NMR T_1-Relaxation Measurements on Paramagnetic Organolanthanides: An Alternative Tool for Structure Determination in Solution

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^{1}H NMR investigations were conducted on four paramagnetic organolanthanides, all bearing the tetraisopropylcyclopentadienyl ligand Cp^{4i} (HC_5iPr_4) in order to verify whether or not interactions observed in the solid state are maintained in solution. In some cases variable-temperature experiments were necessary to enhance the resolution and determine the best conditions for the study. The 1D NMR spectrum could be interpreted in every case. Complementary 2D COSY experiments allowed the full attribution of the signals. T_1 (^{1}H) relaxation values were determined for all the paramagnetic complexes at the most suitable temperature, and compared with those of the diamagnetic KCp^{4i}. The same tendency was observed, with particular features concerning the isopropyl groups. Among the four methyl groups, one exhibits a much higher T_1 value and one a much lower value; the two others are intermediate. This was interpreted as the result of a privileged conformation of the Cp^{4i} ligand: the two α-isopropyl groups take up a spatial orientation with one methyl group in the *exo* position, opposite to the metal atom, whereas the methyl groups of the two β-isopropyl groups are equidistant from the metal atom. Whatever the nature of the metal (Nd, Sm), the oxidation state (Sm^{II}, Sm^{III}) or the temperature (298, 363 K), this conformation is retained. The structure in solution seems to be different from that previously determined in the solid state.

Introduction

Organolanthanide complexes have recently received a growing interest, due in part to their use as catalysts for polymerisation.[1–4] Investigations of the catalytic mechanisms are conducted starting from their molecular structures usually computed from X-ray diffraction data. However, these data reflect a solid-state organisation that is often different from the solution structure involved during reactions.

We recently synthesised a series of complexes bearing the voluminous Cp^{4i} ligand (Cp^{4i} = HC_5iPr_4).[5,6] X-ray studies showed a particular behaviour for several of them: one methyl(Cp^{4i})–lanthanide interaction, possibly agostic, was observed in the X-ray structure of [Ln(Cp^{4i})$_2$(BH_4)] (Ln = Nd, Sm), as well as in divalent [Sm(Cp^{4i})$_2$], whereas [Ln(cot)Cp^{4i}] (cot = C_8H_8) displays an unusually short cot–metal distance. We also established that organolanthanides bearing this Cp^{4i} ligand afford highly *trans*-stereospecific catalysts toward isoprene polymerisation upon activation with BuLi,[6] which is in accordance with the steric hindrance around the metal atom.[7,8] Moreover, [Sm(Cp^{4i})$_2$] was found to be efficient for ε-caprolactone polymerisation, whereas it remained unsolvated in the presence of THF.[5] It was therefore of interest to study thoroughly the stereoelectronic environment of the metal atom in such complexes, and whether or not the interactions observed were maintained in solution, since molecular complexes of lanthanides often behave differently in solution with respect to the solid state.[9]

NMR spectroscopy is a powerful technique that can give additional information, and is thus a complement to X-ray diffraction for studying three-dimensional structures in solution.[10] NMR studies on organolanthanide compounds are still mainly restricted to the diamagnetic derivatives (La, Lu, Y, Sc),[11] while the best catalysts are obtained in the more paramagnetic neodymium and samarium series.[12–14] However, even if the results usually suffer from the loss of resolution of the spectra due to the intrinsic properties of the lanthanide atom, this paramagnetism is able to give some information concerning the complex geometry.[15,16] NMR spectroscopy of paramagnetic molecules has been widely studied and discussed, particularly in terms of chemical shifts,[17] and many lanthanide complexes are used as shift reagents. Paramagnetic metals are also involved in a large number of natural compounds, such as proteins, and their presence usually complicates the study of such compounds. Bertini and co-workers have recently reviewed the

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Table 1. Molecular complexes under study.

