

Correlation of optical and NMR spectral information with coordination variation for axially symmetric macrocyclic Eu(III) and Yb(III) complexes: axial donor polarisability determines ligand field and cation donor preference

Rachel S. Dickins,* David Parker,* James I. Bruce† and David J. Tozer

Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE.

E-mail: r.s.dickins@dur.ac.uk; david.parker@dur.ac.uk

Received 2nd December 2002, Accepted 17th February 2003

First published as an Advance Article on the web 7th March 2003

In Bleaney's theory of magnetic anisotropy, the second-order crystal field coefficient, B_0^2 , is predicted to determine the dipolar NMR shift of paramagnetic lanthanide complexes in solution. This parameter has been measured directly, by analysing the europium emission spectra for a series of eight- and nine-coordinate axially symmetric complexes based on cyclen including aza-carboxylate ligands (e.g. DOTA), phosphonates (DOTP), phosphinates and several carboxamides (e.g. DOTAM). For both Yb and Eu complexes with a common coordination number and geometry (square antiprism (SAP) or twisted square antiprism (TSAP)), the dipolar NMR shift correlates very well with this parameter, which also determines the sign and magnitude of a major CD band in the near-IR CD spectra of a series of enantiopure Yb complexes. Measurements of the free energy change associated with axial ligand exchange in a cationic europium tetraamide complex, [Eu(DOTAMPh)](CF₃SO₃)₃, supported by a simple electrostatic perturbation model, have been interpreted in terms of a predominant donor atom polarisation model which affords a simple assessment of Ln ion donor atom preference and ranks the axial second-order ligand field coefficient.

Introduction

It is widely appreciated that the optical and NMR spectral properties of paramagnetic complexes of the f-block series are determined by the nature and local symmetry of the coordination environment.^{1,2} Most studies have examined one ligand type in detail and varied the lanthanide ion, seeking to understand the nature of charge density, coordination number and ligand field variations across the series. The majority of these reports deal with ¹H, ¹³C and ³¹P NMR properties,³⁻⁶ although there is one compelling report of ligand field/optical emission variation from Ce to Lu for the nine-coordinate tris(oxydiacetate) complexes.⁷ However, there have been very few attempts to correlate⁸ such information between different complexes and to pinpoint the relative importance of varying donor atom charge or polarisability (ligand field effects) when other important factors such as coordination number and geometry are held constant, or *vice versa*. Such issues are very difficult to unravel if the complexes undergo intramolecular or intermolecular exchange processes, for example involving an interconversion between complexes of differing coordination number or geometry. Recently, an increasing amount of spectral information has been reported for related series of well-defined lanthanide complexes, whose constitution and exchange dynamics are appreciated in some detail.⁹ The best example of this class is that based on C₄-symmetric complexes derived from 1,4,7,10-tetrazacyclododecane (cyclen), in which the ligand is octadentate and the complex adopts a coordination number of eight or nine. In the latter case, a regular or twisted square antiprismatic geometry is adopted with the twisted geometry being favoured for nine-coordinate systems as well. Examples of ligands in this class include the anionic systems e.g. DOTA,⁴ gDOTA,¹⁰ DOTP⁶ and the phosphinate analogue DOTPBn^{11,12} and the neutral tetraamide ligands, DOTAM,¹³⁻¹⁵ DOTMA,¹⁵ DOTAMPh^{16,17} and DOTTA^{15,18} (Fig. 1).

On considering this series, we chose to study in detail their europium and ytterbium complexes. In emission, Eu spectra are amongst the simplest to examine and interpret owing to the

absence of degeneracy of the emissive ⁵D₀ excited state. Furthermore, the splitting of the two magnetic dipole allowed ⁷F₁-⁵D₀ transitions in axial symmetry provides a direct measure of the second-order crystal field parameter, B_0^2 . Crystal field parameters of higher order are smallest for Eu, amongst the lanthanides.¹⁹ The parameter B_0^2 also determines the dipolar ¹H NMR shift that dominates the spectral behaviour of Eu and Yb complexes: for europium, the analysis of shifted proton resonances that are more distant from the paramagnetic centre removes any problems arising from a contact shift contribution. In particular, for complexes based on cyclen (Fig. 1), Sherry and Geraldes and co-workers have unequivocally shown²⁰ that the paramagnetic proton NMR shifts for H-4, H-1 and H-5 in [Ln(DOTP)]⁵⁻, [Ln(DOTA)]⁻ (and by analogy the related cyclen-based complexes) are purely dipolar in origin, *i.e.* they are free from any contact shift contribution. The paramagnetic lanthanide induced shift is generally considered as the sum of contact and pseudo-contact terms (eqn. (1))

$$\delta^{\text{para}} = F_i + C_j B_0^2 G_i = \delta_{ij}^{\text{c}} + \delta_{ij}^{\text{pc}} \quad (1)$$

where, C_j are Bleaney factors dependent on the given 4fⁿ electronic configuration, G_i is a geometrical term containing structural information ($G_i = (3\cos^2\theta - 1)/r^3$), F_i is the contact term proportional to the hyperfine Fermi constant (A_i) and $\langle S_z \rangle_j$ is the spin expectation value of the S_z operator. In axial symmetry, eqn. (2) provides a good approximation for the pseudocontact or dipolar NMR shift,

$$\delta_{ij}^{\text{pc}} = \frac{-2C_j\beta^2}{(kT)^2} \left[\frac{3\cos^2\theta - 1}{r^3} \right] B_0^2 \quad (2)$$

where $C_j = g^2 J(J+1)(2J-1)(2J+3)\langle J|a|J' \rangle$, and θ and r define polar coordinates with respect to the principal axis. Europium emission spectra allow information to be gleaned concerning the dipolar polarisability of the ligand donors. Analysis of the form and relative intensity of the electric-dipole allowed $\Delta J = 2$ transition reveals information on the site symmetry and especially the polarisability of the donor atoms.

