cations are present. Because of the large isotopic Gd family, the three signals are mixed. In order to check that point, we prepared the $LTbEu(NO_3)_3{\cdot}(H_2O)_2$ complex. The FAB^+ analysis confirms that the signal centered at 981 u does correspond to the expected $LTbEu(NO_3)_2]^+$ cation (Figure S1, Supp Mat). So in a dimethylformamide solution, we only observe traces of the signals due to the homodinuclear $LTbTb(NO_3)_2]^+$ (*m/z* = 987) and $LEuEu(NO_3)_2]^+$ (*m/z* = 973) species. According to the initial structural determinations, it is expected that an ancillary solvent molecule (acetone, water) is coordinated to the Ln^{III} ion present in the N_4O_3 site and that two nitrate anions are chelated to the Ln^{III} ion linked to the outer site, so that the Ln^{III} ions are respectively eight-coordinate (N_4O_3 + O) and ten-coordinate ($O_3O_3 + O_2 + O_2$). But these complexes can also be characterized by use of the ^{155}Gd Mössbauer spectroscopy, which is able to indicate, thanks to the isomer shift parameter, the nature of the coordination site. As large amounts of each sample are needed to record the ^{155}Gd Mössbauer spectra, around 1000 mg, this study was performed with the family of $LLnLn'(NO_3)_3(H_2O)_2$ complexes that can be prepared in large amounts.

Magnetic properties

The thermal dependences of the $\chi_M T$ products for complexes $LGdEu(NO_3)_3{\cdot}(H_2O)_2$ and $LLuEu(NO_3)_3{\cdot}(H_2O)_2$(iPrOH) are reported in the Figure 1. For the Lu-Eu pair, a constant $\chi_M T$

decrease is observed, going from 2.2 $cm^3\,mol^{-1}\,K$ at 300 K to 0 $cm^3\,mol^{-1}\,K$ at 2 K. The 300 K value is larger than expected for a free Eu^{III} ion (1.54 $cm^3\,mol^{-1}\,K$). A similar variation is observed for the Gd–Eu pair, with a $\chi_M T$ product varying from 9.77 $cm^3\,mol^{-1}\,K$ at 300 K to 6.98 $cm^3 mol^{-1} K$ at 2 K. The $\Delta\chi_M T$ difference between these two curves gives a straight line with a constant value of 7.4 $cm^3\,mol^{-1}\,K$ from 300 to 4 K, followed by a slight decrease to 7.0 $cm^3\,mol^{-1}\,K$ at 2 K. The observed value, which corresponds to the $\chi_M T$ product for a non interacting gadolinium ion, is slightly lower than expected for a free ion (7.8 $cm^3\,mol^{-1}\,K$) but such a difference comes from the $\chi_M T$ value of the Lu–Eu pair, which is larger than expected. This continuous thermal dependence does confirm that our $LGdEu(NO_3)_3{\cdot}(H_2O)_2$ complex is a pure complex and not a mixture of Gd–Gd and Eu–Eu pairs, that would be characterized by a slight $\Delta\chi_M T$ curvature in the 10–2 K temperature range due to an antiferromagnetic Gd–Gd interaction in the Gd–Gd pair [3a].

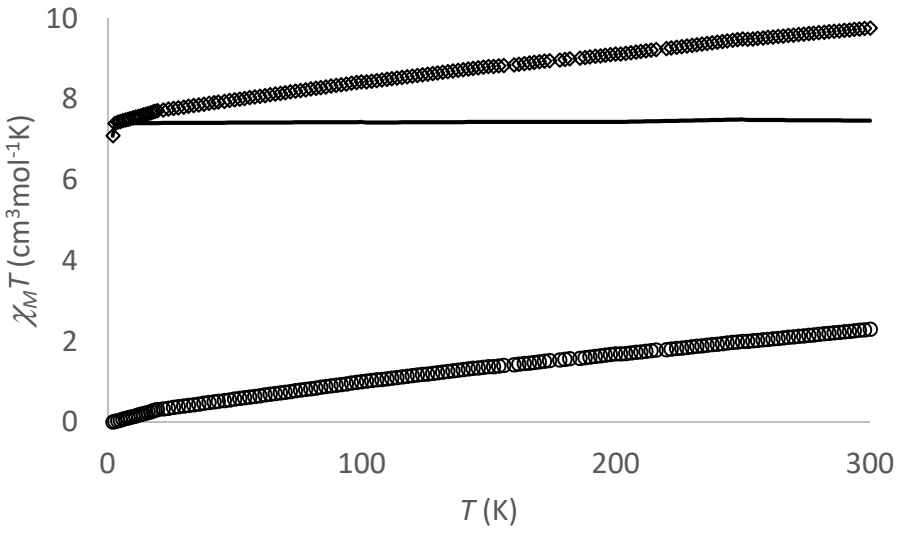


Figure 1. Thermal dependence of $\chi_M T$ for the Gd–Eu (diamonds) and Lu–Eu (circles) complexes along with the $\Delta\chi_M T = (\chi_M T_{Gd\text{-}Eu} - \chi_M T_{Lu\text{-}Eu})$ (line).