Complex[a]	Metal (ox. state)	Ligand 1 (charge)	Ligand 2 (charge)	Ligand 3 (charge)	Temperature for T_1 measurements [K]
KCp^{4i}	K (+I)	Cp^{4i} (–I)			298
$[Sm(cot)Cp^{4i}]$	Sm (+III)	Cp^{4i} (–I)	cot (–II)		298
$[Sm(Cp^{4i})_2(BH_4)]$	Sm (+III)	Cp^{4i} (–I)	Cp^{4i} (–I)	BH_4 (–I)	298/363
$[Nd(cot)Cp^{4i}]$	Nd (+III)	Cp^{4i} (–I)	cot (–II)		363
$[Sm(Cp^{4i})_2]$	Sm (+II)	Cp^{4i} (–I)	Cp^{4i} (–I)		373

[a] cot = C_8H_8, Cp^{4i} = HC_5iPr_4.

field of paramagnetic NMR spectroscopy of biological compounds.[18] It has been increasingly recognized that, besides contributing to line broadening, the electron–nucleus interactions contain useful structural information. Many of the relevant effects that the presence of paramagnetic metals has on the behaviour of the compound nuclei have to do with the metal's magnetic susceptibility. Most of these effects have been well known since the1950s and 1960s, but a few have been described more recently. Concerning lanthanide complexes, the effect of paramagnetism on the spin–lattice relaxation has been studied but mostly with coordination complexes in aqueous media.[19]

Different techniques have been found to calculate distances from T_1 relaxation rates.[20,21] These methods are, however, complicated to undertake due to the high number of parameters they involve. In particular, the comparison of T_1 values obtained for different compounds should be made at the condition of T_{1min}. This is an important problem in the case of paramagnetic compounds because the T_{1min} is usually only reached at low temperature, which induces an additional loss of resolution, and the poor resolution observed prevents the computation of T_1.

In the present study we compare the molecular structures of several organolanthanide complexes in solution, based on their paramagnetic ^1H NMR spectroscopic data. Moreover, we examine paramagnetic samarium and neodymium complexes to overturn the general idea that comprehensive NMR studies are not possible for compounds of these metals.

The choice of organometallic complexes, presented in Table 1, allows the study of different parameters and their influence on the structure. These parameters are: the metal, the oxidation state of the metal, the nature of the ligands (cot, Cp^{4i}), the solvent and the temperature.

Results and Discussion

Choice of Temperature and Signal Assignment

As a first approach, the temperature dependence of the chemical shifts of the complexes was studied. It is well known that paramagnetic organolanthanides display temperature-dependent NMR spectra with respect to both chemical shifts and resolution.[17]

The goal of this experiment was to determine the best temperature for T_1 measurement, i.e., the temperature at which the spectrum exhibits a good enough resolution with no signal overlaps. For most of the complexes this was reached near the highest temperature of the study, typically a few degrees below the solvent boiling point (near 363 K, Figure 1). This was particularly the case of the neodymium complex $[Nd(cot)Cp^{4i}]$ due to the strong paramagnetic character of this metal. In fact, this latter complex gives broad lines even at high temperature but it was possible to distinguish all signals with only two recovering lines, while at room temperature most of the lines could not be distinguished from the noise.

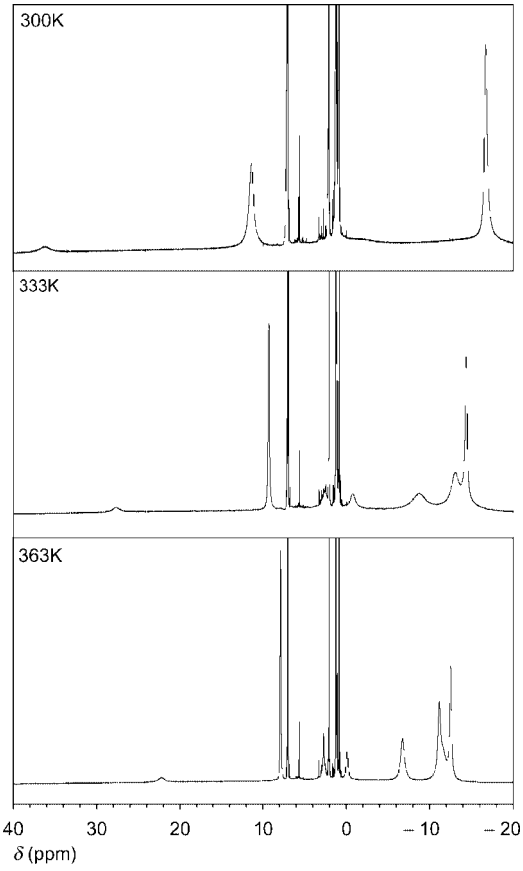
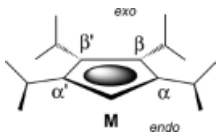


