Anomalous Diamagnetic Behaviour of the ^{1}H NMR Spectra of a Coordinated Imino Nitroxide Radical in Diamagnetic and Paramagnetic Lanthanide(III) Complexes

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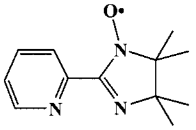
Diamagnetic lanthanide(III) complexes with an imino nitroxide radical IM2py [2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl], [Ln(hfac)$_3$(IM2py)] (Ln = Y and Lu; hfac = hexafluoroacetylacetonate), exhibit ^{1}H NMR chemical shifts for the pyridyl protons of the coordinated IM2py suggesting it behaves as if it were diamagnetic. To a series of paramagnetic lanthanide complexes of this type, the structural analyses of the lanthanide induced shifts (LIS) of the hfac 3-proton and pyridyl protons in IM2py were successfully applied, showing not only the diamagnetic behaviour of the pyridyl protons in the IM2py group, but also the dominant dipolar contribution and isostructural nature with apparent or effective axial symmetry in solution irrespective of the asymmetry in the solid state.

Introduction

There have been a large number of studies of lanthanide complexes and/or radical complexes with much concomitant interest in their potential applications in luminescent probes[1,2] or as building blocks for molecular-based magnetic materials.[3,4] The lanthanide−radical complexes have been mainly investigated in order to reveal the magnetic properties in solid state or absorption and emission spectra.[4,5] Our recent magneto-optical investigations on the nitroxide radical metal complexes were concerned not only with transition metal ions, but also lanthanide(III) ions.[6−12] For the imino nitroxide radical lanthanide complexes, [Ln(hfac)$_3$(IM2py)] [IM2py = 2-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl],[11] we examined the solution spectroscopic properties as well as the magnetic interaction between Gd^{III} and the IM2py radical which is antiferromagnetic, in contrast to the ferromagnetic case[4] of (NIT2py)- and related (NIT)Gd^{III} complexes [NIT2py = 2-(2′-pyridyl)-4,4,5,5-(tetramethyl)-4,5-dihydro-1*H*-imidazolin-1-oxyl 3-oxide]. On the other hand, there have been many NMR studies of lanthanide complexes which have been utilised as lanthanide shift reagents (LSR) with the advantage of bringing about high resolution of complicated NMR spectral patterns of diamagnetic organic compounds, e.g. chiral discrimination and as biological probes since their introduction by Hinckley in 1969.[13] More recently, much attention has been paid to Gd^{III} complexes as contrast agents for magnetic resonance imaging (MRI) due to the short relaxation times encountered in ^{1}H NMR spectroscopy.[14] However, there have been no reports on the NMR spectra of Ln^{III} complexes containing a radical ligand. There have been a number of scattered reports on paramagnetic metal complexes with radical ligands mainly with a limited focus on the coordination effects on the radical ligands with the metal ions.[15,16] In our recent study, the chemical shifts in the ^{1}H NMR spectra of (NIT2py)Ni^{II} complexes were found to correlate with magnetic interactions between paramagnetic Ni^{II} and the NIT2py radical.[6a] In this context, when the diamagnetic complexes or paramagnetic metal complexes are magnetically weakly coupled with a nitroxide radical, the effect of coordination on the NMR spectra or the simple NMR spectroscopic patterns consisting of the original unperturbed signals of the radical and the auxiliary nonradical coligands can be predicted. In the course of the characterisation of Co^{III} or Ln^{III} complexes with IM3py and IM4py [3- and -4-(2′-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl] or IM2py (Scheme 1), we observed unprecedented and apparently diamagnetic ^{1}H NMR behaviour for the imino nitroxide radical ligands in diamagnetic Co^{III} or Y^{III} and Lu^{III} complexes.



Scheme 1. IM2py

In this study, the NMR spectra of (IM2py)Ln^{III} complexes were examined in order to substantiate the diamag-

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netic NMR behaviour. Lanthanide induced paramagnetic shift (LIS) data of the paramagnetic Ln^{III} complexes will be analysed in terms of the classical crystal field dependent and the recently developed crystal field independent methods. The resultant analyses will be compared with the influence of the imino radical on the diamagnetic behaviour as well as the solution structure.