† Present address: Department of Chemistry, Open University, Milton Keynes.

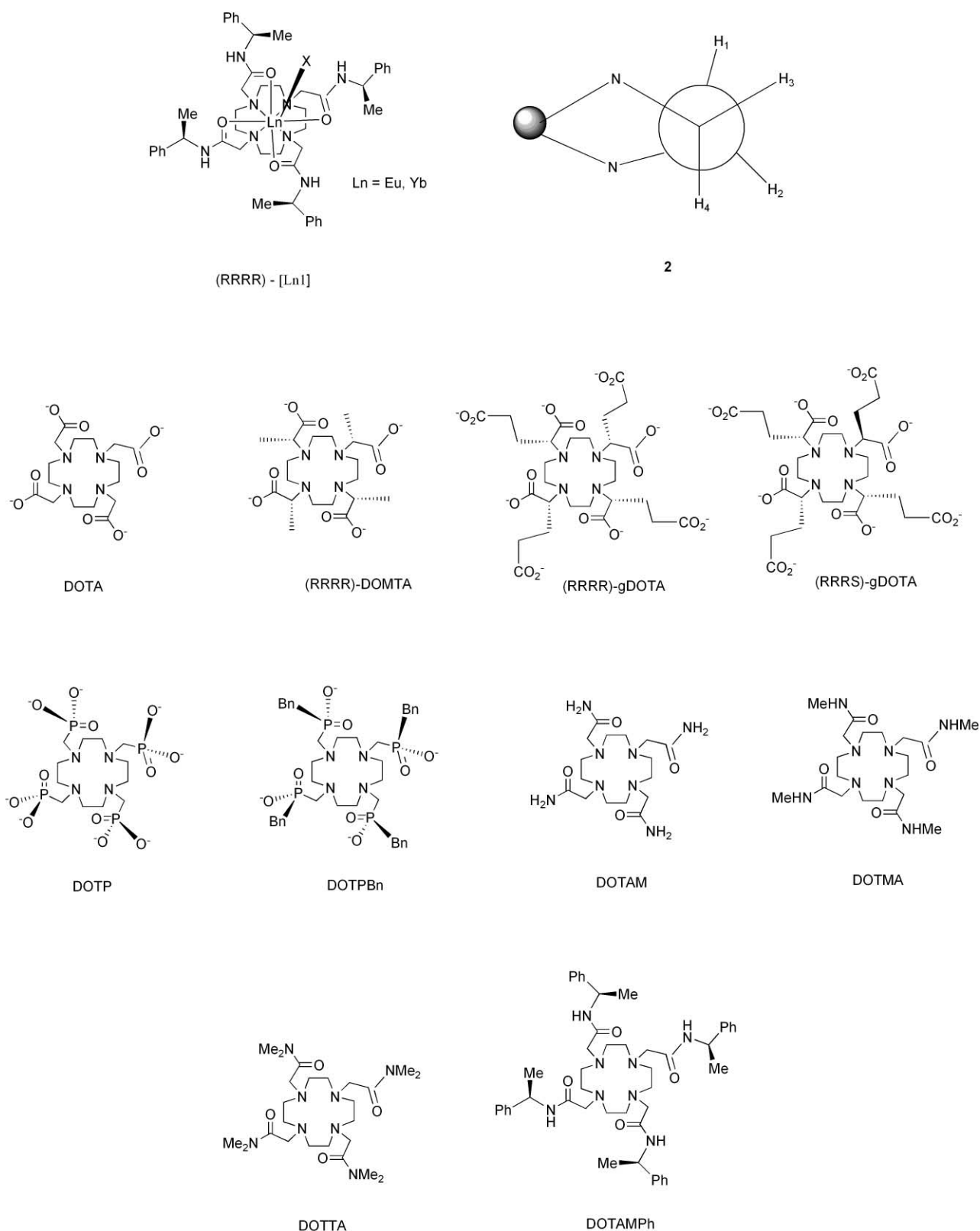


Fig. 1 Structures of octadentate ligands forming Eu and Yb complexes.

Recent work has highlighted the sensitivity of the intensity of this transition to the nature of the axial donor ligand.^{21,22}

The choice of Yb complexes for study is based on both the favourable NMR characteristics and the fact that the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ optical transition, being globally magnetic-dipole allowed, is amongst the most sensitive of the Ln series to circular dichroism analysis.^{23,24} A full interpretation of these CD spectra is difficult because the separation of the sub-levels of the ${}^2F_{7/2}$ ground state is less than $\frac{1}{2}kT$ ($<1.3 \text{ kJ mol}^{-1}$ at 298 K) and considerable band overlap occurs. Nevertheless, the $1-1'$ trans-

ition at 975–980 nm is believed to be quite sensitive to the crystal field in the few examples where the emission or CD spectra have been studied in any detail.^{25–28}

We herein report and collate studies examining two types of Eu and Yb complexes by ${}^1\text{H}$ NMR, emission and CD spectroscopy. Firstly, using the complex $[\text{Ln}(\text{DOTAMPh})](\text{CF}_3\text{SO}_3)_3$, we have systematically varied the nature of the capping axial ligand (X = MeCN, H_2O , MeOH, py, R_2NH , DMF, DMSO, HMPA), taking advantage of the ease of substitution of the axial ligand in acetonitrile solution. Secondly, either with a

