Challenging lanthanide relaxation theory: erbium and thulium complexes that show NMR relaxation rates faster than dysprosium and terbium analogues §

Alexander M. Funk, Peter Harvey, Katie-Louise N. A. Finney, Mark A. Fox, Alan M. Kenwright, Nicola J Rogers, P. Kanthi Senanayake and David Parker *

[a] Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK
email: david.parker@dur.ac.uk

Measurements of the proton NMR paramagnetic relaxation rates for several series of isostructural lanthanide (III) complexes have been performed in aqueous solution over the field range 1.0 to 16.5 Tesla. The field dependence has been modeled using Bloch-Redfield-Wangsness theory, allowing values for the electronic relaxation time, T_{1e} and the magnetic susceptibility, μ_{eff}, to be estimated. Anomalous relaxation rate profiles were obtained, notably for erbium and thulium complexes of low symmetry 8-coordinate aza-phosphinate complexes. Such behaviour challenges accepted theory and can be interpreted in terms of changes in T_{1e} values that are a function of the transient ligand field induced by solvent collision and vary considerably between Ln^{3+} ions, along with magnetic susceptibilities that deviate significantly from free-ion values.

Introduction

Spin relaxation theory of lanthanide complexes is most often addressed by perturbative treatments using Bloch-Redfield-Wangsness (BRW) theory [1] and its extensions. The effective magnetic moments (μ_{eff}) in solution can then be estimated by examining the magnetic field dependence of the longitudinal relaxation rate, R_1. The paramagnetic relaxation arises from rotational and conformational modulation of the electron-nuclear dipolar interaction, eq. (1).

$$R_1 = \frac{2}{15}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_N^2\mu_{eff}^2}{r^6}\left[\frac{7\tau_{R+e}}{1+\omega_e^2\tau_{R+e}^2}+\frac{3\tau_{R+e}}{1+\omega_N^2\tau_{R+e}^2}\right]+\frac{2}{5}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\omega_N^2\mu_{eff}^4}{(3kT)^2 r^6}\frac{3\tau_R}{1+\omega_N^2\tau_R^2} \qquad (1)$$

$$\mu_{eff}^2 = g_e^2\mu_B^2\left\langle \hat{S}^2\right\rangle \qquad \tau_{R+e} = \left(\tau_R^{-1}+T_{1e}^{-1}\right)^{-1}$$

where μ_0 is the vacuum permeability, g_N is the gyromagnetic ratio of the nucleus, g_{Ln} is the Landé factor of the fundamental multiplet J of the free Ln^{3+} ion, μ_B is the Bohr magneton (BM), r is the electron-nuclear distance, τ_r is the rotational correlation time, ω_N is the nuclear Larmor frequency, ω_e is the electron Larmor frequency and T_{1e} is the longitudinal relaxation time of the electron spin. The dependence of R_1 on $(\mu_{\mathrm{eff}})^4$ and $(\omega_{\mathrm{N}})^2$ in the second part of eq. 1 (Curie term) becomes more important at higher magnetic fields, for ions with larger values of μ_{eff} . Thus, at high field, relaxation rates for the second half of the 4f-elements tend to echo the μ_{eff} sequence: Dy/Ho > Tb > Er > Tm > Yb. At fields of less than 3 T, the rate of relaxation is mainly determined by $T_{1\mathrm{e}}$, so that this order can vary significantly.

The major problem of BRW theory is that perturbation theory assumptions are often violated for the electron. The approach also requires knowledge of a large number of empirical parameters that can be difficult to verify independently, for a particular complex system (*e.g.* $T_{1\mathrm{e}}$, τ_{R} and the true value of μ_{eff}). It has been hypothesised recently that the electronic relaxation time, $T_{1\mathrm{e}}$, with values between 0.1 and 1 ps, is a function of the nature of both the lanthanide ion and the transient ligand field induced by solvent collision. Highly symmetric systems showed a direct dependence of $T_{1\mathrm{e}}$ on the second-order ligand field term B_0^2 . [2]