Figure 1. Evolution of the ^1H NMR spectrum of $[Nd(cot)Cp^{4i}]$ (in C_7D_8) with temperature.

After the temperature had been chosen, it was necessary to complete the assignment. Actually, whatever the complex, there are four non-equivalent methyl groups and two non-equivalent methyne groups all belonging to the four isopropyl groups attached to the Cp unit. This indicates that there are two different types of isopropyl groups. Ac-

cording to the symmetry of the Cp^{4i} ligand, two equivalent isopropyl groups are located in an α-position to the Cp methyne group (HCp) and the second type is attributed to both isopropyl groups located in the β-position of the HCp group (Scheme 1).



Scheme 1. Representation of the Cp^{4i} ligand showing the different types of isopropyl groups and the two different sides of the molecule when a metal atom is coordinated.

The presence of four non-equivalent methyl groups for two non-equivalent isopropyl groups means that both methyl groups belonging to the same isopropyl group are non-equivalent (Figure 2). This is explained by the presence of the metal atom located on one side of the Cp plane. Thus, there are two different Cp sides: one *endo* side and one *exo* side. Such a molecular arrangement obviously affords a diastereotopic system of methyl groups.[22,23]

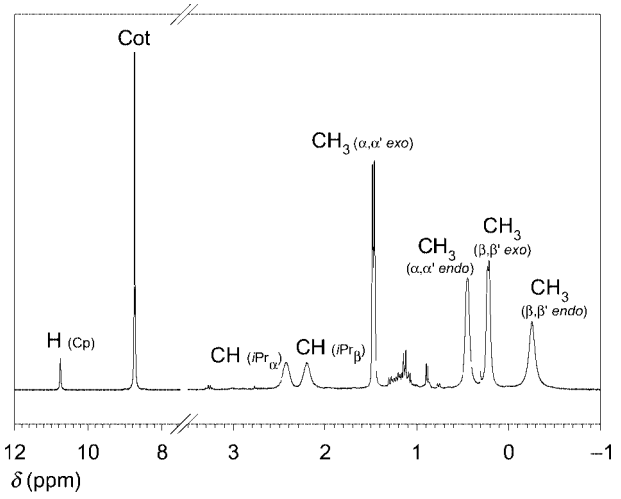


Figure 2. 500 MHz ^{1}H NMR spectrum and assignment of the complex [Sm(cot)Cp^{4i}] recorded at 298 K.

It is noteworthy that the spectrum of KCp^{4i} displays only signals of two types of methyl groups: one type corresponding to the α-isopropyl groups and the other one to the β-isopropyl groups. The geometry of this compound is different from that of the complexes under study as KCp^{4i} is an ionic compound, which means that the potassium ion is not linked to the Cp ring, as neodymium or samarium can be, and therefore *endo* and *exo* sides do not exist. The NMR spectrum can be explained in terms of symmetry if the potassium ion is not coordinated face-on to the Cp ring, with both sides becoming equivalent, or if it alternatively roams quickly from one side to the other in THF.[24] Finally, the methyl groups belonging to the same isopropyl group are enantiotopic in KCp^{4i}.

The next step in the assignment procedure was to connect methyl groups with methyne groups of the same isopropyl group. This was done with a 2D-COSY experiment, which gives correlations between coupled protons (Figure 3). For some complexes, like [Nd(cot)Cp^{4i}], no correlation could be observed due to the very fast relaxation occurring in this compound. As a matter of fact, the incremental delay placed in the 2D sequence to create the second dimension results in a complete relaxation of protons prior to the acquisition step and thus no signal could be detected. Assignment could be achieved for Sm complexes as well as for the potassium salt.