Results and Discussions

Magnetic Properties in Solution

The magnetic moments of [Y(hfac)$_3$(IM2py)] and [Lu(hfac)$_3$(IM2py)] in the solid state at 300 K are 1.81 and 1.90 μ_B, respectively, and those in $CDCl_3$ solution are 2.17 and 2.20 μ_B, respectively. The theoretical value is 1.73 μ_B. The corresponding Yb^{III} complex has values of 5.07 and 4.80 μ_B in the solid state and in solution, respectively, which are close to the theoretical value of 4.80 μ_B. These facts support the existence of the IM2py radical in the solid state and solution, in accordance with the UV/Vis spectra in solution.[11a]

In addition, the solution EPR spectrum of [Y(hfac)$_3$(IM2py)] displays hyperfine splittings to the Y^{III} ion and both nitrogen atoms [N(1) for IM−N and N(2) for IM−N−O] of the IM moiety (Figure 1) where the unpaired electron resides. The coupling of Y^{III} and N(1) is a result of the coordination. These hyperfine coupling constants were estimated by comparing them with the simulated spectra. The nitrogen hyperfine splittings are 4.9 G [N(1) and 7.8 G [N(2)] for [Y(hfac)$_3$(IM2py)]. These values are in contrast to 4.25 G [N(1)] and 9.25 G [N(2)] for free IM2py.[17] This change is due to electron delocalisation from the ligand toward the Y^{III} ion. With ^{89}Y having a nuclear spin of I = 1/2, the expected hyperfine splitting resulting from delocalisation onto the Y ion is only 0.4 G.

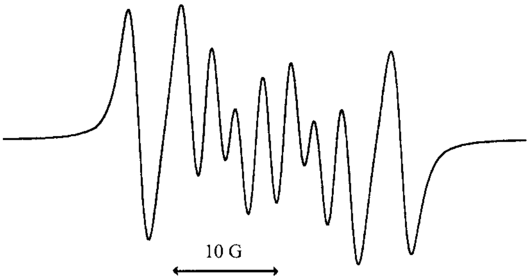


Figure 1. X-band (9.31 GHz) ESR spectrum at 296 K of [Y(hfac)$_3$(IM2py)]

As previously reported,[11a] the UV/Vis spectroscopic changes with the variation of mixing ratios also revealed the stability of the radical Ln^{III} complexes. In view of these results, it is certain that [Y(hfac)$_3$(IM2py)] remains paramagnetic due to the IM2py radical, even in solution.

^1H NMR Spectra of the Diamagnetic Ln^{III} Complexes Containing the IM2py Radical

The ^1H NMR spectra of [Y(hfac)$_3$(IM2py)] and [Lu(hfac)$_3$(IM2py)] should exhibit additive patterns consisting of the signals for the methine proton of hfac (hfac-H) at the diamagnetic Ln^{III} centre and those for the paramagnetic radical IM2py ligand, as if it were a mixture only of the Ln(hfac)$_3$ and IM2py moieties. However, the ^1H NMR spectra of [Y(hfac)$_3$(IM2py)] and [Lu(hfac)$_3$(IM2py)] appear like those of diamagnetic species. As shown in Figure 2 (a, b), the ^1H NMR spectra of [Y(hfac)$_3$(IM2py)] and [Lu(hfac)$_3$(IM2py)] appear in the diamagnetic region (δ = 0 to +10 ppm) associated with line-broadening, whereas no splitting by spin-spin coupling was observed. There is no signal for these Ln complexes in the paramagnetic range at $\delta \approx +20$ or -20 ppm, where the paramagnetic IM2py radical itself exhibits a typical paramagnetic NMR spectroscopic pattern [Figure 2 (c)]. A broad signal at $\delta \approx -15$ ppm is due to the IM methyl groups and the signals at δ = +22, +13 and ca. +4 ppm are due to the pyridyl protons as inferred from the assignments for NIT radicals (4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-3-oxide-1-oxyl).[18]

The signals from δ = +7.5 to +8.5 ppm of the (IM2py)Y and -Lu complexes can be assigned to the pyridyl protons on the basis of the ^1H-^1H COSY spectrum. This exhibits two kinds of cross peaks for the pyridyl protons (Figure 3). There is a discrimination between two pairs of signals corresponding to each proton which are coupled with three ($\delta \approx$ +7.6, +7.9 and +8.5 ppm) and two protons ($\delta \approx$ +8.5 and +8.7 ppm), respectively. Apparently, the former two are due to the 4- and 5-protons of py (py-H4 and py-H5, respectively), the latter two to the 3- and 6-protons of py (py-H3 and py-H6, respectively) (Scheme 2). Since the signal at δ = +8.5 ppm is relatively broader than that at δ = +8.7 ppm, this can be assigned to py-H3 which is closer to the N−O radical moiety. Accordingly, the signals at δ = +7.91 and +7.62 ppm can be assigned to py-H4 and py-H5, respectively. A group of signals at $\delta \approx$ +1.5 ppm arises from the methyl protons of the imidazole ring in IM2py. These assignments are in accordance with the chemical shifts of the analogous diamagnetic complex, *trans*-[Co(acac)(NO$_2$)$_2$(IMH2py)], where IMH2py [2-(2′-pyridyl)-4,4,5,5-tetramethyl-1-hydroxyimidazoline] is a diamagnetic one electron reduced IM2py group.[9] The broad signal at δ = 6.0 ppm should be due to the methine proton of the hfac (hfac-H) function in the (IM2py)Y complex, since its position is close to that in the nonradical [Y(hfac)$_3$(bpy)] complex. The ^1H NMR line widths in [Y(hfac)$_3$(IM2py)] are similar to those of an equimolar mixture of [Y(hfac)$_3$(bpy)] and IM2py, both of which are about five times as large as those of the diamagnetic complex [Y(hfac)$_3$(bpy)]. Therefore, it can be observed that the relaxation times of the hfac methine proton as well as the py protons and imidazole methyl protons of IM2py become shorter by through-space or outer-sphere dipolar interactions with the proximate molecules in solution, substantiating the existence of the IM2py radical in solution.