Mössbauer spectra

Some of the ^{155}Gd Mössbauer spectra of our different complexes, which were run at 12K, appear in Figure 2 while the entire set of spectra are collated in Figure S2. Note that the weak

absorption is due to the large γ-ray energy (86.55 keV) and to the small recoil-free fraction for the molecular compounds. The hyperfine parameters are reported in Table 1, which gives the isomer shift δ (relative to the source), the quadrupole coupling constant e^2qQ and the experimental linewidths Γ_{exp} along with the expected first Gd coordination sphere. The δ values of our different dinuclear Ln complexes are comprised in between the GdF_3 and Gd_2O_3 δ values, 0.67–0.50 mm s^{-1}. We can remark first that this δ extent is not very large but that a relationship between these δ values and the nature of atoms participating in the Gd first coordination sphere has been found. δ decreases on going from O_{10} to N_4O_4 and to N_9 environments. And there is a relationship between the coordination number and δ value if we consider Gd complexes in an environment made of oxygen atoms only [18]. As the $\Delta R/R$ ratio is negative for ^{155}Gd (ΔR being the difference between the nuclear radii of the excited and the ground state), the isomer shift decreases on going from GdF_3 to Gd_2O_3 samples. GdF_3 is considered as an extremely ionic compound, with the Gd ion in a $4f^7$ electron configuration. So an increase of the electron density at the Gd nucleus introduces partial covalency, which corresponds to the observation of a lower δ value because of the negative $\Delta R/R$ ratio. Such a situation can happen by addition of electron density to the 6s Gd orbitals. It is the main contribution to the δ values, the s orbitals being the only ones to transmit an appreciable density to the Gd nucleus.

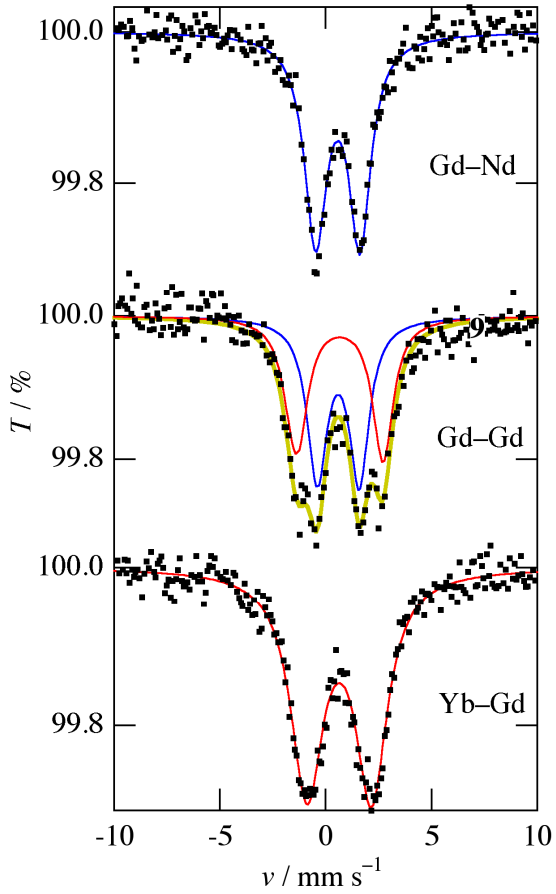


Figure 2 ^{155}Gd Mössbauer spectra at 12 K for LLnLn'$(NO_3)_3\cdot(H_2O)_2$ (Ln-Ln' = Gd–Nd (top), Gd–Gd (middle), Yb–Gd (bottom).

Applied to heterodinuclear Ln complexes, Mössbauer data confirm the existence of such complexes as pure heterodinuclear complexes and also give an information on the location of the Gd ions. The spectra are obviously different between the two series of GdLn or LnGd complexes. The GdLn series corresponds to LGdLn $(NO_3)_3\cdot(H_2O)_2$ (Ln = Ce, Nd, Eu) complexes while the LnGd series is exemplified by LLnGd$(NO_3)_3\cdot(H_2O)_2$ (Ln = Dy, Er, Yb) entities (Figures 2 and S2). The δ values for the former series (0.57–0.60 mm s^{-1}) are clearly smaller than those for the latter one (0.64–0.66 mm s^{-1}). The δ values for the latter series are close to those of the 3d–Gd complexes [21] and the polyethylene glycol complexes having GdO_{10} or GdO_9 coordination configurations [22]. Taking into account the coordination environment for the tripodal ligand, we can definitely assign the Gd sites; the Gd atom in Ln–Gd complexes occupies the outer O_3O_3 site while that in Gd–Ln entities the inner N_4O_3 site of the ligand. This affords a support for the previous conclusion derived from the FAB$^+$-MS experiments [3a]. The smaller δ values in Gd–Ln complexes, suggesting an increase in covalency for the Gd ion located in the N_4O_3 site, are consistent with our previous observations