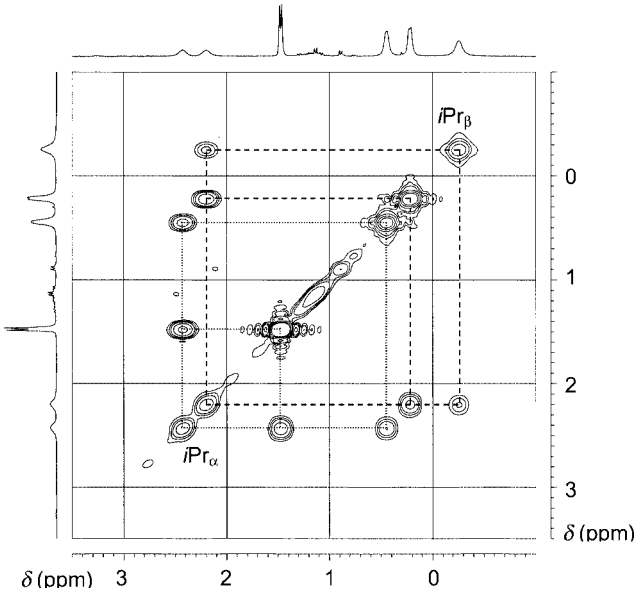


Figure 3. 2D COSY map of the complex [Sm(cot)Cp^{4i}] recorded at 298 K. Assignments of both types of isopropyl groups are shown.

Two uncertainties still remained at this stage of our studies, namely the identification of the α- and the β-isopropyl groups and the *exo*- and *endo*-methyl groups. The first problem was solved by performing an NOE-difference experiment in which the HCp signal was irradiated. We observed a significant variation of one H(*i*Pr) signal intensity, and this isopropyl group was thus assigned to the closest (α and α′) position. Such an experiment could not be conducted on all complexes due to fast relaxation but was unambiguous for [$Sm(BH_4)(Cp^{4i})_2$]. These results were further generalized to the other complexes. The identification of *endo* and *exo* groups was achieved by measuring T_1 values (see below).

Relaxation Study

The non-paramagnetic KCp^{4i} was first studied as a reference. As we remarked previously, the potassium cation does not generate the asymmetry at the Cp ring that is the origin of the *endo* and *exo* sides noticed in the other complexes. Moreover, the metal should have very little influence on the Cp^{4i} relaxation rates since it is not paramagnetic, in contrast with the other complexes under study. The relaxation times of KCp^{4i} are reported in Table 2. These values are similar to those usually observed for small organic molecules. The α- and β-methyne signals exhibit relaxation times

Table 2. T_1 data [ms] of molecular complexes at 298 K.

Complex	H_{Cp}	CH_α	CH_β	CH_3 (α,α′-*exo*)	CH_3 (α,α′-*endo*)	CH_3 (β,β′-*exo*)	CH_3 (β,β′-*endo*)	cot/BH_4
[Sm(cot)Cp^{4i}]	53.4	212.8	236.4	515.5	208.8	303.0	227.8	73.7
[Sm(Cp^{4i})$_2$(BH_4)]	27.5	201.2	152.9	471.7	173.3	–[c]	217.4	3.6
[Sm(Cp^{4i})$_2$(BH_4)][a]	34.5	244.5	240.4	800.0	248.1	392.2	308.6	2.6
[Nd(cot)Cp^{4i}][a]	1.8	7.7	7.1	32.9	9.8	15.3	11.5	6.8
[Sm(Cp^{4i})$_2$][b]	11.4	37.1	–[c]	176.8	34.0	53.0	37.6	–
KCp^{4i}	4169	2775	2111	1605 (α,α′)		1839 (β,β′)		–

[a] Recorded at 363 K. [b] Recorded at 373 K. [c] Signal overlapped.