Since the ^{89}Y NMR spectrum of [Y(hfac)$_3$(IM2py)] gives only a sharp singlet at δ = 72.5 ppm (Figure 1S, Supporting Informations; for Supporting Informations see footnote on the first page of this article), the Y^{III} ion exists only as one

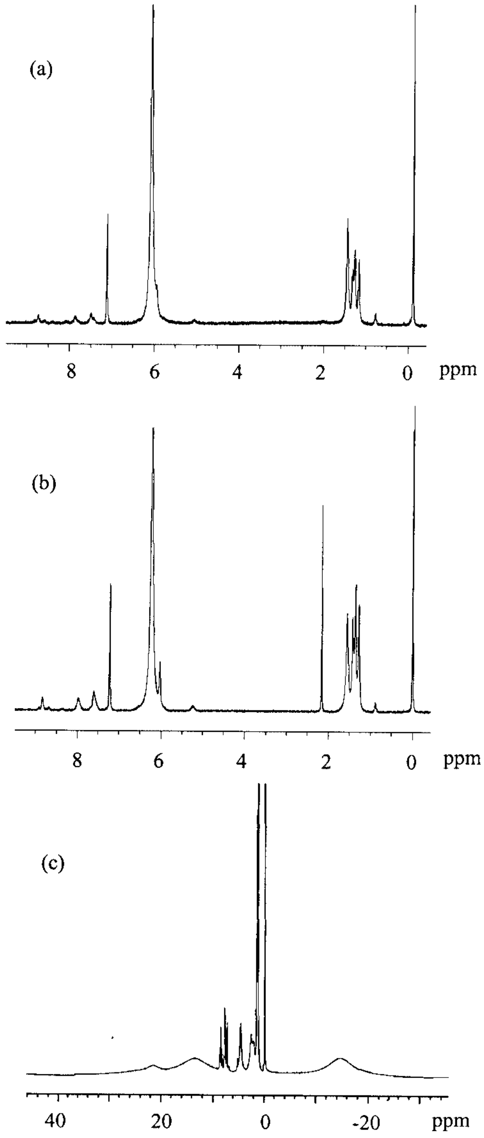


Figure 2. ^{1}H NMR spectra of (a) [Y(hfac)$_3$(IM2py)], (b) [Lu(hfac)$_3$(IM2py)] and (c) free IM2py

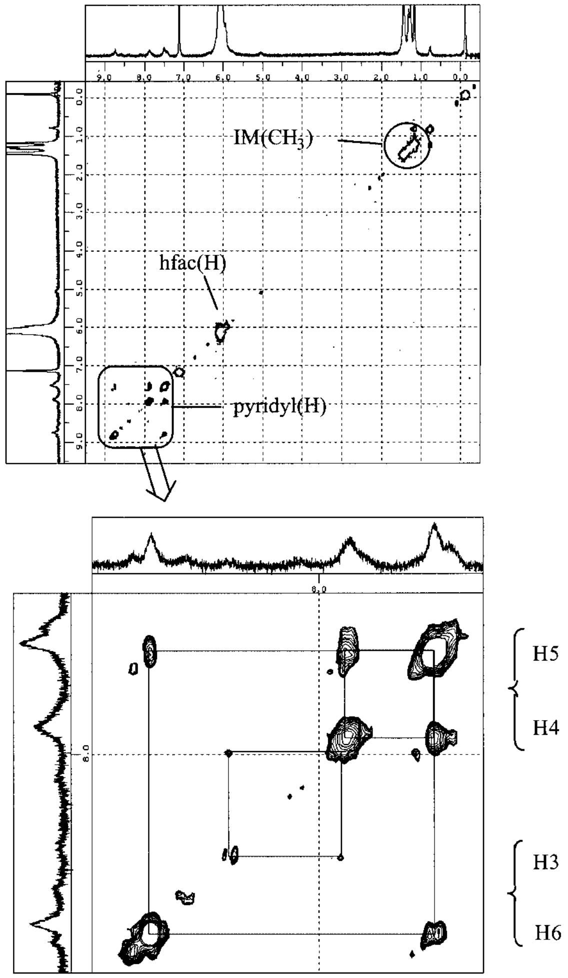
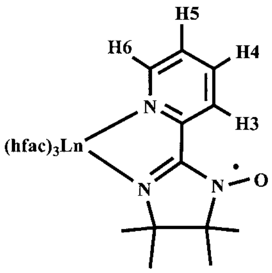