Table 1 Observed ^1H NMR shifts for selected ligand resonances in $[\text{Ln}(\text{DOTAMPh})\text{X}]^{3+}(\text{CF}_3\text{SO}_3^-)_3$ (295 K, CD_3CN , 200 MHz, 1 mM complex, 20-fold excess of axial donor; for assignments see structure 2; shifts are relative to internal $^1\text{BuOH}$)

| Axial donor X | $\text{H}_{4\text{ax}}$ | | $\text{H}_{3\text{eq}}$ | | $\text{H}_{2\text{eq}}$ | | $\text{H}_{1\text{ax}}$ | | H'_{CHCO} | | H''_{CHCO} | |
|---------------------------------|-------------------------|-----------------|-------------------------|-----------------|-------------------------|------|-------------------------|-----------------|---------------------------|-------|----------------------------|-------|
| | Yb | Eu ^d | Yb | Eu ^a | Yb | Eu | Yb | Eu ^d | Yb | Eu | Yb | Eu |
| MeCN | +117.6 | +32.0 | +20.3 | -1.8 | +16.6 | -7.3 | -41.1 | -8.1 | -33.7 | -18.0 | -75.8 | -19.8 |
| MeNO ₂ | +116.2 | +30.1 | +20.2 | -1.6 | +16.5 | -7.6 | -40.9 | -7.4 | -33.6 | -14.9 | -75.6 | -15.8 |
| Pyridine ^b | +115.0 | +31.3 | +20.4 | -1.7 | +16.7 | -7.6 | -39.8 | -7.6 | -32.8 | -15.0 | -75.1 | -15.9 |
| Et ₃ N ^c | +113.4 | - | +19.8 | - | +16.1 | - | -39.8 | - | -32.8 | - | -73.9 | - |
| MeOH | +112.0 | +28.6 | +19.7 | -2.3 | +16.1 | -7.7 | -39.1 | -7.2 | -32.2 | -14.9 | -73.1 | -15.2 |
| Water | +101.3 | +28.1 | +17.8 | -2.5 | +14.5 | -7.8 | -35.3 | -7.4 | -29.1 | -14.9 | -65.8 | -15.4 |
| Me ₂ NH ^c | +101.0 | - | +18.0 | - | +14.8 | - | -34.6 | - | -28.7 | - | -66.7 | - |
| DMAP | +89.2 | +24.4 | +16.2 | -3.6 | +13.3 | -5.8 | -30.0 | -5.5 | -25.0 | -10.8 | -57.6 | -13.3 |
| DMF | +88.1 | +21.5 | +15.6 | -4.1 | +12.8 | -5.4 | -30.3 | -5.4 | -25.1 | -10.6 | -56.7 | -13.0 |
| Octylamine | +75.8 | +20.5 | +13.4 | -3.9 | +10.9 | -4.6 | -25.9 | -4.5 | -21.4 | -9.4 | -48.4 | -12.0 |
| DMSO | +71.1 | +18.2 | +12.7 | -3.8 | +10.4 | -4.3 | -24.1 | -4.2 | -20.1 | -9.1 | -45.2 | -11.6 |
| HMPA | +50.0 | +11.5 | +7.7 | -0.7 | +6.3 | -2.6 | -18.0 | -2.6 | -18.0 | -8.4 | -34.0 | -9.6 |

^a The rather poor correlation (shift/donor type) may be due to local anisotropy associated with the solvent or to a non-zero contact shift contribution. ^b Sterically hindered amines such as 2,6-dimethylpyridine did not bind to Eu, nor did the simple imine *N*-benzylidenemethylamine. ^c For the Eu complex amide deprotonation was observed (assisted by the Eu³⁺ centre acting as a charge sink), leading to a non-C₄ symmetric species of different ligand field. ^d The dipolar proton NMR shift of H-1 and H-4 has been shown to be free of any contact contribution in related complexes $[\text{Ln}(\text{DOTA})]^-$ and $[\text{Ln}(\text{DOTP})]^{5-}$; for H-2 and H-3, however, the contact shift contribution is likely to be significant for the Eu series.

water molecule occupying the axial site or with no axial donor being present (CN = 8), we have correlated NMR shift and optical emission data for the series of ligands in Fig. 1, thereby allowing an assessment of the role of the four pendant atom donors, with a common, rigid N₄ basal set provided by cyclen.

Results and discussion

Correlation of Eu and Yb NMR and optical spectral properties: role of axial donor

Dynamic ^1H NMR studies, X-ray analysis, emission and CD spectral studies of the Yb and Eu complexes, **1**, of the C₄-symmetric ligand (SSSS)-DOTAMPh have established that one major species exists in solution, namely the monocapped square antiprismatic ($\Delta, \lambda\lambda\lambda\lambda$) complex (Fig. 2). In dry acetonitrile solution, the axial ligand is a N-bound acetonitrile molecule which is relatively easily displaced by addition of a ≥ 20 fold excess of a competitive donor ligand. Changes were conveniently monitored by ^1H NMR spectroscopy (5 mM complex, 295 K, CD_3CN) examining differences in the appearance of the paramagnetically shifted spectrum. Resonances were assigned by COSY methods and by reference to the established shift sequence for closely related complexes (Table 1).^{4,6,24} A comparison of the ^1H NMR shifts, as a function of the added axial donor (Fig. 3), strongly suggested that the complex was adopting the same overall structure (*i.e.* a capped square antiprism), as shifts in the diastereotopic ring axial and equatorial protons and the exocyclic methylene protons revealed a proportional change. The behaviour of the amide NH resonance (*viz.* Fig. 1) was different only in the case of an added primary or secondary amine, suggesting that in each of these cases it may act as a hydrogen bond donor to the amine N. In crystal structures of the lanthanide complexes of **1**, the

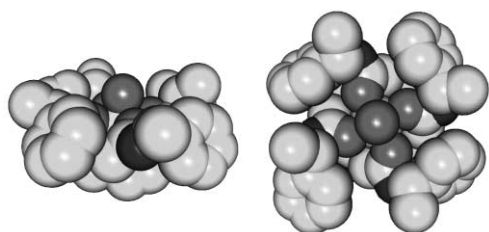


Fig. 2 Views of the crystal structure of $[\text{Eu}(\text{DOTAMPh})(\text{H}_2\text{O})]^{3+}$,¹⁶ showing the monocapped square antiprismatic coordination geometry, the capping water molecule and the partially exposed amide NH protons.