of 2.77 and 2.11 s, respectively, which are rather different. However, in such diamagnetic compounds dipolar relaxation is predominant over other relaxation processes, and this can explain the observed difference. The β-methyne protons feel the influence of methyl groups belonging to the same isopropyl group as well as that of methyl groups belonging to both neighbouring isopropyl groups. In the case of α-methyne protons, however, there is only one neighbouring isopropyl group, which induces a less efficient dipolar relaxation. The α- and β-methyl groups display relaxation times of 1.60 and 1.84 s, respectively; this small difference seems to be not very significant. The relaxation times measured for KCp^{4i} are of no structural interest but are interesting for comparison with those measured for paramagnetic complexes.

As expected, all paramagnetic complexes display relaxation times that are drastically smaller than those reported for KCp^{4i}. This decrease is due to the presence of the paramagnetic metal, although the distances between the protons and the metal atom may also have a strong influence.

Straight lines corresponding to relaxation of [Sm(cot)Cp^{4i}] protons are shown in Figure 4 as an example; the relaxation times of the different complexes under study are reported in Table 2.

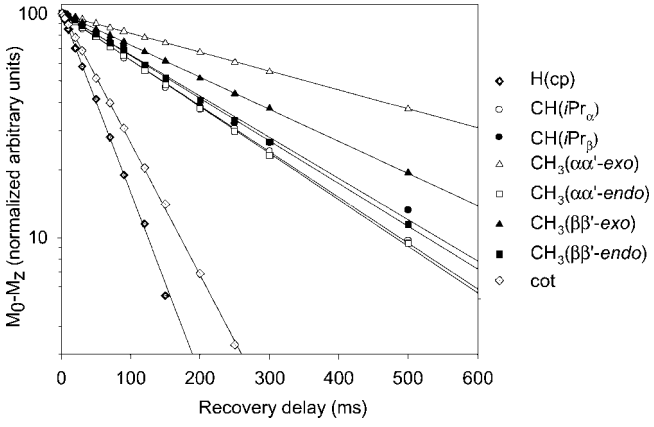


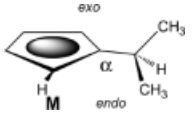
Figure 4. [Sm(cot)Cp^{4i}] T_1 (^{1}H) relaxation plots recorded at 298 K.

As regards to the variety of the complexes under study, the nature of the metal can be evaluated by comparing both [Sm(cot)Cp^{4i}] and [Nd(cot)Cp^{4i}]. Samarium complexes usually give ^{1}H NMR spectra that are better resolved than those corresponding to neodymium derivatives, which display spectra with very broad lines.[5,6,25] From this consideration, one would expect smaller T_1 values for neodymium than for samarium complexes; the T_1 values reported in Table 2 confirm this. As a matter of fact, [Nd(cot)Cp^{4i}] T_1 values are much smaller than those observed for [Sm(cot)Cp^{4i}]. The ratio T_1([Sm(cot)Cp^{4i}])/T_1([Nd(cot)Cp^{4i}]) has values of between 10, for the cot protons, and 30, for the isopropyl methyne groups. Nevertheless, it is noteworthy that in both complexes the same tendency in the T_1 distribution is observed: the HCp proton has the shortest T_1 relaxation in both compounds, followed by the cot protons. Such small HCp T_1 values were not observed for KCp^{4i}. Obviously, the diamagnetic character of the compound explains the larger T_1 values, but in the case of KCp^{4i} HCp exhibits the largest T_1 value. As explained previously, dipolar relaxation is the most important relaxation mechanism in KCp^{4i} and HCp is the most distant proton from the other ones, thus explaining the lack of efficiency in its relaxation mechanism. In the cases of both [Sm(cot)Cp^{4i}] and [Nd(cot)Cp^{4i}], paramagnetic relaxation dominates and the smaller HCp T_1 values, as compared to those of other nuclei, indicate that HCp is the nearest proton to the metal ion. This is valid for all complexes under study since they all display very small HCp T_1 values.

