

Preliminary communication / Communication

Covalent tripods for assembling triple-helical lanthanide podates

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Abstract

The nonadentate podands L^7 , L^8 et L^9 have been prepared according to a multi-step strategy using the flexible 3-(2-hydroxy-ethyl)-pentane-1,5-diol, 4-(3-hydroxy-propyl)-heptane-1,7-diol and 3-(2-hydroxy-ethyl)-3-méthyl-pentane-1,5-diol covalent tripods, respectively. Minor changes in the structure of the ligands, i.e. the replacement of the apical hydrogen atom with a methyl group, or the introduction of an extra methylene in the capping moiety, induce dramatic effects in the structures of the resulting lanthanide complexes $[Ln(L^x)]^{3+}$ ($x = 7-9$). The complexes $[Ln(L^7)]^{3+}$ and $[Ln(L^9)]^{3+}$ exist as mixtures of two *endo* isomers which do not interconvert on the NMR time scale, whereas $[Ln(L^8)]^{3+}$ exhibits a single *exo* isomer. **To cite this article: S. Koeller et al., C. R. Chimie 9 (2006).**

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Résumé

Les podands nonadentés L^7 , L^8 et L^9 ont été préparés selon une stratégie de synthèse multi-étape à partir des tripodes covalents 3-(2-hydroxy-éthyl)-pentane-1,5-diol, 4-(3-hydroxy-propyl)-heptane-1,7-diol et 3-(2-hydroxy-éthyl)-3-méthyl-pentane-1,5-diol, respectivement. Des changements mineurs dans la structure des ligands – la substitution de l'atome d'hydrogène apical par un groupe méthyle ou l'introduction d'un méthylène supplémentaire dans la partie coiffante du tripode – induisent des effets importants dans la structure des complexes de lanthanides résultants $[Ln(L^x)]^{3+}$ ($x = 7-9$). Les complexes $[Ln(L^7)]^{3+}$ et $[Ln(L^9)]^{3+}$ existent dans un mélange de deux isomères *endo* qui ne s'interconvertissent pas à l'échelle de temps de la RMN, alors que les complexes $[Ln(L^8)]^{3+}$ existent sous la forme d'un seul isomère *exo*. **Pour citer cet article : S. Koeller et al., C. R. Chimie 9 (2006).**

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1. Introduction

Lanthanide complexes possessing a high degree of structural organization associated with tunable electronic and magnetic properties are promising precursors for molecular and supramolecular devices [1–3]. As a result of the poor stereochemical preferences and variable coordination numbers of Ln(III) ions, the structural control of the final architecture essentially arises from weak, but crucial interactions between the wrapped ligand strands according to the *induced fit* concept [1–3]. In this context, semirigid symmetrical tridentate units containing a central pyridine ring \mathbf{L}^{1-4} (Scheme 1) have been shown to produce nine-coordinate pseudo-tricapped trigonal prismatic sites [4–9] but an improved control of the electronic properties requires the development of unsymmetrical tridentate units (such as $\mathbf{L}^{5,6}$, scheme 1) possessing two different side arms connected to the 2- and 6-positions of the central pyridine ring [7, 10–13]. However, the controlled facial arrangement of three unsymmetrical tridentate binding units around Ln(III) implies the use of non-covalent d-block based tripods (\mathbf{L}^6) or their connection to a tripod [14–17] which prevents facial/meridional isomerization [18].

2. Synthesis of the ligands

The ligands tris- $\{2-[2-(6\text{-diethylcarbamoyl-pyridin-2-yl})-1\text{-ethyl-1}H\text{-benzimidazol-5-ylmethoxy}]\text{-ethyl}\}$ -methane (\mathbf{L}^7) [19], 1,1,1-tris- $\{2-[2-(6\text{-diethylcarbamoyl-pyridin-2-yl})-1\text{-ethyl-1}H\text{-benzimidazol-5-ylmethoxy}]\text{-ethyl}\}$ -ethane (\mathbf{L}^8) [20] and tris- $\{3-[2-(6\text{-diethylcarbamoyl-pyridin-2-yl})-1\text{-ethyl-1}H\text{-benzimidazol-5-ylmethoxy}]\text{-propyl}\}$ -methane (\mathbf{L}^9) were obtained according to a convergent multi-step strategy (Scheme 2). The $^{13}\text{C-NMR}$ spectra of \mathbf{L}^x ($x = 7-9$) in acetonitrile display the signals expected for trigonal symmetry (C_3 or C_{3v} point groups). The $^1\text{H-NMR}$ signals confirm three-fold symmetry and the systematic observation of enantiotopic methylene protons points to flexible side arms providing a dynamically average C_{3v} for \mathbf{L}^x ($x = 7-9$) in solution (Figs. 1a, 2a and 3a).