on the nitrogen coordinating compounds including the N_9 environment of the $Gd(Pr^nTBP)_3(OTf)_3$ complex involving three N_3-tridentate ligands [21-22]. Concomitance of two Gd ions with a different location in $LGdGd(NO_3)_3\cdot(H_2O)_2$ is confirmed by the existence of two well-resolved absorptions characterized by different δ (0.59 and 0.65 mm s^{-1}) and e^2qQ (4.25 and 8.80 mm s^{-1}) values. The ratio of the absorption area for outer site/inner site (A_{outer}/A_{inner}) is 0.93(2), not far from the expected theoretical 1 value, so suggesting that the Gd^{III} ions occupy the two sites equally. The slightly larger absorption area of the inner site is attributable to stronger Gd interaction with the chelating donor atoms of the N_4O_3 coordination site, induced by the increased covalency through a larger recoil-free fraction. This also agrees with the structural determinations of $[LYb(OCMe_2)La(NO_3)_2][La(NO_3)_5]$ [2a] and $[LDy(H_2O)Dy(ovan)(H_2O)](NO_3)_2(H_2O)_2$ [3b]. The (equivalent isotropic) temperature factors U_{eq} for the inner site are slightly smaller than those for the outer site. It is well-known that the recoil-free fraction derived from the Mössbauer spectra has a good relation with the thermal factors of X-ray structural determinations [23]. An even larger deviation in the ratio of the absorption area has been recently reported for Gd ions belonging to different coordination sites of $Gd_2CoGe_4O_{12}$ entities [24].

The e^2qQ value reflects the symmetry of the coordination geometry because the equal occupation of the seven 4f orbitals counteracts to compensate the electrical field gradient induced by the 4f electrons. The e^2qQ values for $LGdLn(NO_3)_3\cdot(H_2O)_2$ (Ln = Ce, Nd, Eu; 4.11–4.48 mm s^{-1}) entities are obviously smaller than those for $LLnGd(NO_3)_3\cdot(H_2O)_2$ (Ln = Dy, Er, Yb; 5.66–6.62 mm s^{-1}) compounds. The narrow distribution of the e^2qQ values for the $N_4O_3 + O$ configuration indicates that the coordination geometries of the inner Gd site in $LGdLn(NO_3)_3\cdot(H_2O)_2$ are essentially similar, implying that the size of the Ln^{3+} in the outer site scarcely affects the coordination of the inner site. Although we have no crystal structure of the Gd-containing dinuclear complex, the crystal structures of related complexes, $LYb(acetone)La(NO_3)^{2+}$ [2] and $LDyDy(H_2O)_2(ovan)^{2+}$ (ovan = orthovanillin) [3b], are known. Application of the "SHAPE" program [25] indicates that the Yb and Dy ions in the inner N_4O_3 + O coordination spheres are in a slightly deformed biaugmented trigonal prism geometries, with small values for the shape measure parameter S_{BTPR}, equal to 1.6 (complex YbLa) and to 2.3 (complex DyDy). The corresponding e^2qQ values agree with this observation. The e^2qQ values for the O_{10} configuration ($O_3O_3 + O_2 + O_2$) are large, being even larger than those of 3d–4f complexes (4.40–4.82 mm s^{-1}) in the GdO_9 configuration ($O_2O_2 + O + O_2 + O_2$) [21], in agreement with larger deformations from regular polyhedron.