Other interesting T_1 values are those of the methyl groups. In all complexes T_1 values corresponding to the four non-equivalent types of methyl groups could be measured, leading each time to the same tendency: i) one value is much higher than the others; ii) two types of methyl groups have intermediate values of the same order; iii) the last type of methyl groups exhibits a T_1 value a little bit smaller than the intermediate value; iv) the methyl groups exhibiting the smallest and largest T_1 values belong to the same type of isopropyl groups located in the α-position to HCp, and thus methyl groups with intermediate T_1 values belong to isopropyl groups in the β-position to HCp.

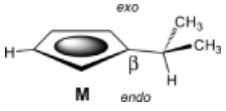
These results give important information concerning the complexes' geometry. It seems that α-isopropyl groups take an orientation in which one methyl group is far from the paramagnetic centre while the other one is much closer to the metal atom. Taking into consideration that the metal atom is located beneath the Cp ring plane, this means that the α-isopropyl groups take an orientation in which one methyl group (with the largest T_1 value) is located on the *exo* side of the Cp ring plane while the other one (with the smallest T_1 value) is located on the *endo* side of this plane. This conformation most likely places the *exo*-methyl group in the plane perpendicular to the Cp ring. In this situation, this methyl group is located as far as possible from the para-

magnetic centre. It is noteworthy, given the tetrahedral geometry of sp^3-carbon atoms, that in this case the *endo*-methyl groups are not as close as possible to the metal atom. Also, this conformation places the α-isopropyl methyne groups slightly on the *endo* side but not far from the Cp ring plane (Scheme 2). Thus, whereas the diastereotopic nature of the methyl groups does not give any information about possible free rotation of isopropyl groups on the basis of chemical shifts, the fact that such a T_1 difference can be observed for methyl groups belonging to the same isopropyl groups clearly indicates a tendency to hindered rotation.



Scheme 2. Conformation of the α-isopropyl group, with one methyl group as far as possible from the metal atom.

We can see that β-isopropyl methyne groups have relaxation times close to those measured for α-methyne groups. If we consider that paramagnetic relaxation, and thus the proximity of the metal atom, is the predominant mechanism of relaxation, this indicates that α- and β-methyne groups are approximately at the same distance from the metal atom. Nevertheless, β-methyl groups adopt a quite different orientation from their α homologues, since they display relaxation times between both values observed for α-methyl groups. Moreover, the difference between both methyl groups belonging to the same β-isopropyl group is smaller than that measured between α-isopropyl methyl groups. This suggests an orientation of the β-isopropyl groups in which the methyl groups probably have positions not far from the plane of the Cp ring. According to the fact that the α-*endo*-methyl groups have the shortest relaxation time (as compared to other methyl groups), the β-methyl groups might be on the *exo* side due to their larger T_1 value (Scheme 3).



Scheme 3. Conformation of the β-isopropyl group, with the two methyl groups nearly equidistant to the metal atom.

All these structural considerations are valid for the complete series of paramagnetic complexes under study, whatever the metal or its oxidation state. A comparison of [Sm(cot)Cp^{4i}] and [Sm(Cp^{4i})$_2$(BH_4)] shows the influence that other ligands might have on the Cp^{4i} relaxation. In fact, replacing the cyclooctatetraenyl ligand by a borohydride and a second Cp^{4i} ligand induces a small decrease of the T_1 values. This indicates that if the general geometry of Cp^{4i} is the same, the distances between the metal atom and the Cp^{4i} ligand should be different in both complexes. Actually, the Sm–CP distances have been found to be 2.40 Å in [Sm(cot)Cp^{4i}][5] and 2.44 and 2.47 Å in [Sm(Cp^{4i})$_2$(BH_4)][6] (CP is the centroid of the Cp^{4i} ring). Although the distance is slightly shorter in the cot complex, the T_1 values are higher. However, the geometry of the two complexes is different: [Sm(cot)Cp^{4i}] is a metallocene of Sm^{III}, while [Sm(Cp^{4i})$_2$(BH_4)] bears one additional ligand.