Figure 3. ^{1}H-^{1}H COSY spectrum of [Y(hfac)$_3$(IM2py)]



Scheme 2. Ln(hfac)$_3$(IM2py) with atom numberings of the pyridyl ring

species coordinated by IM2py. Thus, the ^{1}H and ^{89}Y NMR spectroscopic behaviour originates from the radical complex itself, but not from complexes containing decomposed nonradical ligands such as [Y(hfac)$_3$(H$_2$O)] and/or [Y(hfac)$_3$(IMH2py)]. It is clear that the protons in the IM2py moiety show diamagnetic ^{1}H NMR behaviour with respect to chemical shift but remain paramagnetic in line-width due to the outer-sphere interaction.

In the ^{1}H NMR spectra of diamagnetic *trans*-[Co(acac)$_2$(NO$_2$)(IM3py or IM4py)], only the methine and methyl proton signals of the acac ligand were previously considered when making the assessment of the geometrical structures. The coordinated pyridyl and imidazole protons of the IM*n*py group were not considered.[10] A re-examination of the ^{1}H NMR spectra of these Co^{III} complexes revealed the existence of the signals at $\delta \approx +8$ ppm and $\delta \approx +1.5$ ppm, respectively, which correspond to the diamagnetic pyridyl and imidazole protons both in terms of chemical shift and splitting pattern as in *trans*-[Co(acac)(NO$_2$)$_2$(IMH2py)] and [Y- or Lu(hfac)$_3$(IM2py)] [Figure 2 (a, b)]. Thus, it is from the *coordination* in the complexes containing diamagnetic metal ions that the diamagnetic NMR behaviour of IM radicals arises, but it does *not* necessarily depend on whether the coordination mode is monodentate or bidentate. The paramagnetic radicals coordinated in diamagnetic lanthanide and/or diamagnetic transition metal ions may hamper paramagnetic shifting of the ^{1}H NMR signals in the radical compounds or make them behave as if they were diamagnetic. This gives the appearance of complete disappearance of the unpaired electron around the protons in the IM radicals with respect to the ^{1}H NMR chemical shifts.

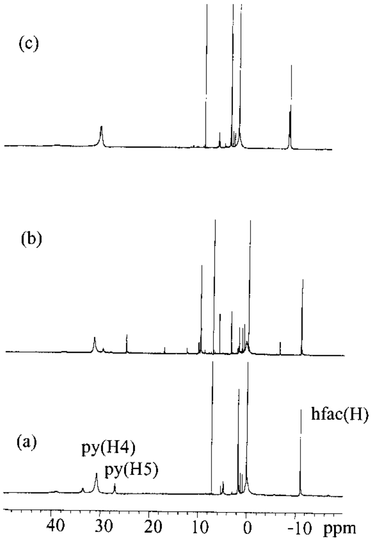


Figure 4. ^{1}H NMR spectra of (a) [Yb(hfac)$_3$(IM2py)], (b) [Yb(hfac)$_3$(IM4Me2py)] and (c) [Yb(hfac)$_3$(IM5Me2py)]

^{1}H NMR Spectra of the Paramagnetic Ln^{III} Complexes Containing the IM2py Radical