3. Solution structure of the complexes $[\text{Ln}(\mathbf{L}^x)](\text{ClO}_4)_3$ ($x = 7$, Ln = La; $x = 8$, Ln = Eu; $x = 9$, Ln = Eu)

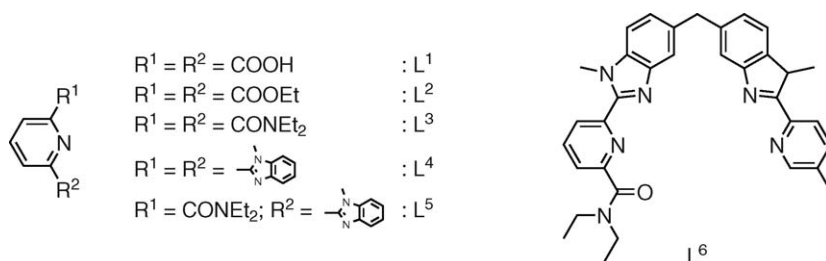
ESI-MS titrations of \mathbf{L}^x ($x = 7-9$, 10^{-4} mol/dm $^{-3}$, acetonitrile) with $\text{Ln}(\text{ClO}_4)_3 \cdot n \text{H}_2\text{O}$ (Ln = La, Eu, Lu; $n = 1-4$) for Ln: \mathbf{L}^x ($x = 7-9$) ratios in the range 0.5–2.0 show the exclusive formation of the complex

$[\text{Ln}(\mathbf{L}^x)]^{3+}$ ($x = 7-9$) together with their adduct ions $[\text{Ln}(\mathbf{L}^x)(\text{CF}_3\text{SO}_3)_i]^{(3-i)+}$ ($i = 1-2$). On the other hand, the $^1\text{H-NMR}$ spectra of $[\text{La}(\mathbf{L}^7)]^{3+}$ and $[\text{Eu}(\mathbf{L}^9)]^{3+}$ systematically display two different sets of signals corresponding to two different C_3 -symmetrical species in approximately 7:3 and 13:1 ratios, respectively (Figs. 1b and 3b).