X-ray diffraction analyses also indicate that [Sm(Cp^{4i})$_2$(BH_4)] exhibits one very short Sm–H(CH_3) distance (2.50 Å). This could be due to an agostic interaction. A similar feature, though less pronounced, has also been detected in other [Ln(cot)Cp^{4i}] complexes (Ln = Nd, Sm). According to our NMR experiments, it seems that such an interaction, which should lead to a much smaller T_1 value, is not retained in solution.

Changing the oxidation state of the metal also has important effects on the relaxation times. [Sm(Cp^{4i})$_2$] has a much lower relaxation time than [Sm(Cp^{4i})$_2$(BH_4)], while its Sm–CP distances are slightly longer, as expected for Sm^{II} (2.51 Å);[5] the more pronounced paramagnetism of Sm^{II} against Sm^{III} is responsible for the important decrease of the T_1 values.

As previously noticed, these changes do not influence the Cp geometry; the differences in relaxation times are undoubtedly due to the different electronic configurations of the metal to which the paramagnetism is strongly bound.

Finally, [Sm(Cp^{4i})$_2$(BH_4)] was submitted to T_1 measurements at two different temperatures (room and high temperature), while other complexes were generally studied at high temperature only due to the better resolution under these conditions. This was done mainly to verify that the geometry of the complexes does not change in the range 298–373 K. Obviously, some differences are to be expected when comparing T_1 values measured at both temperatures since temperature influences the motion of the complexes. However, whatever the temperature of the study, the same conclusions can be drawn concerning the [Sm]-Cp^{4i} geometry. The most probable conformation of the Cp^{4i} ligand in all the complexes under study is represented in Figure 5.

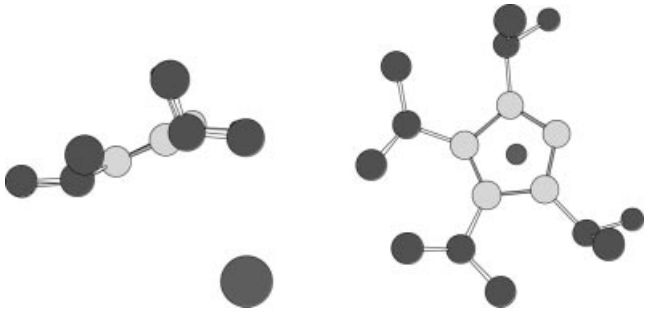


Figure 5. 3D representation of the [Cp^{4i}-Sm] moiety of [Sm(cot)-Cp^{4i}] orthogonally to the Cp ring (left) and in the Cp ring plane (right).

In order to validate our approach, Ln–H distances were calculated from T_1 data. It is well known that relaxation rates are proportional to $1/r^6$, where r can be considered as the metal–H distance, since paramagnetic relaxation is the dominant relaxation process.[21] Under our experimental conditions, only relative distances are easily accessible. For each complex under study, we took as reference the Ln–H(Cp) distance found in its X-ray structure. Among all Ln–

Table 3. Metal–H distances [Å] (calculated from NMR T_1/determined from X-ray).

Complex	H_{Cp}[a]	CH_α	CH_β	CH_3 (α,α′-*exo*)	CH_3 (α,α′-*endo*)	CH_3 (β,β′-*exo*)	CH_3 (β,β′-*endo*)	cot/BH_4
[Sm(cot)Cp^{4i}]	3.19	4.02/3.87	4.09/3.95	4.65/5.39	4.00/4.11	4.26/5.39	4.06/3.82	3.37/3.29
[Sm(Cp^{4i})$_2$(BH_4)][b]	3.19	4.45/4.06	4.25/3.90	5.13/5.46	4.34/4.31	–/5.49	4.51/4.13	2.28/2.68
[Nd(cot)Cp^{4i}]	3.26	4.15/3.95	4.10/4.01	5.29/5.44	4.32/4.10	4.66/5.40	4.44/3.79	4.07/3.32
[Sm(Cp^{4i})$_2$]	3.27	3.98/3.92	–/4.04	5.16/5.49	3.92/4.20	4.22/5.43	3.99/3.76	–/–

[a] X-ray data, used as reference for NMR-computed distances. [b] From T_1 recorded at 363 K.