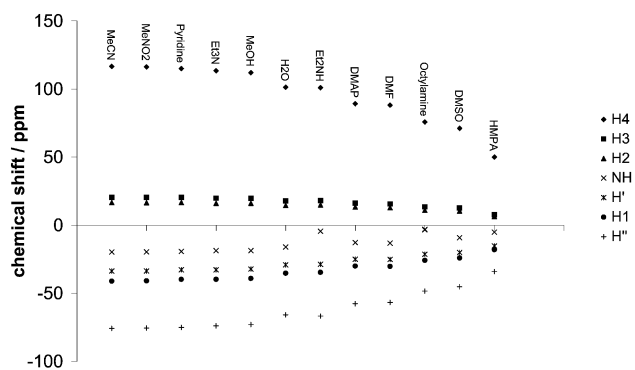


Fig. 3 Comparison of ^1H NMR shifts in $[\text{Yb}(\text{DOTAMPh})\text{X}]^{3+}$ (295 K, 200 MHz, CD_3CN) as the axial donor X is varied. Typically a 50-fold excess of the donor X was added to a 5 mM solution of the complex.

amide NH has been observed to act as a H-bond donor, for example to water or MeOH solvent molecules.^{17,24}

Similar behaviour was defined for $[\text{Eu}(\text{DOTAMPh})\text{X}]^{3+}$, and under identical conditions the same pattern of shift changes was observed (Table 1), consistent with a common coordination geometry and a profound influence of the axial donor ligand on the magnetic anisotropy. For the case of the most shifted ligand resonance²⁰ (*i.e.* the axial ring proton H₄, **2**; Table 1), a linear correlation was obtained, comparing the observed NMR shift for the Yb vs. Eu complex as the axial donor X was permuted (Fig. 4). Given the scope of the observed shift variation, such behaviour indicates that the second-order crystal field coefficient, B_0^2 that determines the magnetic susceptibility anisotropy of these axially symmetric paramagnetic complexes (eqn. (1)), is primarily determined by the axial ligand field for both the Eu and Yb complexes. In the case of Eu complexes, the splitting of the two components of the $\Delta J = 1$ transition in emission spectra provides a direct measure^{19,20} of the parameter B_0^2 . In Bleaney's model of magnetic susceptibility, higher order terms may also contribute (*e.g.* terms in T^{-3} , T^{-4}). They are generally considered to be small¹⁹ and have been excluded from the analysis here. By plotting the chemical shift of the most shifted axial ring proton, H₄, vs. the splitting (energy difference in cm^{-1}) of the $\Delta J = 1$ bands determined on the same samples, a linear correlation was obtained, (Fig. 5). This is cogent and direct experimental proof to justify Bleaney's theory of magnetic susceptibility anisotropy.^{20,29}

For ytterbium complexes, spectral analysis of the $^2\text{F}_{5/2} - ^2\text{F}_{7/2}$ transition is not straightforward owing to the large number of

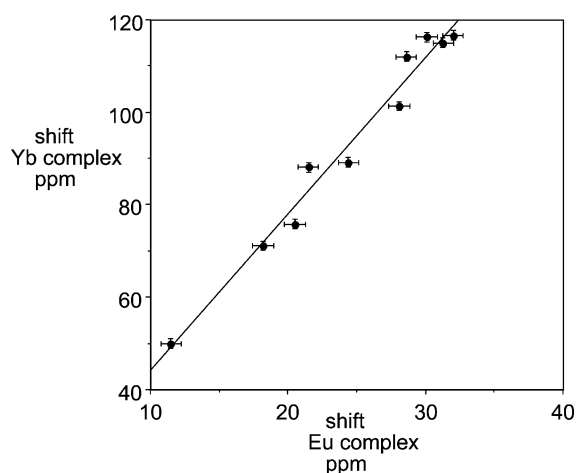


Fig. 4 Correlation of the most shifted ligand resonance in $[\text{Ln}(\text{DOTAMPh})\text{X}]^{3+}$ ($\text{Ln} = \text{Eu}$ vs. Yb ; 295 K, CD_3CN , 200 MHz) as a function of the axial donor X.

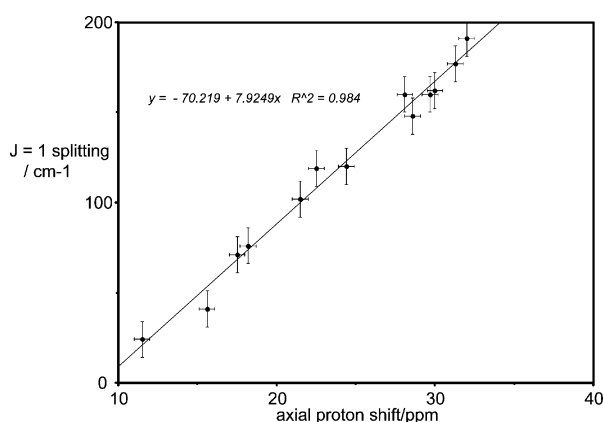


Fig. 5 Correlation of the ^1H NMR shift of the most shifted axial ring proton, H_4 , in $[\text{Eu}(\text{DOTAMPh})\text{X}]^{3+}$ with the separation of the $\text{A}_2\text{--A}_1$ and E--A_1 optical transitions in the $\Delta J = 1$ emission band ($\pm 10 \text{ cm}^{-1}$) for thirteen different O and N axial donors (295 K, 1 mM complex).