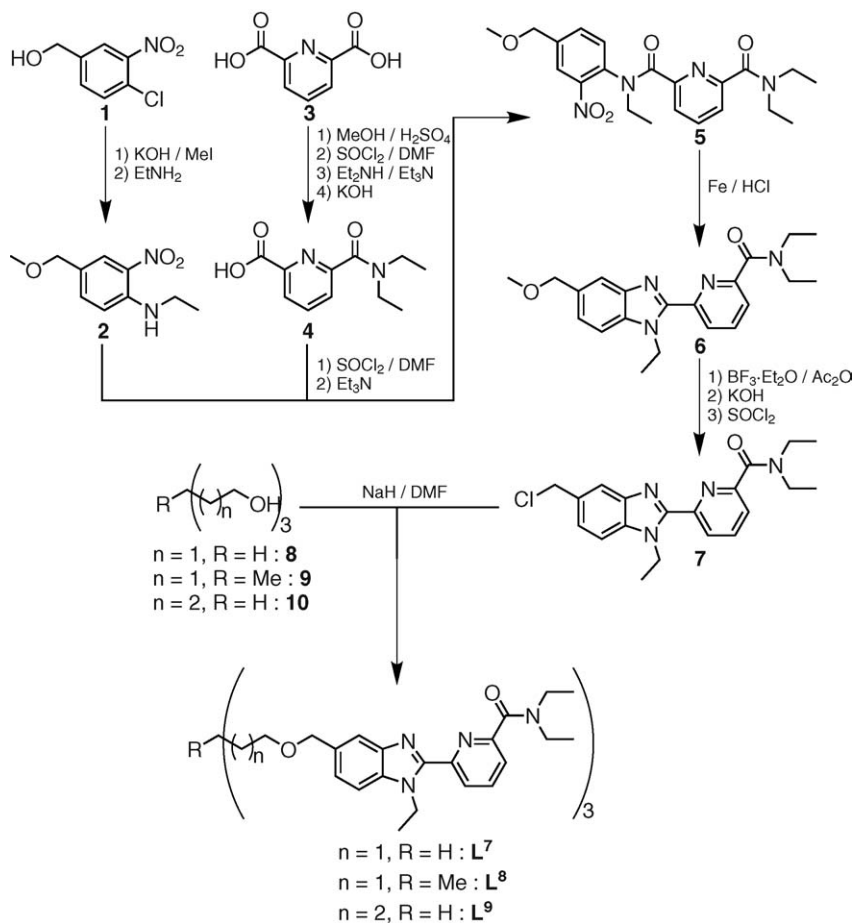
The minor variation of the chemical shifts of the same nucleus in the two isomers points to similar chemical environments and closely related arrangements of the strands. We have shown that these two isomers did not result from an *endo/exo* isomerization of the apical proton, but from a blocked conformation (on the NMR time scale) of the ethyleneoxy spacers of the capping moiety [19]. The 13:1 ratio observed for the two isomers in the $^1\text{H NMR}$ spectrum of $[\text{Ln}(\mathbf{L}^9)]^{3+}$ – versus the 7:3 ratio observed for $[\text{Ln}(\mathbf{L}^7)]^{3+}$ – reflects the gain of flexibility induced by the longer spacer in \mathbf{L}^9 . The high activation energy ($[\text{Ln}(\mathbf{L}^7)]^{3+}$, $\Delta G^\ddagger > 71 \text{ kJ mol}^{-1}$; $[\text{Ln}(\mathbf{L}^9)]^{3+}$, $\Delta G^\ddagger > 67 \text{ kJ mol}^{-1}$) estimated for this interconversion suggests that it requires the partial decomplexation of the ligand. On the other hand, the $^1\text{H-NMR}$ spectrum of $[\text{Eu}(\mathbf{L}^8)]^{3+}$ displays a single set of 22 signals which confirms the formation of a single C_3 -symmetrical species (Fig. 3b), in contrast with the systematic detection of two different inert conformers for $[\text{Ln}(\mathbf{L}^x)]^{3+}$ ($x = 7, 9$). The formation constants $\log(\beta_{11}^{\text{Ln}}) = 7.2-8.2$, observed for the complexes $[\text{Ln}(\mathbf{L}^8)]^{3+}$ (Ln = La–Lu) do not vary significantly along the lanthanide series within experimental errors and point to negligible size-discriminating effects (Fig. 4). These constants are slightly larger than $\log(\beta_{11}^{\text{Ln}}) = 6.5-7.6$ obtained in the same conditions for the analogous nine-coordinate podates $[\text{Ln}(\mathbf{L}^7)]^{3+}$ (Ln = La–Lu), which suggests that the methylation of the remote capping carbon atom influences the binding of the tridentate side arms and slightly increases their affinity for Ln(III) [19,20].

4. Crystal and molecular structure of the podates $[\text{Ln}(\mathbf{L}^x)](\text{ClO}_4)_3$ ($x = 7$, Ln = La [19]; $x = 8$, Ln = Eu [20])

In the solid state, the complexes $[\text{La}(\mathbf{L}^7)]^{3+}$ and $[\text{Eu}(\mathbf{L}^8)]^{3+}$ display similar metallic environments in which the metal atom is nine-coordinate in a distorted tricapped trigonal prismatic site with the three oxygen atoms of the carboxamide groups and the three nitrogen atoms of the benzimidazole rings occupying the vertex of the prism, and the three nitrogen atoms of the pyridine rings capping the rectangular faces (Fig. 5). The



Scheme 1.



Scheme 2.

striking difference between the crystal structure of $[\text{Eu}(\mathbf{L}^8)]^{3+}$ and that of the analogous podate $[\text{La}(\mathbf{L}^7)]^{3+}$ concerns the *exo* conformation of the apical carbon resulting from its methylation in $[\text{Eu}(\mathbf{L}^8)]^{3+}$ [20].

5. Conclusion

To the best of our knowledge, the methylated covalent tripod \mathbf{L}^8 produces the first unambiguous nine-co-

ordinate podates $[\text{Ln}(\mathbf{L}^8)]^{3+}$ in which the three helically wrapped aromatic tridentate binding units are connected to a single capping atom displaying no acid-base property. This covalent tripod can be considered as a valuable alternative to the delicate self-assembly processes with post-modification required for assembling identical nine-co-ordinate lanthanide sites in non-covalent podates, and in which the capping atom is an inert d-block ion (Cr^{III} , Co^{III}) [12,21].

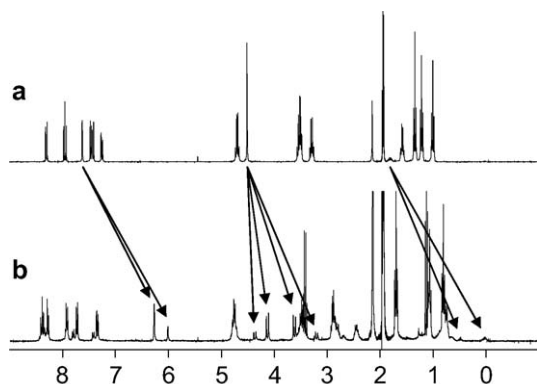


Fig. 1. $^1\text{H-NMR}$ spectra of a) L^7 and b) $[\text{La}(\text{L}^7)]^{3+}$ in CD_3CN (298 K).