H distances, the latter is supposed to fluctuate the least from the solid state to the solution due to the rigid plane structure of the Cp ring. All other distances given in Table 3 were calculated from this reference. One can see that the computed distances fit quite well with those determined from X-ray studies. As expected, a significant difference is found between *endo*- and *exo*-CH_3αα′. On the other hand, whereas in the solid state the Cp^{4i} ligand displays *endo*- and *exo*-CH_3ββ′, this seems to be no longer the case in solution. The Ln–H(CH_3ββ′) distances take values that are quite similar, which corresponds well to methyl groups both located close to the plane of the Cp ring.

Conclusions

Structural information for four paramagnetic organolanthanides has been deduced by ^{1}H NMR spectroscopy. Despite the paramagnetism, the molecular conformation of the hyperbulky tetraisopropylcyclopentadienyl ligand involved in these complexes was fully resolved from 1D, 2D COSY and T_1 relaxation experiments.

The specific conformation is retained at high temperature, whatever the other surrounding ligands and the nature (neodymium or samarium) and the oxidation state (divalent or trivalent) of the lanthanide atom. The molecular structure in solution differs from that previously observed in the solid state. Such a conclusion can be drawn thanks to T_1 relaxation experiments.

This contribution shows that structural features may not be retained in solution in the case of the bigger early lanthanides, and this should be taken into consideration when performing mechanistic studies. Finally, the paramagnetism of lanthanide complexes does not necessarily preclude extensive NMR investigations for the determination of their conformation in solution.

Experimental Section

General Remarks: All complexes were prepared as published.[5,6] The potassium derivative KCp^{4i} was obtained by the classical reaction of KH with HCp^{4i} in THF. All samples were dissolved in [D_8]-toluene previously dried with Na/K alloy. Toluene was chosen as solvent due to its higher boiling point than benzene. Toluene transfer was performed by vacuum distillation into NMR tubes equipped with a Teflon valve (Young). After transfer, samples were stored under argon pressure. For KCp^{4i} [D_8]THF was used as solvent due to its poor solubility in toluene or benzene. All NMR experiments were recorded with a Bruker Avance 500 spectrometer working at a field of 11 T. Initially, several spectra were recorded as a function of temperature in order to determine the best conditions for the relaxation-time measurements. The highest resolution, and thus the best conditions, were usually reached at 363 or 373 K, depending on the nature of the complex. Assignment of the proton signals was performed with a 2D COSY experiment. The classical sequence using magnitude correction was used. No gradients were used for the complexes containing a paramagnetic metal because the additional delays involved in the pulse sequence result in a complete loss of magnetisation due to the very short relaxation time of the compounds under study. A gradient field 2D-COSY pulse sequence was used for the only non-paramagnetic complex (KCp^{4i}). In this case, the *Z*-gradient powers were set to 10% while the gradient pulse and the delay for gradient recovery were 1 ms and 100 μs, respectively. In order to complete the assignment of the *exo* and *endo* substituents, a 1D NOE-difference experiment was performed; the HCp signal was irradiated to indicate the closest α-and α′-isopropyl groups. Pulse lengths were calibrated prior to each relaxation-time measurement. Typically, the 90° proton pulse was 5.6 μs at an attenuation of 0 dB. T_1 measurements were performed by using the conventional inversion recovery technique. Several experiments of 256 scans were recorded with 20 different durations between the 180° and the 90° pulses. These experiments were recorded in a random order of the durations to minimize errors due to adjustment drifts occurring as a function of the time. The delay between each scan was chosen to be much larger than five times T_1. After Fourier transformation, the intensities of the different signals were collected and the curves $\ln(M_0 - M_Z)$ were drawn as a function of the delay between the 180° and the 90° pulses. The constant M_0 was evaluated by averaging two experiments involving long delays much larger than five times the T_1. The slopes of the obtained straight lines were then computed and led thus to the T_1 values, which are known to be the opposite reverse of the slopes ($-1/T_1$).

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