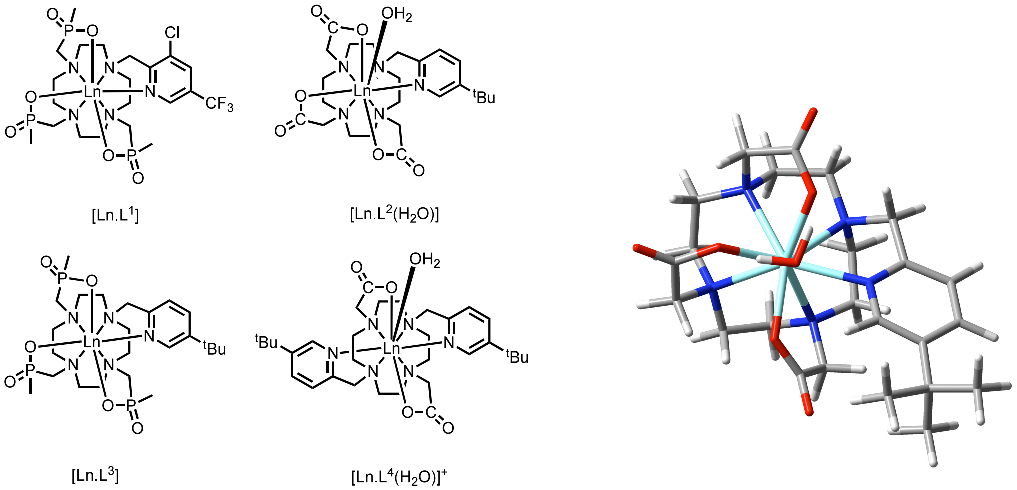
In lanthanide ion electronic structure theory, the effect of spin-orbit coupling on electronic energy levels is usually assumed to be much greater than the splitting due to the ligand field, which separates the J multiplets into individual m_J projections. Indeed, in the Landé and van Vleck approximations generally used to treat lanthanide paramagnetism, J is considered a good quantum number, allowing experimental values of magnetic susceptibility for the 'free ions' to be calculated directly. Such values are then predicted to be independent of coordination environment, i.e. not perturbed by the ligand field. [3] Typically, spin-orbit coupling values range from 600 to 2000 cm^{-1} across the 4f series. However, values for the second order crystal field term, B_0^2, can vary from near zero to 2000 cm^{-1}, [4] and higher order terms may have even greater size, suggesting that the Landé and van Vleck approximations will not hold consistently. [5] In such cases, the concept of J-mixing can be invoked, and has been reported in interpreting lanthanide total and circularly polarised emission spectra to explain unusual oscillator strengths and transitions for Eu(III) compounds and complexes. [6] Even where J is a good quantum number, the ligand field splittings within the ground multiplet can be much greater than kT at room temperature. In either case, the general approximation that a room temperature magnetic moment can be derived simply from J and the Landé factor g_J is not strictly valid. Examples of lanthanide compounds with large ligand fields have not often been studied in detail. However, using SQUID magnetometry for the LnOBr series where values of B_0^2 vary from -1200 (Tb) to -1350 cm^{-1} (Yb), Horsa has shown that the room temperature magnetic moments are systematically lower than the free-ion values, especially for Ho(III), (-11%). [7]

Lanthanide(III) ions have different electron distributions within the 4f shell depending on the coordination ligand field. For example, electron density clouds for the maximum $|m_J|$ projections are prolate for Yb, Tm, Er, Eu and oblate for Ce, Tb, Pr, Dy, Nd and Ho. Hence, ligand electron density on the molecular z axis has been suggested to destabilise maximum $|m_J|$ for the former ions and stabilise them for the latter. [8] Therefore, it is to be expected that room temperature magnetic moments for Ln(III) ions in coordination complexes will vary with the coordination environment, especially when ligand field splittings are large.

Results and Discussion

In this work, the variation of experimental relaxation rate data [2,9] with field has been used to estimate values of μ_{eff} and $T_{1\mathrm{e}}$ using iterative minimisation methods and assuming classical BRW theory. Four isostructural series of complexes were examined, [Ln.L$^{1\text{-}4}$], [10,11] (Scheme 1) holding constant the Ln-proton average distance, r, and the complex rotational correlation time, τ_{r}, for each of the six complexes examined (Tb-Yb) within a given series. These sets of complexes were chosen as they have known values of B_0^2, (taken from analysis of their Eu emission spectra: [Eu.L^1], -550; [Eu.L^2], -450; [Eu.L^3], -570; [Eu.L^4], -355 cm^{-1}) [5,12] and they possess NMR reporter groups, in relatively rigid coordinated pyridyl moieties, that reside at a convenient distance from the paramagnetic centre, allowing measurement of longitudinal relaxation rates in solution at up to six magnetic fields from 1.0 to 16.5 T.