^{151}Eu Mössbauer data are limited to LGdEu$(NO_3)_3 \cdot (H_2O)_2$ (Table 2 and Figure S3). Two remarks can be made. First the $\Delta R/R$ ratio is positive for ^{151}Eu, so that the isomer shift increases on going from EuF_3 to Eu_2O_3 samples. Then the δ range is larger than in the ^{155}Gd Mössbauer spectroscopy, from 0.00 for EuF_3 to 0.93 mm s^{-1} for Eu_2O_3. The low isomer shift, 0.14 mm s^{-1} along with the large experimental e^2qQ value (7.50 mm s^{-1}) are in accordance with a coordination of the Eu^{III} ion in the outer O_3O_3 coordination site of the ligand, in a O_{10} environment. But the main interest of this ^{155}Gd and ^{151}Eu Mössbauer study consists in showing that the LGdEu$(NO_3)_3 \cdot (H_2O)_2$ heterodinuclear complex is not a mixture of LGdGd$(NO_3)_3 \cdot (H_2O)_2$ and LEuEu$(NO_3)_3 \cdot (H_2O)_2$ compounds. Although the ionic radii of the Eu^{III} and Gd^{III} ions are very close, the ^{155}Gd and ^{151}Eu δ values do agree with a location of the Gd^{III} ion in the inner N_4O_3 coordination site and of the Eu^{III} ion in the outer O_3O_3 coordination site of the ligand. This result highlights the efficiency of the experimental process for the preparation of heterodinuclear Ln–Ln' complexes, which is quite uncommon till now for two consecutive ions of the periodic table [6e, 26].

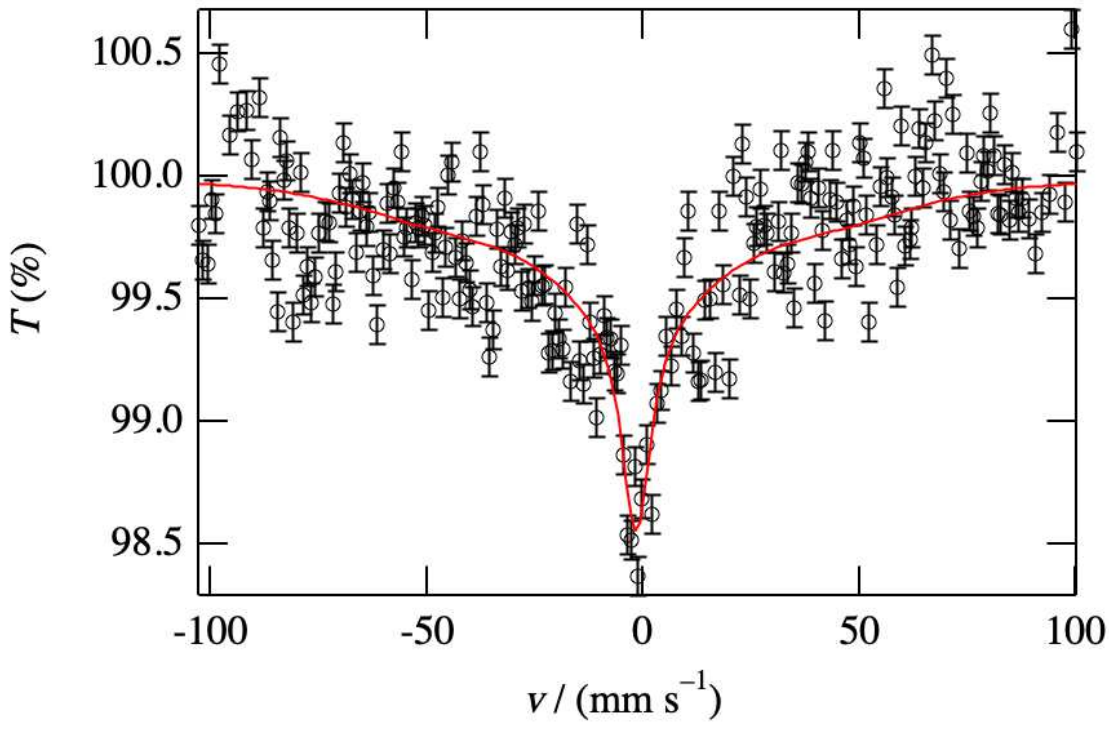


Figure 3. ^{166}Er Mössbauer spectrum of the LErGd$(NO_3)_3 \cdot (H_2O)_2$ complex at 12 K.

Hyperfine parameters: Γ_{exp} = 8.3(6) mm s^{-1}, τ = 45(7) ps, B_{hf} = 765(81) T, e^2qQ = 0 mm s^{-1} (fixed).