The ^{1}H NMR spectra of the paramagnetic lanthanide complexes [Ln(hfac)$_3$(IM2py)] deserve examination in relation to the diamagnetic NMR behaviour of the coordinated IM2py ligand in the complexes. Slightly broad NMR signals were observed for [Yb(hfac)$_3$(IM2py)] with the chemical shifts ranging from $\delta = +60$ to -30 ppm [Figure 4 (a)]. If there were little or no magnetic interaction between Yb^{III} and IM2py, the ^{1}H NMR spectra would appear as a sum of each paramagnetically shifted signal due to the Yb^{III} ion and IM2py. This is in contrast to the case of the paramagnetic Ni^{II} complexes, [Ni(β-diketonato)$_2$(NIT2py)], where the chemical shifts of the β-diketonato methine protons are given by a product of the NMR contact shifts of the nonradical Ni^{II} complexes and the fractional contribution to the Ni^{II} moiety arising from the magnetic interaction between the Ni^{II} ion and the NIT2py radical.[6a] By analogy with the diamagnetic ^{1}H NMR behaviour of [Y(hfac)$_3$(IM2py)] and [Lu(hfac)$_3$(IM2py)], it can be assumed that one unpaired electron of IM2py has no influence to the paramagnetic shift of Ln^{III}. In other words, the ^{1}H NMR signals of the IM2py coordinated to paramagnetic Yb^{III} suggest it might behave as a *diamagnetic* ligand in the complex. In order to assess this assumption, the ^{1}H NMR spectra could be analysed in the same manner as a series of isostructural paramagnetic lanthanide(III) complexes with diamagnetic ligands. The methine protons of the hfac (hfac-H) moiety can be assigned readily by comparison with the ^{1}H NMR spectra of the analogous nonradical complexes [Ln(hfac)$_3$(bpy)]. The NMR signals of the pyridyl protons of the IM2py group can be assigned in comparison with those of [Yb(hfac)$_3$(IM4- or -5Me2py)] (IM4- or -5Me2py = methyl-substituted pyridyl at the 4- or 5-position in IM2py). Though the ^{1}H NMR spectra of the (IM4Me2py)- and (IM5Me2py)-Yb^{III} complexes [Figure 4 (b, c)] are similar, on the whole, to that of [Yb(hfac)$_3$(IM2py)], the py-H4 and py-H5 signals of [Yb(hfac)$_3$(IM2py)] disappear in the NMR spectra of the (IM4Me2py)- and (IM5Me2py)Yb^{III} complexes, respectively. In the same manner, the assignments of the py-H4 and py-H5 signals for other paramagnetic Ln^{III} complexes were also made. The chemical shifts for py-H4 and -H5 in [Yb(hfac)$_3$(IM*n*Me2py)] are entirely different from those of free IM2py [Figure 4 (a)], whereas those of hfac-H in the (IM*n*Me2py)Yb^{III} complexes at $\delta \approx -10$ ppm are mostly unshifted relative to those of the corresponding nonradical Yb^{III} complex as shown in Figure 4 (b, c). In view of the latter behaviour, there is little influence on the hfac-H signal from the IM2py unpaired electron in the coordinated IM2py, whereas a large magnetic interaction between the paramagnetic Yb^{III} and the IM2py radical may be inferred from the significant change in the IM2py signals. This contradicts the fact that the magnetic interactions are very small, as deduced from the examination of the variable-temperature magnetic susceptibility measurements.[11] This discrepancy may be resolved by assuming that the ^{1}H NMR spectra of the coordinated IM2py ligands are affected by the paramagnetism of the Yb^{III} ion or the lanthanide induced shifts (LIS). In order to examine the ^{1}H NMR spectroscopic behaviour of the IM2py moiety in the paramagnetic Ln^{III} complexes, it is appropriate to make a quantitative structural analysis for the LIS of the NMR spectroscopic data on the basis of the above-mentioned assignments. The LIS, $\delta_{ij}{}^{\mathrm{LIS}}$, is given as the difference between the chemical shifts (δ^{para}) in the paramagnetic Ln^{III} complexes and those (δ^{dia}) of the corresponding diamagnetic Y^{III} complexes [Equation (1)].

$$\delta_{ij}{}^{\mathrm{LIS}} = \delta^{\mathrm{para}} - \delta^{\mathrm{dia}} \tag{1}$$

As a result of the dipolar and contact interactions between the electron spins on the Ln^{III} and the proton nuclear spin of the ligand, the chemical shifts of a given proton are shifted from the position observed in the corresponding diamagnetic environment [Equation (2)].

$$\delta_{ij}{}^{\mathrm{LIS}} = \delta(\mathrm{contact}) + \delta(\mathrm{dipolar}) \tag{2}$$

The dipolar interaction contains the information on the geometrical positions in space of the ligand nuclei [Equation (3)], where F_i is the hyperfine coupling constant of the nucleus (i) in the ligand independent of Ln^{III} ions (j),[20] $<S_z>_j$ is the spin expectation value for Ln ions (j),[22] D_j is a magnetic constant proportional to Bleaney's constant C_i which is characteristic of a given Ln^{III} ion, $<B_2^0> = <A_2^0(r^2)>$ is a crystal field coefficient of the Ln^{III} complex and G_i is a geometric function of the ligand nucleus which is equal to $(3\cos^2\theta - 1)/r^3$ assuming the axial symmetric magnetic susceptibility.[19−21]

$$\delta_{ij}^{\mathrm{LIS}} = F_i\langle S_z\rangle_j + \langle B_2^0\rangle D_j{\cdot}G_i \qquad (3)$$