Values of the mean distance r from the paramagnetic centre to the t-butyl protons were estimated by optimised geometries using *ab initio* and DFT methods without symmetry constraints, based on the yttrium analogue of a published X-ray structure (Scheme 1 and ESI). The ionic radius of Ln^{3+} ions, in both 8 and 9 coordination, contracts by only 0.06 Å from Tb to Yb, so the use of a constant distance between the metal ion and the reporter resonances, CF_3 for [Ln.L^1] (6.1 Å) and the ^{t}Bu group for the other three complexes (6.6 Å), is a reasonable approximation. Estimates of τ_{R} were based on previously established values for these or closely related systems [2,10]; if allowed to vary by ±10%, changes in μ_{eff} and T_{1e} of less than 3% were found at 9.4 and 4.7 T (ESI).



Scheme 1 Structures of [Ln.L$^{1-4}$] and a view of the DFT optimised structure of [Y.L^2(H$_2$O)]

The experimental data (Tables 1 and 2) showed that the longitudinal relaxation rates for the erbium complexes of L^1 and L^3 were significantly faster than for Dy, Ho and Tb, both at low and at high field, whereas for the nine-coordinate carboxylate series of complexes, rates for Dy were fastest, and fell in the sequence: Dy > Ho/Tb> Er > Tm > Yb. Indeed, the rate of relaxation for [Er.L^3] was over 90% higher than the corresponding Dy complex at 1 T, and the thulium complexes of L^1 and L^3 relaxed faster than their Tb analogues, between 4.7 and 16.5 T. Such field dependent behaviour is unprecedented and suggests that the theory used to interpret paramagnetic relaxation may be imprecise and/or that values of μ_{eff} for the systems examined differ considerably from 'free-ion' values (Tb, 9.8; Dy, 10.3; Ho, 10.4; Er, 9.4; Tm, 7.6; Yb, 4.5 BM) [3].

Table 1 ^{19}F shift and relaxation rate data for the CF$_3$ resonance of [Ln.L^1] (295 K, D$_2$O, τ_r 240 ps, r 6.1 Å) to give the 'best fit' μ_{eff} and T_{1e} values

Ln^{3+}	δ_F/ppm[a]	R_1/s^{-1} 4.7 T	 9.4 T	 11.7 T	 14.1 T	 16.5 T	μ_{eff}/BM	T_{1e}/ps
Tb	–158.4	56±1	89±1	117±3	133±1	150±4	8.54(04)	0.37(03)
Dy	–162.4	64±2	114±1	142±1	166±1	192±1	9.11(03)	0.35(02)
Ho	–107.8	67±1	129±1	154±2	189±1	218±1	9.43(03)	0.32(02)
Er	–16.9	94±1	136±1	175±1	188±1	219±3	9.35(03)	0.64(03)
Tm	17.1	59±1	107±1	132±1	152±1	173±1	8.89(01)	0.36(03)
Yb	–41.5	14.2±0.5	15.1±0.1	17.3±1.1	18.0±0.1	19.4±0.3	4.69(06)	0.43(04)

[a] diamagnetic Y complex resonates at -63.0 ppm; [b] values of μ_{eff} for the free ions are usually considered to be within 5 % of the following: Tb, 9.8; Dy, 10.3; Ho, 10.4; Er, 9.4; Tm, 7.6; Yb, 4.5 BM. [3]

Table 2 ^{1}H NMR ^{t}Bu shift data and estimated best-fit values of T_{1e} and μ_{eff} for the later lanthanide(III) complexes of ligands L^2-L^4 (295 K, D_2O, r = 6.6 Å; see ESI for full data)[a]

Complex	δ_H/ppm	μ_{eff}/BM	T_{1e}/ps
[LnL^2(H$_2$O)]			
Tb	–11.6	9.68(02)	0.59(02)
Dy	–20.5	10.22(02)	0.49(02)
Ho	–7.4	9.82(02)	0.22(02)
Er	+7.0	8.95(01)	0.17(01)
Tm	+10.8	8.12(03)	0.29(02)
Yb	+6.3	4.44(08)	0.29(03)
[LnL^3]			
Tb	–75.9	8.81(03)	0.49(02)
Dy	–75.0	9.47(02)	0.45(02)
Ho	–31.8	9.77(02)	0.37(02)
Er	+38.2	9.70(02)	0.85(01)
Tm	+67.0	9.51(01)	0.30(01)
Yb	+16.3	4.57(09)	0.53(02)
[LnL^4(H$_2$O)]			
Tb	–7.2	10.26(03)	0.96(04)
Dy	–17.8	10.84(03)	0.93(04)
Ho	–7.0	10.03(03)	0.25(02)
Er	+3.4	b	b
Tm	+6.2	7.84(04)	0.16(05)
Yb	+9.1	4.70(10)	0.15(04)

[a] τ_r values were estimated to be 260 ps for [LnL^{2,3}] and 280 ps for [LnL^4]; [b] satisfactory minimisation did not occur.