The broad linewidths of ^{155}Gd spectra observed in our Ln–Gd binuclear complexes are ascribed to the broadening due to the paramagnetic relaxation. Thus we measured the ^{166}Er Mössbauer spectrum of the LErGd$(NO_3)_3\cdot(H_2O)_2$ complex at 12 K, the same temperature as the ^{155}Gd spectra (Table 3). The ^{166}Er nucleus is very sensitive to magnetic ordering and suitable for such a purpose. The observed broad and structureless spectrum is typical of a slow paramagnetic relaxation (Figure 3). The spectrum analysis using the Nowik-Wickman model for the paramagnetic relaxation gave the relaxation time (τ) to be 45(7) ps and an internal magnetic field (B_{hf}) of 765(81) T. The e^2qQ value was rather arbitrary fixed to 0 mm s^{-1} for the fitting of the spectrum. Although this assumption is not proper in that case, we could not find an optimal solution for the unfixed e^2qQ value. A small and negative e^2qQ value gives a better fitting but does not affect the relaxation time. The τ value is much smaller than those for some mononuclear complexes including Er^{3+}–β-diketonato and EDTA complexes (0.1–1.7 ns) and Er metal (6.1 ns) [19]. τ strongly depends on the metal distance, here Er–Gd and the coordination number. Since the antiferromagnetic interaction becomes noticeable below 15 K, our observation is quite reasonable, and the broadening of ^{155}Gd Mössbauer spectra is also expected (Figure S2). Note again that the δ and e^2qQ values for the Gd ion in this Er-Gd complex do agree with the presence of the Gd ion in the outer coordination site of the ligand.

Conclusion

The ^{155}Gd Mössbauer data bring new information on the behaviour of complexes involving Gd ions. In the case of heterodinuclear Gd–Ln or Ln–Gd complexes and on the basis of ^{155}Gd Mössbauer spectra, we have been able to assign unambiguously the location of Gd ions in the N_4O_3 or O_3O_3 coordination site of the tripodal ligand used for their preparation. These results bring an experimental proof for the presence of a partial covalent character corresponding to a partial occupation of the 6s orbitals when the Gd ion is in the inner N_4O_3 coordination site. On the contrary an ionic character is prevailing for Gd^{III} ions in the outer coordination site. These two different behaviours are also concomitant in the homodinuclear Gd–Gd complex. Eventually these Mössbauer results highlight existence of a pure and unique heterodinuclear Gd–Eu complex involving two consecutive ions of the periodic table and confirm the efficiency of our experimental process to prepare heterodinuclear Ln complexes. The very rapid relaxation time observed in the ^{166}Er Mössbauer spectrum of the Er–Gd complex confirms presence of an antiferromagnetic interaction in the genuine Er–Gd complex.

Acknowledgement

A part of this study was supported by the Inter-University Program for the Joint Use of JAEA Facilities (Proposal No. 6101).

References

1 (a) N. André, R. Scopelliti, C. Hopfgartner, C. Piguet, J.-C. G. Bünzli. Discriminating between lanthanide ions: self-assembly of heterodimetallic triple-stranded helicates. Chem. Commun. 2002, 214–215;
(b) N. André, T. B. Jensen, R. Scopelliti, D. Imbert, M. Elhabiri, G. Hopfgartner, C. Piguet, J.-C. G. Bünzli. Supramolecular recognition of heteropairs of lanthanide ions: a step toward self-assembled bifunctional probes. Inorg. Chem. 43 (2004) 515–529.
(c) S. Floquet, M. Borkovec, G. Bernardinelli, A. Pinto, L.-A. Leuthold, G. Hopfgartner, D. Imbert, J.-C. G. Bünzli, C. Piguet. Programming heteropolymetallic lanthanide helicates: thermodynamic recognition of different metal ions along the strands. Chem. - Eur. J. 10 (2004) 1091–1105 ;
(d) N. Dalla-Favera, J. Hamacek, M. Borkovec, D. Jeannerat, G. Ercolani, C. Piguet. Tuneable intramolecular intermetallic interactions as a new tool for programming linear heterometallic 4f–4f complexes. Inorg. Chem. 46 (2007) 9312-9322.

2 J. P. Costes, F. Dahan, A. Dupuis, S. Lagrave, J. P. Laurent. Homo- (4f, 4f) and heterodimetallic (4f, 4f') complexes. The first structurally characterized example of a heterodimetallic (Yb, La) complex (1'). Magnetic properties of 1' and of a homodinuclear (Gd, Gd) analogue. Inorg. Chem. 37 (1998) 153–155;

3 (a) J. P. Costes, F. Nicodème. Unequivocal synthetic pathway to heterodinuclear (4f,4f') complexes: magnetic study of relevant (Ln^{III}, Gd^{III}) and (Gd^{III}, Ln^{III}) complexes. Chem. - Eur. J. 8 (2002) 3442–3447;
(c) J. P. Costes, F. Dahan, F. Nicodème. Structure-based description of a step-by-step synthesis of homo- and heterodinuclear (4f, 4f') lanthanide complexes. Inorg. Chem. 42 (2003) 6556–6563.