In order to obtain the dipolar and contact parts from the experimental LIS, the graphical separation methods or classical one-nucleus crystal field dependent methods are given [Equations (4) and (5)].[19,20]

$$\delta_{ij}^{\mathrm{LIS}}/\langle S_z\rangle_j = F_i + \langle B_2^0\rangle G_i{\cdot}D_j/\langle S_z\rangle_j \qquad (4)$$

$$\delta_{ij}^{\mathrm{LIS}}/D_j = F_i\langle S_z\rangle_j/D_j + \langle B_2^0\rangle G_i \qquad (5)$$

If the lanthanide complexes were isostructural, a plot of $\delta_{ij}^{\mathrm{LIS}}/\langle S_z\rangle$ against $D_j/\langle S_z\rangle_j$ according to Equation (4) would be linear for a particular nucleus (i) of the ligand in the corresponding complexes across the entire Ln series. A linear plot of Equations (4) and (5) can be assumed for the dominant dipolar and constant contribution, respectively. In the case of multi-spin systems such as [Ln(hfac)$_3$(IM2py)], the magnetic interaction between unpaired spins of Ln^{III} and IM2py must be taken into consideration. This could be significantly large, unless the plots were linear. Thus, the intramolecular magnetic interaction in the (IM2py)Ln^{III} complexes may be tested by the application of the LIS analysis for nonradical complexes to the NMR spectroscopic data of [Ln(hfac)$_3$(IM2py)] (Table 1S, Supporting Information). In view of the correlation coefficients (r) in Figure 5, the linearity was found to be excellent for hfac-H and fairly good for py-H5 and py-H4 in the IM2py moiety for a series of Ln^{III} complexes according to Equation (4). According to Equation (5), however, the plots deviate significantly from linearity for py-H4 (r = 0.72) and hfac-H (r = 0.76) but not for py-H5 (r = 0.97). This suggests that the LIS for three protons are more dominantly contributed from the dipolar contribution than the contact one. The slopes for the two neighbouring protons (py-H4 and py-H5) in the plots of Equation (4) are similar to each other and have the same sign which is opposite to that of hfac-H, reflecting the differences in the geometrical dispositions of the three protons. The agreement factors $\{AF_i = [\Sigma(\delta^{\mathrm{LIS}} - \delta^{\mathrm{calcd.}})^2/\Sigma(\delta^{\mathrm{LIS}})^2]^{1/2}\}$ were found to be 0.1, 0.6 and 0.48 for hfac-H, py-H4 and py-H5, respectively, from the plots of Equation (4). The small AF value for hfac-H shows no significant influence from the IM2py radical. The fairly large AF values for py-H4 and py-H5 may result from less invariance in the crystal field coefficient and/or the influence of the unpaired electron of the IM2py group.

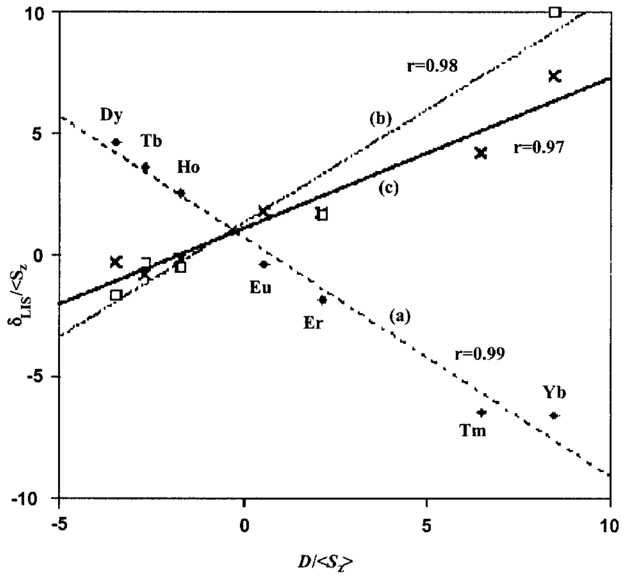


Figure 5. Plots of $\delta_i^{\mathrm{LIS}}/\langle S_z\rangle$ versus $D_j/\langle S_z\rangle$ according to Equation (4) ($\delta_i^{\mathrm{LIS}}/\langle S_z\rangle = F_i + G_iB_2^0D_j/\langle S_z\rangle$); hfac-H (a), py-H4 (b) and py-H5 (c)

In order to examine these causes, the two- and three-nuclei crystal field independent separation methods[23] were applied to the LIS. These are represented by Equation (6)[22] and Equation (7)[23], respectively.