The fits to equation 1 of the sets of experimental data for each complex converged to well-defined minima, (Tables 1 and 2, Figure 1 and ESI), allowing values of μ_{eff} and T_{1e} to be estimated. The magnetic susceptibilities for complexes of L^1 and L^3 followed the unusual order Ho > Er > Dy > Tm > Tb, in accord with the high field rate data with enhancements (*vs* the free-ion literature values) of up to 24% for Tm, and variations of up to 11% for the other ions. Only the values for the Yb complexes fell within ±5% of the classical values.

Variable temperature studies (Figure 1) of [Dy.L^3] revealed the expected linear dependence of the longitudinal relaxation rate with 1/T^2 at 11.7 T (high field), over the temperature range 290-315 K. No significant variation of R_1 was observed at 1 T over a 5 K temperature range, associated with the vanishing impact of the Curie term (eq. 1). At low field the order of the measured relaxation rates echoed the sequence of T_{1e} values, in accord with the diminishing contribution of Curie relaxation (eq. 1). The fast, low-field relaxation of the Er complexes of L^1 and L^3 is particularly striking and can be attributed to a relatively large T_{1e} value. [2] The low field behaviour of [Tm.L^3] fitted the least well of all the systems studied.

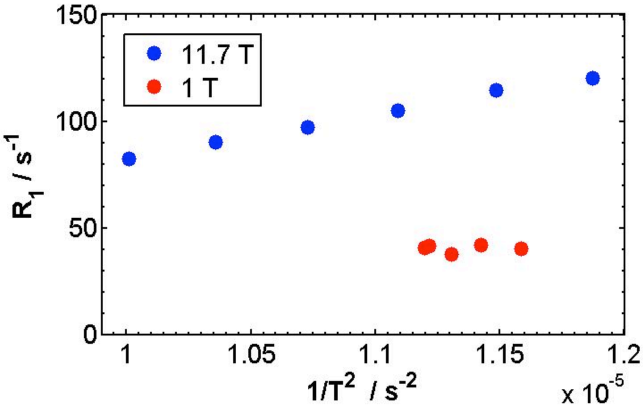


Figure 1 ^{1}H NMR relaxation rates (R_1/s^{-1}) for the ^{t}Bu resonance in [Dy.L^3] measured at 11.7 T (blue) and 1 T (red) as a function of 1/T^2 (D_2O). Temperatures for 1 T measurements were calibrated from the ^{t}Bu resonance chemical shift (ESI)

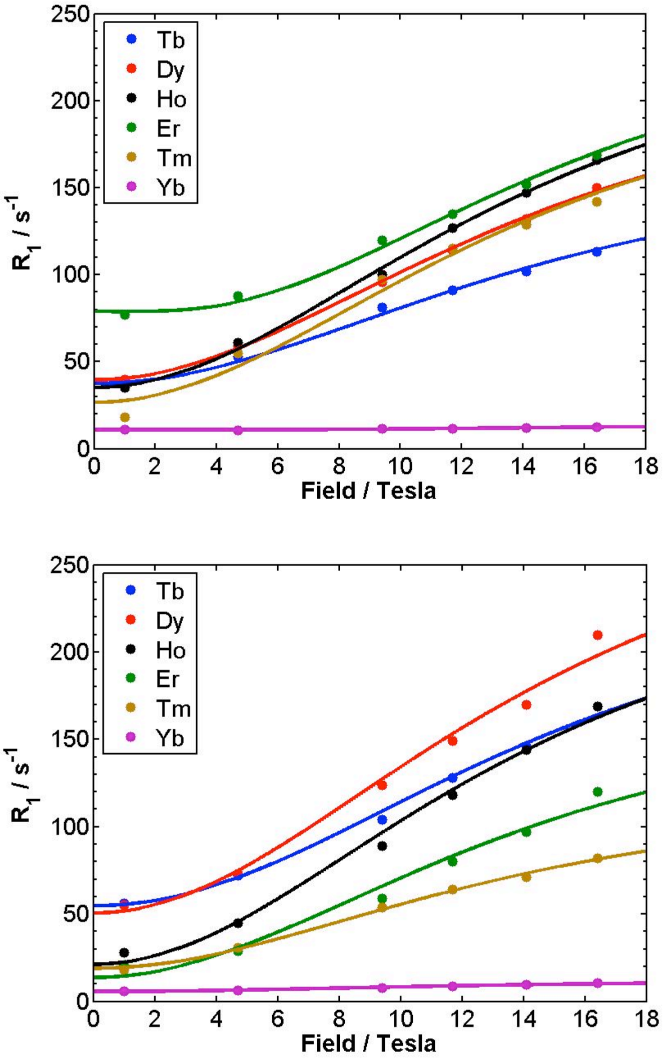
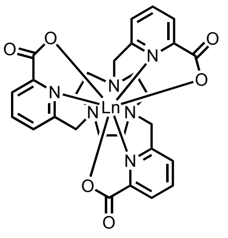