sub-levels present.^{23–28} Simplification is achieved by examining ytterbium CD^{22,24,28} or CPL³⁰ spectra, and the former have been examined here for the series of complexes with differing axial donors. Spectra measured for twelve different axial donors (Fig. 6) reveal a pronounced sensitivity in the intensity of the transition at 975 nm. With increasing polarisability of the axial donor, the intensity of this CD band falls from a large positive value for harder σ -donors to zero for DMSO and a small negative value for HMPA. This change in relative CD intensity has been correlated to the variation of the axial ring proton shift (Fig. 7). Although not a perfect linear correlation ($R^2 = 0.954$), the trend is sufficiently clear that it may be concluded that the same axial ligand effect is manifest in each parameter and is most probably to be associated with the same second-order crystal field coefficient, B_0^2 , that has been shown to determine the features of Eu optical and NMR spectra.

Nature of the axial donor: polarisability, donor preference and relative binding affinity

The axial donor exchange process for $[\text{Eu}(\text{DOTAMPh})\text{X}]^{3+}$ in dry acetonitrile was monitored by emission spectroscopy, measuring changes in the intensity of the $\Delta J = 2$ transition at 618 nm as a function of added donor concentration. A representative binding isotherm is shown in Fig. 8, and a simple non-linear least squares fitting procedure allowed an estimate of the equilibrium constant and hence the free energy associated with this axial donor interchange process. Parallel experiments with a variety of differing N and O donors were

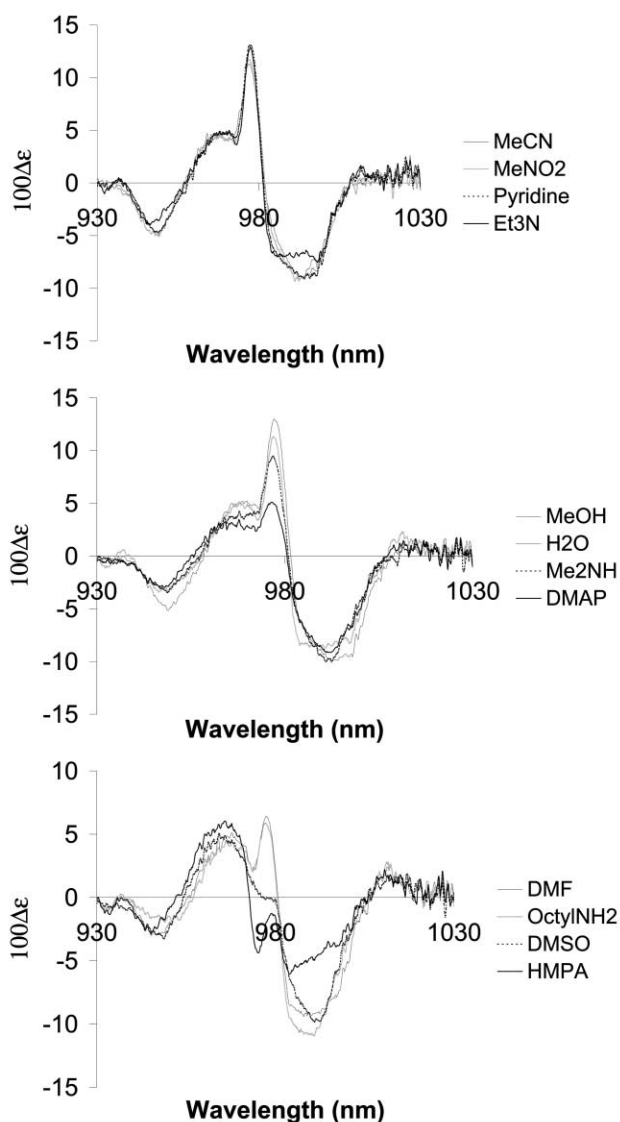


Fig. 6 Variation of the circular dichroism spectra of $[\text{Yb}(\text{DOTAMPh})\text{X}]^{3+}(\text{CF}_3\text{SO}_3^-)_3$ as the axial donor is permuted (5 mM complex, 295 K, 250 mM axial donor).

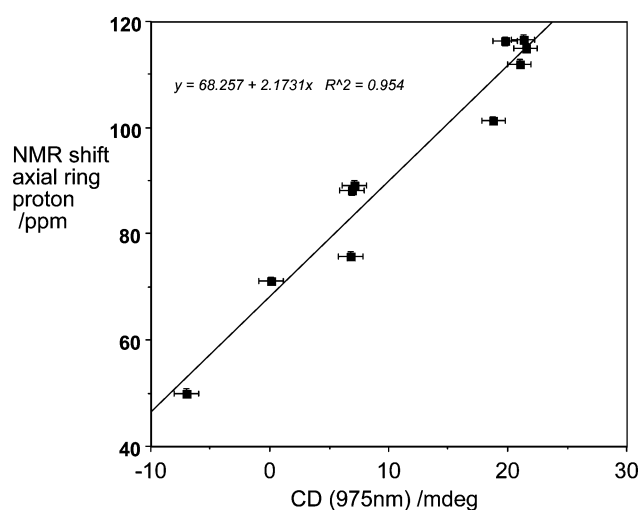


Fig. 7 Correlation of the proton NMR shift for the axial ring proton, H_4 , with the intensity of the CD band at 975 nm for $[\text{Yb}(\text{DOTAMPh})\text{X}]^{3+}(\text{CF}_3\text{SO}_3^-)_3$ (295 K, 5 mM complex, 250 mM axial donor, CD_3CN).