$$\delta^{\mathrm{LIS}}(\mathrm{pyH}_i)/\langle S_z\rangle = (F_{\mathrm{py\text{-}H}i} - F_{\mathrm{hfac\text{-}H}}R_i) + R_i\delta^{\mathrm{LIS}}(\mathrm{hfac\text{-}H})/\langle S_z\rangle \qquad (6)$$

where $R_i = G_{\mathrm{py\text{-}H}i}/G_{\mathrm{hfac\text{-}H}}$

$$\delta^{\mathrm{LIS}}(\mathrm{py\text{-}H}_i)/\delta^{\mathrm{LIS}}(\mathrm{hfac\text{-}H}) = \alpha\delta^{\mathrm{LIS}}(\mathrm{py\text{-}H}_j)/\delta^{\mathrm{LIS}}(\mathrm{hfac\text{-}H}) + \beta \qquad (7)$$

where $\alpha = (F_{\mathrm{py\text{-}H}i}/F_{\mathrm{hfac\text{-}H}} - R_i)/(F_{\mathrm{py\text{-}H}j}/F_{\mathrm{hfac\text{-}H}} - R_j)$ and $\beta = [(F_{\mathrm{py\text{-}H}i}/F_{\mathrm{hfac\text{-}H}})R_i - (F_{\mathrm{py\text{-}H}i}/F_{\mathrm{hfac\text{-}H}})R_j]/(F_{\mathrm{py\text{-}H}j}/F_{\mathrm{hfac\text{-}H}} - R_j)$

The plots for $\delta^{\mathrm{LIS}}(\mathrm{py\text{-}H}_i)/\langle S_z\rangle$ versus $\delta^{\mathrm{LIS}}(\mathrm{hfac\text{-}H})/\langle S_z\rangle$ according to Equation (6) for the two-nuclei crystal field independent analysis show fairly good linearity with high r values (r = 0.95 for py-H4 and 0.93 for py-H5). In addition, the three-nuclei crystal field independent analysis given by a plot of $\delta^{\mathrm{LIS}}(\mathrm{py\text{-}H4})/\delta^{\mathrm{LIS}}(\mathrm{hfac\text{-}H})$ versus $\delta^{\mathrm{LIS}}(\mathrm{py\text{-}H5})/\delta^{\mathrm{LIS}}(\mathrm{hfac\text{-}H})$ in terms of Equation (7) exhibits good linearity (r = 0.93), confirming the invariance of the crystal field coefficient and the isostructural nature of the Ln^{III} complexes. Moreover, in order to check the invariance in the hyperfine coupling constant and the geometric factor, a crystal field independent method was employed according to Equations (8) and (9). This is based on the shift modulation, Y, using Yb^{III} as the reference Ln complex as defined in Equations (8) and (9).[20d,25]

$$Y_{\mathrm{Ln},j} = \delta^{\mathrm{LIS}}_{\mathrm{Yb},j}\langle S_z\rangle_{\mathrm{Ln}}/\langle S_z\rangle_{\mathrm{Yb}} - \delta^{\mathrm{LIS}}_{\mathrm{Ln},j} \qquad (8)$$

$$Y_{\mathrm{Ln,py\text{-}H}i} = Y_{\mathrm{Ln,hfac\text{-}H}}G_{\mathrm{py\text{-}H}i}/G_{\mathrm{hfac\text{-}H}} \qquad (9)$$

The plots of $Y_{\mathrm{Ln,py\text{-}H}i}$ of py-H4 and py-H5 with reference to $Y_{\mathrm{Ln,hfac\text{-}H}}$ of hfac-H give excellent conformities (Figure 6). Internal conformity for the F_i and $R = G_{\mathrm{py\text{-}H}i}/G_{\mathrm{hfac\text{-}H}}$ values was also found from Equations (4), (6) and (7) (Table 2S, Supporting Information), reconfirming the invariance of the parameters and isostructural pattern. From these structural analyses of the LIS, no change in the geometrical structures or isostructure with axial symmetry in solution was found and little or negligible magnetic interactions between Ln and IM2py were observed through the Ln series. This fact means that there is little effect on the ^{1}H NMR properties from the unpaired electron spin in the IM2py radical. Accordingly, the paramagnetic shifts of the IM2py ligand in the paramagnetic Ln^{III} ions are induced only by unpaired 4f electrons in the Ln^{III} ions and are hardly affected by the unpaired spin in IM2py. The present LIS analyses suggest that there is a difference in symmetry between the solid-state and solution structures of the complexes. That is, the present complexes in the solid state do not have actual axial symmetry as revealed by the X-ray analysis[11] and they exhibit no effect due to the magnetic asymmetry in solution. This can be re-emphasized from the fairly good linear relationships [$r = 0.80$ (py-H4), 0.86 (py-H5), and 0.98 (hfac-H)] in terms of the structural analyses according to plots of δ^{LIS}/D' versus D/D' derived from Equation (10), where D and G are given in Equation (3) and D' is an asymmetric magnetic constant and $G' = (\sin^2\theta\cos2\varphi)r^{-3}$.[26]