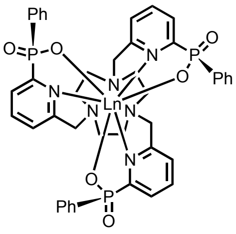
Figure 2 ^{1}H NMR relaxation rates (R_1/s^{-1}) for the ^{t}Bu resonances in [Ln.L^3] (*upper*) and [Ln.L^2(H_2O)] (*lower*) as a function of magnetic field, showing the fits (line) to the experimental data points (295K, D_2O).

Control experiments in small ligand field systems

As a control, parallel analyses have been carried out with the isostructural nine-coordinate complexes of L$^{5-7}$ [13-15] that possess time-averaged C$_3$ symmetry, in which the ligand field is much smaller and values of B_0^2 are considerably lower (70, 110 and 235 cm^{-1} respectively for the Eu(III) analogues). For each of these complexes, iterative fitting of the field-dependent rate data gave estimated values of μ_{eff} that fell within ±5% of calculated values, (Table 3), except for [Er.L^3]$^{3+}$ where the deviation was -7%. Furthermore, each of the values of T_{1e} was considerably smaller than in the low-symmetry complex series, consistent with the hypothesis that electronic relaxation in these highly symmetric systems is directly proportional to the static ligand field or the transient ligand field induced by solvent collision. [2]

Our earlier work with [Ln.L^6] [14] had examined ^{31}P relaxation rate data over the field range 4.7 to 16.5 T. In this case, fitted values of T_{1e} fell within two standard deviations of the values given in Table 3. Larger discrepancies were found in the fitted values of μ_{eff} , notably for Ho, Er and Tm. The discrepancy relates to the fact that these earlier analyses did not use a fixed distance. Indeed, the fitted value for the Ln-P distance was 0.2 Å shorter than found by X-ray crystallography. Refitting the rate data, fixing r = 3.91 Å, gave closer correspondence for μ_{eff} values (yet Tb/Dy 10 and 12% different), and similar T_{1e} values (Table 3, footnote b).


[Ln.L^5]


[Ln.L^6]

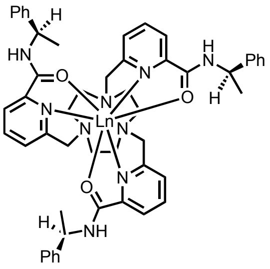

[Ln.L^7]$^{3+}$

Table 3 Estimated effective magnetic moments^a, μ_{eff}, and electronic relaxation times, T_{1e}, for the lanthanide complexes [Ln.L$^{5-7}$], based on analysis of ^{1}H NMR relaxation rate data over the field range 4.7 to 16.5 T [10,11,7] (295 K, D$_2$O, CD$_3$OD; D$_2$O for [Ln.L^5]) ^{a}.