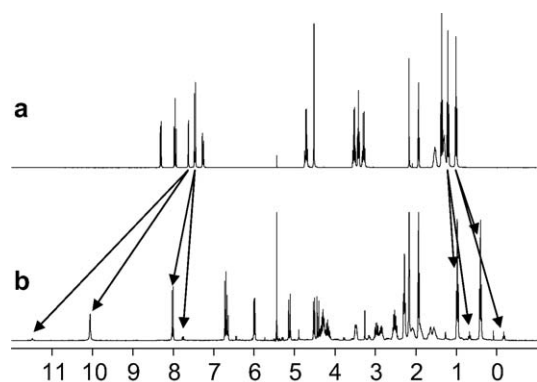


Fig. 2. $^1\text{H-NMR}$ spectra of a) L^9 and b) $[\text{Eu}(\text{L}^9)]^{3+}$ in CD_3CN (298 K).

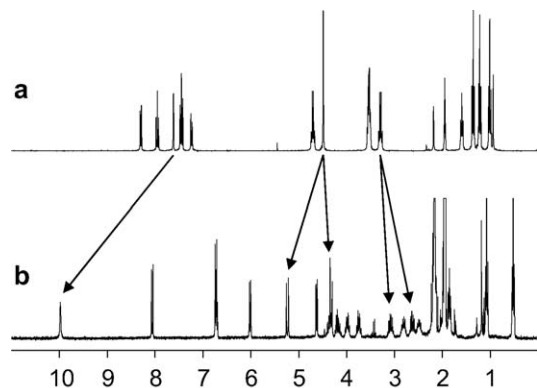


Fig. 3. $^1\text{H-NMR}$ spectra of a) L^8 and b) $[\text{Eu}(\text{L}^8)]^{3+}$ in CD_3CN (298 K).

6. Supporting information

Detailed experimental procedures for the preparation of the tripod L^9 and its precursors (including references

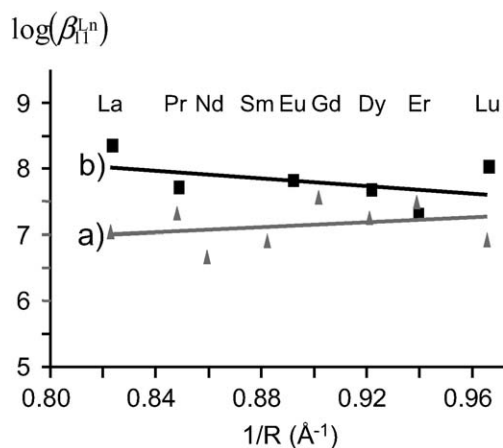


Fig. 4. Formation constants $\log(\beta_{11}^n)$ for the complexes a) $[\text{Ln}(\text{L}^7)]^{3+}$ and b) $[\text{Ln}(\text{L}^8)]^{3+}$ in acetonitrile ($10^{-2} \text{ mol}\cdot\text{dm}^{-3}$ $[\text{N}(\text{tBu})_4]\text{ClO}_4$, 293 K) versus the inverse of nine-coordinate ionic radii (\AA^{-1}).

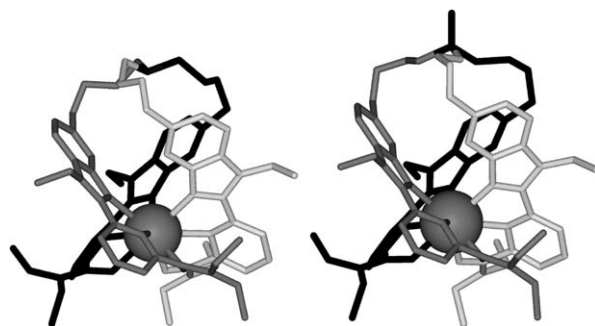


Fig. 5. Perspective views of the crystal structure of a) $[\text{La}(\text{L}^7)]^{3+}$ (major conformer) and b) $[\text{Eu}(\text{L}^8)]^{3+}$ perpendicular to the C_3 axis.

for each known compounds), and relevant spectroscopic characterizations (^1H and $^{13}\text{C-NMR}$ spectra).

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Annexe A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: 10.1016/j.crci.2005.12.001.

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