undertaken. In each case, the ratio of the integrated emission intensities for the $\Delta J = 2/\Delta J = 1$ spectral bands was also measured, (Table 2). This ratio is generally regarded as a useful

Table 2 Role of the axial donor in determining the difference in free energy for exchange of MeCN in [Eu(DOTAMPh)(MeCN)](CF₃SO₃)₃, compared to the ratio of integrated emission intensities ($\Delta J = 2/\Delta J = 1$ manifolds) and the calculated charge on the donor heteroatom in the absence (q) or presence of a single (q^+) or double (q^{2+}) point charge fixed at 2.5 Å^a

| Axial donor | $\Delta J = 2/\Delta J = 1$ intensity ratio | $\Delta G^{295}/\text{kJ mol}^{-1}$ | q | q^+ | q^{2+} |
|-----------------------------------|---|-------------------------------------|------|-------|----------|
| MeCN | 1.1 | 0 | 0.12 | 0.28 | 0.45 |
| MeNO ₂ ^b | 0.95 | <5 | 0.04 | 0.16 | 0.28 |
| MeOH | 1.0 | 6.6 | 0.13 | 0.20 | 0.26 |
| H ₂ O | 0.6 | 7.8 | 0.20 | 0.26 | 0.31 |
| DMF | 1.9 | 11.7 | 0.20 | 0.31 | 0.42 |
| DMSO | 2.8 | 14.3 | 0.27 | 0.41 | 0.54 |
| HMPA | 3.2 | 18.8 | 0.28 | 0.42 | 0.55 |
| Pyridine | 1.8 | 10.7 | 0.08 | 0.23 | 0.38 |
| 4-Mepy | 1.9 | 13.0 | 0.09 | 0.24 | 0.40 |
| PhCH ₂ NH ₂ | 1.8 | 13.0 | 0.19 | 0.28 | 0.38 |
| 4-NMe ₂ py | 3.5 | 15.7 | 0.11 | 0.26 | 0.40 |
| py <i>N</i> -oxide | 5.2 | 17.9 | 0.28 | 0.41 | 0.53 |

^a Values of q were calculated in the gas phase for the isolated donors; values of q^+/q^{2+} represent the relative charge density on the donor atom in the presence of a single or double point charge held 2.5 Å away, with the donor atom oriented towards it along its stereoelectronically preferred coordination vector. ^b Only unidentate coordination was assumed for MeNO₂.

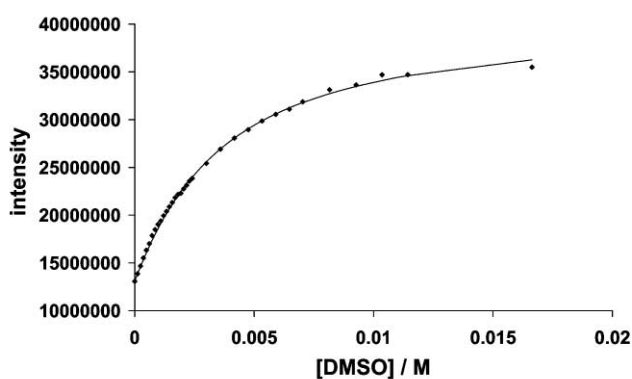


Fig. 8 Changes in the intensity of the 618 nm emission band for [Eu(DOTAMPh)X](CF₃SO₃)₃ (1 mM complex, dry CH₃CN 295 K), following incremental addition of dry DMSO; the line shows the fit to the experimental data points, for $\Delta G_{295} = -14.3 \text{ kJ mol}^{-1}$.

parameter in evaluating changes in the Eu coordination environment.^{1,31,32} The $\Delta J = 1$ transition is magnetic dipole allowed and its oscillator strength is relatively independent of the ligand environment whereas the $\Delta J = 2$ manifold is electric-dipole allowed. To a first approximation, the oscillator strength of this transition is considered to be proportional to the square of the ligand dipolar polarisability, $|a|$.³² Thus, the $\Delta J = 2/\Delta J = 1$ intensity ratio may afford a measure of the polarisability difference between [Eu(DOTAMPh)(MeCN)]³⁺ and the complexes in which the N-bound MeCN molecule is replaced by the donors listed in Table 2. The order of bonding affinities correlates quite well with the $\Delta J = 2/\Delta J = 1$ ratio, especially for the oxygen donor series (HMPA > DMSO > DMF > H₂O ~ MeOH > MeNO₂; $R^2 = 0.91$). Within the short series of pyridine donors, the $\Delta J = 2/\Delta J = 1$ ratio followed the sequence 4-NMe₂py \gg 4-Mepy > py, consistent with the measured change in the free energy of binding.

In seeking to rationalise this behaviour in terms of a simple electrostatic model, calculations of donor atom charge densities have been performed, by spatially partitioning the charges on each of the axial donor's atoms. Using the CADPAC programme,³³ Kohn–Sham density functional theory calculations were performed using the B97–1³⁴ exchange–correlation functional and the DZP³⁵ basis set. In order to reduce the basis set dependence of the calculated charges, each molecule was partitioned into atom-centred Voronoi polyhedra³⁶ and atomic charges were assessed by integrating the charge density within each polyhedron. In the absence of any polarising point charge, calculations were carried out at fixed geometries corresponding to the theoretically optimised structures, to give the values

of q for the O or N donor atom listed in Table 2. In addition, the charge on each donor atom was also calculated in the presence of an arbitrary single or double point charge, 2.5 Å away from the ligating donor. Here, the donor atom was oriented so that the donor lone pair was directed towards the charge centre, along its stereoelectronically preferred coordination direction. For the series of oxygen donors (Table 2), the correlation of q^+ and q^{2+} with donor affinity (ΔG_{295} values) was reasonably good ($R^2 = 0.93, 0.92$), whilst the $q/\Delta G$ correlation was significantly inferior ($R^2 = 0.80$). Such behaviour is consistent with the idea that it is the polarisability of the axial donor atom, which not only plays a dominant role in defining metal ion affinity, but also governs the magnitude of the crystal field coefficient, B_0^2 (Table 1 vs. Table 2).