Ln^{3+}	[Ln.L^5]		[Ln.L^6]^b		[Ln.L^7]$^{3+}$	
	μ_{eff}/BM	T_{1e}/ps	μ_{eff}/BM	T_{1e}/ps	μ_{eff}/BM	T_{1e}/ps
Tb	9.65(02)	0.26(03)	9.00(06)	0.25(02)	9.59(03)	0.29(02)
Dy	10.47(02)	0.28(02)	9.83(03)	0.27(04)	10.09(03)	0.25(03)
Ho	10.40(01)	0.17(02)	10.94(01)	0.14(07)	10.31(02)	0.23(03)
Er	9.23(02)	0.23(03)	9.59(02)	0.32(06)	8.80(03)	0.26(04)
Tm	7.43(01)	0.08(02)	8.25(03)	0.09(02)	7.77(02)	0.13(03)
Yb	4.27(02)	0.09(04)	4.75(03)	0.10(03)	4.56(03)	0.12(03)

[a] Data for the following ^{1}H resonances were analysed here: [Ln.L^5], pyH^{3,4}; [Ln.L^6], H$_{ax}$, H$_{eq}$, pyH^{3,5}; [Ln.L^7], pyH^{3,4}. Similar values (± 10%) were found by examining other resonances. Distances used in these analyses were taken from published X-ray data [10-12] and the values of τ_r used were: [Ln.L^1], 135 ps; [Ln.L^2], 190 ps; [Ln.L^3]$^{3+}$, 188 ps. Earlier studies have examined the solvent dependence of the estimated T_{1e} values in several related isostructural series of complexes. Little or no solvent effect on the size of T_{1e} was observed; the major impact of solvent variation is in determining the τ_r value, via viscosity modulation and has been allowed for here. [2] [b] Fitting the published ^{31}P rate data [14] for [Ln.L^6] with r held at 3.91Å, gave μ_{eff} and T_{1e} values as follows: Tb: 9.91(0.32); Dy, 11.0(0.31); Ho, 10.6 (0.15); Er, 9.63(0.37), Tm, 7.65 (0.07); Yb, 4.38 (0.07).

Summary and Conclusions

In summary, application of BRW theory suggests that the fast relaxation of Er and Tm(III) complexes of the 8-coordinate low-symmetry phosphinate ligands L^1 and L^3 can be attributed to their long electronic relaxation times and relatively high μ_{eff} values, compared to the Dy and Ho analogues. These features are important in devising PARASHIFT relaxation probes for use in MRI, where consideration needs to be given to both the size of the dipolar shift and the relaxation behaviour of a lanthanide complex, for use at a particular magnetic field. [10,11,16] A large dipolar shift allows bigger bandwidths to be used in imaging, permitting the selective observation of a shifted ligand resonance. For the complexes of [Ln.L^3], the *t*-butyl group in the Tm and Er complexes resonates at +67 and + 38 ppm, compared to -75 and -76 ppm for the Dy and Tb analogues. The fast relaxation of the same resonance permits more rapid data acquisition per unit time in spectroscopy and imaging. [9,11] Given that modern clinical MR imaging fields are 1.5 and 3 T, the unusually fast relaxation of the erbium complexes at low field merits further attention, and helps guide lanthanide ion selection and ligand design in PARASHIFT probe development. Examples of the use of thulium PARASHIFT probes for cell tracking *in vivo* have recently appeared. [17]

This study also suggests that independent variable temperature ESR and SQUID magnetometry measurements are warranted, addressing the anisotropy of the magnetic susceptibility tensor in the 8-coordinate systems lacking an axial donor. Such studies are required in order to explore in more detail the origins of the differing magnetic susceptibility behaviour, with respect to the 9-coordinate analogues where a water molecule occupies the capping axial site.

In addition, a better theory of paramagnetic relaxation may be required, in which allowance is made for the anisotropy of the ligand field and the differing contributions of the m_J states to the overall susceptibility. Related thinking is evident in the recent rebuttal of Bleaney's theory of magnetic anisotropy in paramagnetic lanthanide(III) complexes,[11] where the directional dependence of the magnetic susceptibility tensor has a profound impact on the observed chemical shift. The NMR paramagnetic shift behaviour of ligand resonances can be understood in terms of a change in the relative size of the mutually orthogonal components (axial/rhombic) of the overall susceptibility tensor, corresponding to a shift in the principal axis of magnetization, as the ligand or the lanthanide ion is permuted. Such a conclusion accords with the important work reported recently for lanthanide complexes of the macrocyclic ligand DOTA, in low temperature, single-crystal magnetometry studies. [18]

Acknowledgements

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§ Supplementary information is available: NMR spectral figures, tables of shift and relaxation rate data at five or six magnetic field strengths and a discussion of error analyses.

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