4 (a) S. Faulkner, S. J. A. Pope. Lanthanide-sensitized lanthanide luminescence: terbium-sensitized ytterbium luminescence in a trinuclear complex. J. Am. Chem. Soc. 125 (2003) 10526–10527;
(b) L. S. Natrajan, A. J. L. Villaraza, A. M. Kenwright, S. Faulkner. Controlled preparation of a heterometallic lanthanide complex containing different lanthanides in symmetrical binding pockets. Chem. Commun. (2009) 6020–6022;
(c) M.P. Placidi, A. J. L. Villaraza, L. S. Natrajan, D. Sykes, A. M. Kenwright, S. Faulkner. Synthesis and spectroscopic studies on azo-dye derivatives of polymetallic lanthanide complexes: using diazotization to link metal complexes together. J. Am. Chem. Soc. 131 (2009) 9916–9917;
(d) J. A. Tilney, T. J. Sørensen, B. P. Burton-Pye, S. Faulkner. Self-assembly between dicarboxylate ions and a binuclear europium complex: formation of stable adducts and heterometallic lanthanide complexes. Dalton Trans. 40 (2011) 12063–12066.

5 P. Zhu, N. Pan, R. Li, J. Dou, Y. Zhang, D. Y. Y. Cheng, D. Wang, D. K. P. Ng. Jiang, J. Electron-donating alkoxy-group driven synthesis of heteroleptic tris(phthalocyaninato) lanthanide(III) triple-deckers with symmetrical molecular structure. Chem. - Eur. J. 11 (2005) 1425–1432.

6 (a) D. Aguilà, L. A. Barrios, F. Luis, A. Repollés, O. Roubeau, S. J. Teat, G. Aromí. Synthesis and properties of a family of unsymmetric dinuclear complexes of Ln^{III} (Ln = Eu, Gd, Tb). Inorg. Chem. 49 (2010) 6784–6786;

(b) D. Aguilà, L. A. Barrios, V. Velasco, L. Arnedo, N. Aliaga-Alcalde, M. Menelaou, S. J. Teat, O. Roubeau, F. Luis, G. Aromí. Lanthanide contraction within a series of asymmetric dinuclear[Ln_2] complexes. Chem. - Eur. J. 19 (2013) 5881–5891;
(c) D. Aguilà, L. A. Barrios, V. Velasco, O. Roubeau, A. Repollés, P. J. Alonso, J. Sesé, S. J. Teat, F. Luis, G. Aromí. Heterometallic [LnLn'] lanthanide complexes: towards a chemical design of two-qubit molecular spin quantum gates. J. Am. Chem. Soc. 136 (2014) 14215–14222;
(d) J. Gónzalez-Fabra, N. A. G. Bandeira, V. Velasco, L. A. Barrios, J. Gónzalez-Fabra, C. Bo, S. J. Teat, O. Roubeau, G. Aromí. Thermodynamic stability of heterometallic [LnLn'] complexes: synthesis and DFT studies. Chem. - Eur. J. 23 (2017) 5117–5125;
(e) D. Aguilà, V. Velasco, L. A. Barrios, S. J. Teat, O. Roubeau, G. Aromí. Inorg. Chem. 57 (2018) 8429-8439.

7 D. J. Lewis, P. B. Glover, M. C. Solomons, Z. Pikramenou. Purely heterometallic lanthanide(III) macrocycles through controlled assembly of disulfide bonds for dual color emission. J. Am. Chem. Soc. 133 (2011) 1033–1043.

8 R. Sato, K. Suzuki, M. Sugawa, N. Mizuno. Heterodinuclear lanthanoid containing polyoxometalates: stepwise synthesis and single-molecule magnet behavior. Chem. - Eur. J. 19 (2013) 12982–12990.

9 Y. Lan, S. Klyatskaya, M. Ruben, O. Fuhr, W. Wernsdorfer, A. Candini, V. Corradini, A. Lodi Rizzini, U. del Pennino, F. Troiani, L. Joly, D. Klar, H. Wende, M. Affronte. Magnetic interplay between two different lanthanides in a tris-phthalocyanato complex: a viable synthetic route and detailed investigation in the bulk and on the surface. J. Mater. Chem. C, 3 (2015) 9794–9801.

10 F. Artizzu, F. Quochi, L. Marchio, R. F. Correja, M. Saba, A. Serpe, A. Mura, M. L. Mercuri, G. Bongiovanni, P. Deplano. Ln_3Q_9 as a molecular framework for ion-size-driven assembly of heterolanthanide (Nd, Er, Yb) multiple near-infrared emitters. Chem. -Eur. J. 21 (2015) 3882–3885.

11 M. A. Polovkova, A. G. Martynov, K. P. Birin, S. E. Nefedov, Y. G. Gorbunova, A. Y. Tsivadze. Determination of the structural parameters of heteronuclear (phthalocyaninato)bis(crownphthalocyaninato)lanthanide(III) triple-deckers in solution by simultaneous analysis of NMR and single-crystal X-ray data. Inorg. Chem. 55 (2016) 9258–9269.