The sequence of binding affinities defined in Table 2, do not correlate well with other empirical measurements of Lewis basicity, such as Gutmann's donor number³⁷ which is based on the strength of the interaction with SbCl₅, nor with the alternative scale devised by Maria and Gal³⁸ based on Lewis base donation to BF₃. The sequence of donor affinities established here may serve as a useful basis for ordering Lewis basicity in cases where ligand polarisation dominates, *i.e.* in lanthanide ion donor preferences and for related charge dense ions such as Mg²⁺, Ca²⁺, Li⁺, Sc³⁺, Ga³⁺ and Y³⁺.

Correlation of Eu/Yb NMR optical-spectral properties: role of 'equatorial' donor set

The above discussion highlights the importance of the axial donor in defining the ligand field and the magnetic susceptibility anisotropy. For a common water axial donor, or in the absence of any axial donor, there is a large body of information for complexes of the cyclen-based octadentate ligands, in which the four equivalent pendant arm donors are carboxylates, α -alkyl carboxylates, phosphonates, phosphinates, or 1°/2°/3° carboxamides (Fig. 1 above). The chemical shift of the most shifted 'axial' ring proton (H₄ in **2**) in this series has proved a reliable probe of the local magnetic anisotropy²⁰ (*ut supra demonstravimus*), and so for the sake of simplicity, it is used here rather than analyses based on the full shift data set. Data are collected in Tables 3 and 4 for the europium and ytterbium complexes, respectively, and in the former case, a comparison is also made with the B_0^2 parameter, which is directly proportional to the separation of the two emission bands observed for the $\Delta J = 1$ transition around 590 nm in the C₄-symmetric complexes. The coordination number for each isomer is also listed, as deduced by independent measurements of hydration number (¹⁷O NMR, Eu/Tb luminescence)^{45,46} or revealed by X-ray crystallography.^{45,47}

For the series of Eu complexes, with a common monocapped square antiprismatic coordination geometry (SAP: Table 3), the correlation of the shift of H_4 with the splitting of appropriate $\Delta J = 1$ emission bands is good (Fig. 9; $R^2 = 0.98$). This result echoes the axial donor variation correlation seen earlier and is again a direct consequence of each parameter's dependence on B_0^2 .²⁸ A good correlation was also observed in the TSAP series of nine-coordinate complexes. With the analogous Yb complexes, only the SAP series has been proved to adopt a coordination number of nine in aqueous solution. Shift data for these nine-coordinate species again correlate well with corresponding values for the SAP Eu series ($R^2 = 0.97$). The ligand field splitting for these nine-coordinate species follows the order below:



in which the α -substituted carboxylate ligands give rise to the largest B_0^2 term, which is approximately 70% greater than for the amide series of ligands.

Table 3 Optical emission band splittings ($\Delta J = 1$) and ^1H NMR shifts for the most shifted ring proton (H_4 in **2**) for isomeric nine-coordinate Eu complexes^{ab} (D_2O 295 K, 300 MHz, 1 mM complex)

| Complex | H_4 shift/ppm ^c | | $\Delta J = 1$ splitting/cm ⁻¹ | |
|--|------------------------------|------|---|------|
| | SAP | TSAP | SAP | TSAP |
| <i>[Eu(DOTA)]^{-d}</i> | 34.0 | 13.1 | 190 | 120 |
| <i>(RRRR)-[Eu(gDOTA)]⁵⁻</i> | 41.5 | 21.6 | 229 | 128 |
| <i>(RRRS)-[Eu(gDOTA)]⁵⁻</i> | 42.7 | 22.7 | 235 | 134 |
| <i>[Eu(DOTP)]^{5-e}</i> | – | 28.5 | – | 200 |
| <i>[Eu(DOTPBn)]^{-e}</i> | – | 34.4 | – | 214 |
| <i>[Eu(DOTAM)]^{3+d}</i> | 27.5 | 6.0 | 142 | 62 |
| <i>[Eu(DOTMA)]^{3+d}</i> | 26.3 | 5.6 | 136 | 60 |
| <i>[Eu(DOTAMPh)]³⁺</i> | 28.1 | – | 140 | – |
| <i>[Eu(DOTTA)]^{3+d}</i> | 28.7 | 5.4 | 135 | ≤60 |

^a Axial donor is a water molecule in each case, except for Eu complexes of DOTP and DOTPBn; major isomeric species is italicised. ^b Luminescence data from refs. 39–41. ^c Data from refs. 4, 6, 10, 11, 12, 15 and 16. ^d Shift data extrapolated to 298 K from 270 K measurement (to freeze out isomer interconversion) and relative to $^1\text{BuOH}$ ($\delta = 0$ ppm). ^e Eight-coordinate complex *i.e.* no axial donor.