$$\delta^{\mathrm{LIS}}/D' = D/D'G + G' \qquad (10)$$

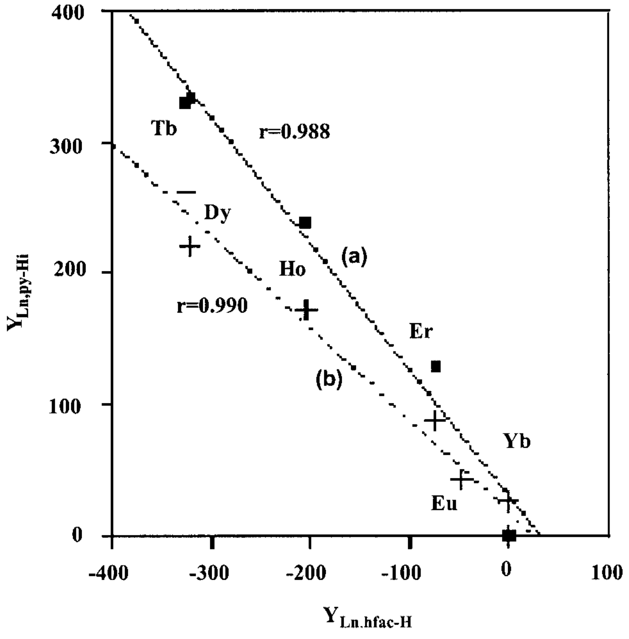


Figure 6. Plots of $Y_{\mathrm{Ln,pynH}}$ versus $Y_{\mathrm{Ln,hfacH}}$ according to Equation (9); py-H4 (a) and py-H5 (b)

The evidence for the effective magnetic axial symmetry of the Ln complexes can be accounted for by the intramolecular motions and/or rearrangements leading to the dynamic averaging on a faster time scale than that of NMR spectroscopy. This dynamic aspect is consistent with the observation of only one NMR signal for hfac-H, revealing the equivalence of three hfac ligands which are not symmetrically correlated in the solid state as found by the X-ray analysis.[11]

Conclusions

It has been found that the ^{1}H NMR spectra for the (IM2py)Ln^{III} complexes behave as if the IM2py radical was diamagnetic. For the diamagnetic Ln^{III} complexes, the ^{1}H NMR signals of the coordinated IM2py radical come in the range observed for the diamagnetic compounds, whereas in the paramagnetic Ln^{III} complexes their chemical shifts exhibit only shifts induced by the lanthanide ion's unpaired 4f electron spin(s) and not by the IM2py radical spin. In order to elucidate the peculiar diamagnetic behaviour of the coordinated IM2py ligand, more NMR spectroscopic data are needed for the coordinated radicals in diamagnetic and/or paramagnetic metal complexes.

Experimental Section

General: All chemicals were reagent grade and were used without purification. Lanthanide or yttrium trichloride hexahydrate and Hhfac were purchased from Wako Pure Chemical Industries Ltd. and Tokyo Chemical Industry Co. Ltd., respectively. The radical ligands IM2py, methyl-substituted pyridyl ligands IM*n*Me2py[27] and the complexes [Ln(hfac)$_3$(IM2py)][11] were prepared by previously reported methods.

Measurements: Magnetic susceptibility data of solids and solutions were measured using a magnetic balance (Sherwood Scientific, MSB-AUTO) and the Evans method[28] (^{1}H NMR spectra), respectively, at 23 °C. Pascal's constants were used to determine the constituent atom diamagnetism. The EPR spectrum was measured using a JES-RE1X ESR spectrometer at 296 K in CH$_2$Cl$_2$ and was analysed with WinFonia EPR Spectrum Simulation Software Ver. 1.25 (Bruker Analytische Messtechnik GmbH, Germany, **1996**). ^{1}H NMR spectra were recorded with a JEOL EX-270 spectrometer in CDCl$_3$ at 23 °C with concentrations of about 15 mM. The internal standard of tetramethylsilane (TMS) was assigned a chemical shift of $\delta = 0$ ppm. ^{89}Y NMR spectra were recorded with a JEOL Lambda-500 spectrometer in CDCl$_3$ at 30 °C, where the external standard of Y(NO$_3$)$_3$ in D$_2$O was assigned a chemical shift of $\delta = 0$ ppm.

Supporting Information: See footnote on the first page of this article. Table 1S with lists of the chemical shifts and LIS values for the IM2py complexes; Table 2S with F, B_2^0G, R, $(F_i - RF_i)$, α, β. Figure 1S with Y NMR spectra.

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