12 P. D'Angelo, A. Zitolo, V. Migliorati, G. Chillemi, M. Duvail, P. Vitorage, S. Abadie, R. Spezia. Revised ionic radii of lanthanoid(III) ions in aqueous solution. Inorg. Chem. 50 (2011) 4572–4579.

13 G. A. Stewart, Some applications of rare earth Mössbauer spectroscopy. Mater. Forum 18 (1994) 177.

14 For example: (a) M. A. Albedah, F. Nejadsattari, Z. M. Stadnik, Y. Liu, G.-H. Cao, Mössbauer spectroscopy measurements on the 35.5 K superconductor $Rb_{1-\delta}EuFe_4As_4$. Phys. Rev. B97 (2018) 144426-1–144426-9;
(b) S. Klenner, L. Heletta, R. Pöttgen, Diluting europium spins – a magnetic and ^{151}Eu Mössbauer spectroscopic investigation of the solid solution $Eu_{1-x}Sr_xPtIn_2$. Dalton Trans. 48 (2019) 3648–3657;
(c) R. Pöttgen, K. Latka, ^{155}Gd Mössbauer spectroscopy on intermetallics – An overview. Z. Anorg. Allg. Chem. 636 (2010) 2244–2255;

(d) P. Lemoine, N. R. Lee-Hone, D. H. Ryan, A Vernière, B. Malaman, G. Le Caër, Neutron powder diffraction and Mössbauer spectroscopy (^{119}Sn and ^{155}Gd) studies of the CeScSi-type GdMgSn and GdMgPb compounds. Phys. Rev. B89 (2014) 174428-1–174428-9;
(e) G. A. Stewart, J. M. Cadogan, W. D. Hutchison, D. H. Ryan, A Mössbauer study of $DyCrO_4$ and $ErCrO_4$. AIP Adv. 9 (2019) 035320-1–4;
(f) A. Legros, D. H. Ryan, P. Dalmas de Réotier, A. Yaouanc, C. Marin, ^{166}Er Mössbauer spectroscopy study of magnetic ordering in a spinel-based potential spin-ice system: $CdEr_2S_4$. J. Appl. Phys. 117 (2015) 17C701-1–17C70103.

15 S. Liu, L. W. Yang, S. J. Rettig, C. Orvig. Bulky ortho 3-methoxy groups on N_4O_3 amine phenol ligands producing six-coordinate bis(ligand)lanthanide complex cations $[Ln(H_3L)_2]^{3+}$ (Ln = Pr, Gd; H_3L = tris(((2-Hydroxy-3-Methoxybenzyl)amino)ethyl)-amine. Inorg. Chem. 32 (1993) 2773–2778.

16 E. Lucaccini, J. J. Baldoví, L. Chelazzi, A. L. Barra, F. Grepioni, J. P. Costes, L. Sorace. Electronic structure and magnetic anisotropy in lanthanoid single-ion magnets with C_3 symmetry: the Ln(trenovan) series. Inorg. Chem. 56 (2017) 4728–4738.

17 P. Pascal. Magnochemical studies. Ann. Chim. Phys. 19 (1910) 5–70.

18 J. Wang, J. Abe, T. Kitazawa, M. Takahashi, M. Takeda. ^{155}Gd Mössbauer spectroscopic study of $GdM(CN)_6{\cdot}4H_2O$ (M = Cr^{III}, Fe^{III} and Co^{III}) and $KGdM(CN)_6{\cdot}3H_2O$ (M = Fe^{II} and Ru^{II}). Z. Naturforsch. 57a (2002) 581–585.

19 J. Wang, M. Takahashi, M. Takeda. Crystal structures and ^{166}Er Mössbauer spectra for some β-diketonatoerbium(III) complexes. Bull. Chem. Soc. Jpn. 75 (2002) 735–740.

20 I. Nowik, H. H. Wickman. Relaxation phenomena in Mössbauer spectra of magnetically ordered erbium ions in $ErFeO_3$. Phys. Rev. Lett. 17 (1966) 949 − 951.

21 T. Ayabe, J. P. Costes, L. Vendier, A. Geist, M. Takeda, M. Takahashi, Contribution of ^{155}Gd Mössbauer data to the study of the magnetic interaction in heterodinuclear (3d-Gd) coordination complexes. Dalton. Trans. 48 (2019) 6872–6878.

22 M. Takeda, J. Wang, T. Nishimura, K. Suzuki, T. Kitazawa, M. Takahashi. ^{155}Gd Mössbauer isomer shifts and quadrupole coupling constants of gadolinium complexes. Hyperfine Interact. 156/157 (2004) 359–364.

23 (a) C. I. R. Magalhães, A. C. Gomes, A. D. Lopes, I. S. Gonçalves, M. Pillinger, E. Jin, I. Kim, Y. H. Ko, K. Kim, I. Nowik, R. H. Herber, Ferrocene and ferrocenium inclusion compounds with cucurbiturils: a study of metal atom dynamics probed by Mössbauer spectroscopy. Phys. Chem. Chem. Phys. 19 (2017) 21548.
(b) B. Bogolsavsky, I. Nowik, R. H. Herber. Hyperfine interactions and metal atom dynamics in a number of stannyl phosphide compounds and the detailed crystal structure of triphenyltin chloride revisited. Eur. J. Inorg. Chem. (2016) 1619.
(c) R. H. Herber, I. Nowik. Mean-square amplitudes of vibration and anisotropic motion of metal atoms in iron organometallics. Hyperfine Interct. 144/145 (2002) 249.

24 D. Xu, M. Avdeev, P. D. Battle, D. H. Ryan. Magnetic properties of $Ln_2CoGe_4O_{12}$, $LnCoGe_4O_{12}$ (Ln = Gd, Tb, Dy, Ho, Er; B = Sc, Lu). Dalton Trans. 46 (2017) 15778–15788.

25 M. Llunell, D. Casanova, J. Cirera, J., J. M. Bofill, P. Alemany, S. Alvarez, M. Pinsky, D. Avnir, D. SHAPE, v1.1b; University of Barcelona: Barcelona, Spain, 2005.

26 M. A. Polovkova, A. G. Martynov, K. P. Birin, S. E. Nefedov, Y. G. Gorbunova, A. Yu. Tsivadze, Determination of the structural parameters of heteronuclear (phthalocyaninato)bis(crownphthalocyaninato)lanthanide(III) triple deckers in solution by

simultaneous analysis of NMR and single-crystal x-ray data. Inorg. Chem. 55 (2016) 9258–9269.

Table 1. ^{155}Gd Mössbauer parameters for dinuclear Ln–Ln' complexes containing Gd^{III} ions at 12 K.[a]

compounds	δ [b] mm s^{-1}	e^2qQ [c] mm s^{-1}	Γ_{exp} mm s^{-1}	coord. config.	reference
Gd_2O_3 (site1)	0.50	11.02	0.80	GdO_6	
(site2)	0.49	5.71	0.80	GdO_6	
$LGdCe(NO_3)_3\cdot(H_2O)_2$	0.59	4.11	1.56	GdN_4O_4	2b
$LGdNd(NO_3)_3\cdot(H_2O)_2$	0.57	4.48	1.24	GdN_4O_4	
$LGdEu(NO_3)_3\cdot(H_2O)_2$	0.60	4.39	1.56	GdN_4O_4	
$LGdGd(NO_3)_3\cdot(H_2O)_2$ (inner site)	0.59	4.25	1.11	GdN_4O_4	2a
(outer site)	0.65	8.80	1.14	GdO_{10}	2a
$LDyGd(NO_3)_3\cdot(H_2O)_2$	0.66	6.62	2.10	GdO_{10}	2a
$LErGd(NO_3)_3\cdot(H_2O)_2$	0.65	5.66	1.92	GdO_{10}	2b
$LYbGd(NO_3)_3\cdot(H_2O)_2$	0.64	6.56	1.81	GdO_{10}	2b
GdF_3	0.67	5.68	0.92	GdF_9	2b

[a] Experimental errors, δ: ± 0.02 mm s^{-1}, e^2qQ and Γ_{exp} : 0.05 mm s^{-1}. [b] Relative to the $^{155}Eu/^{154}SmPd_3$ source and at 12 K. [c] Asymmetry parameters were fixed to be 0.0.

Table 2. ^{151}Eu Mössbauer parameters at 78 K for heterodinuclear complexes with Eu^{III} ions.[a]

compounds	δ [b] mm s^{-1}	e^2qQ [c] mm s^{-1}	Γ_{exp} mm s^{-1}	Coordination configuration
Eu_2O_3	0.93(2)	7.7(5)	3.5(1)	EuO_6
$LGdEu(NO_3)_3 \cdot (H_2O)_2$	0.14(3)	7.5(7)	2.9(1)	EuO_{10}
EuF_3	0.0(1)	6.9(8)	3.4(1)	EuF_9

[a] Experimental errors, δ: ±0.03 mm s^{-1}, e^2qQ: ±0.8 mm s^{-1}, Γ_{exp}: ±0.3 mm s^{-1}. [b] Relative to EuF_3 at 78 K. [c] Asymmetry parameters were fixed to be 0.0.

Graphical Abstract