For the eight coordinate Yb complexes in a TSAP geometry, the order of dipolar shifts follows the order: tetraphosphinate > gDOTA ~ DOMTA > phosphonate > DOTA, suggesting that the phosphinate ligand gives rise to the largest crystal field splitting term in agreement with the sequence of relative B_0^2 values for the TSAP isomers measured by emission spectroscopy for the two eight-coordinate TSAP Eu complexes (Table 3: 214 cm^{-1} for $[\text{Eu}(\text{DOTPBn})]^-$, 200 cm^{-1} for $[\text{Eu}(\text{DOTP})]^{5-}$). Finally, although more difficult to pick out for the ytterbium series because of accompanying coordination number variation, the shift and splitting data for Eu complexes (Table 3) clearly indicate that TSAP isomers possess a B_0^2 term that is, on average 55% of the value found for the SAP series ($\Delta J = 1$ splitting data). This accounts for the greater NMR spectral width associated with the larger magnetic susceptibility anisotropy that occurs for the latter series of complexes. Given that the mixing of the magnetic and electronic transition moments is governed by the twist angle of the complex ($40^\circ/29^\circ$ for SAP/TSAP isomers, examining the N_4/O_4 distortion from a cubic array^{9,10,13,17}), it is tempting to speculate that the twist angle, which also governs the $g_{\text{cm}}/g_{\text{abs}}$ values for chiral complexes in CD/CPL,⁴⁸ also may be determining the B_0^2 parameter.

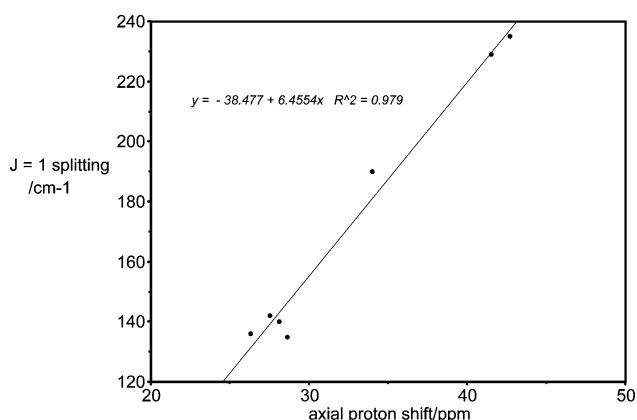


Fig. 9 Correlation of the ^1H NMR shifts (± 0.5 ppm) of the most shifted 'axial' ring proton, H_4 , in C_4 -symmetric Eu complexes (see Fig. 1) with the separation of the $\Delta J = 1$ components in emission spectra (± 10 cm^{-1}) for seven different complexes that adopt a common SAP geometry with a capping water molecule.

Table 4 ^1H NMR Shifts of the H_4 'axial' ring proton in diastereoisomeric ytterbium complexes^a (298 K D_2O , major isomer italicised)

| Complex | H_4 Shift ^b /ppm | | Coordination number | | Magnetic anisotropy, ^c $D/\text{ppm } \text{Å}^3$ | |
|---|-------------------------------|-----------------|---------------------|------|---|------|
| | SAP | TSAP | SAP | TSAP | SAP | TSAP |
| <i>[Yb(DOTA)]^{-d}</i> | 126 | 74 | 9 | 8 | – | – |
| <i>(RRRR)-[Yb(gDOTA)]⁵⁻</i> | 157 | 100 | 9 | 8 | – | – |
| <i>(RRRR)-[Yb(DOMTA)]⁻</i> | 161 | 94 | 9 | 8 | 5300 | 5200 |
| <i>[Yb(p-NO₂PhDOTA)]⁻</i> | 138 ^e | 84 ^e | 9 | 8 | 5250 | 3190 |
| <i>[Yb(DOTP)]⁵⁻</i> | – | 87.4 | – | 8 | – | 3210 |
| <i>[Yb(DOTPh)]⁻</i> | – | 102 | – | 8 | – | – |
| <i>[Yb(DOTAM)]³⁺</i> | 104 | – | 9 | – | 3300 | – |
| <i>[Yb(DOTMA)]^{3+e}</i> | 101 | – | 9 | – | – | – |
| <i>[Yb(DOTAMPh)]³⁺</i> | 102 | – | 9 | – | – | – |
| <i>[Yb(DOTTA)]^{3+f}</i> | 120 | – | 9 | – | – | – |

^a SAP = Monocapped square antiprismatic isomer; TSAP = twisted square antiprismatic species. ^b Data from refs. 4, 6, 10, 11, 15, 16, 42 and 43; shift data for $[\text{Yb}(\text{DOTA})]^-$ is extrapolated from lit. value at 275.5 K, assuming T^{-2} dependence, to avoid shift variation with isomer exchange. ^c The $\Delta J = 0$ transition for the SAP complexes of $[\text{Eu}(\text{DOTA})]^-$, $(\text{RRRR})\text{-}[\text{Eu}(\text{gDOTA})]^{5-}$ and $(\text{RRRS})\text{-}[\text{Eu}(\text{gDOTA})]^{5-}$ occurred at 17244, 17271 and 17270 cm^{-1} , respectively; for the DOTAM, DOTMA, DOTAMPh and DOTTA complexes, values were: 17241, 17245, 17243 and 17244 cm^{-1} . For DOTP and DOTPBn Eu complexes, the measured values were 17256 and 17263 cm^{-1} . No significant correlation was noted between the position of this 0–0 band and the $\Delta J = 1$ splitting value (see ref. 44 for empirical correlations of the 0–0 band position). ^d In CD_3CN , H_4 in the SAP isomer resonates at +113 ppm, and the TSAP isomer is evident at +77 ppm. ^e Mean shift of the four observed resonances. ^f In CD_3OD : SAP –124 ppm; TSAP +66 ppm; in CD_3CN , SAP +140 ppm, TSAP +85 ppm.

Conclusions

By examining structurally similar, europium and ytterbium complexes with eight-coordinate ligands based on a common N_4 basal plane, the relative importance of the nature of the axial donor and the equatorial plane donor atom type on the magnetic susceptibility anisotropy has been evaluated. The second-order crystal field parameters, B_0^2 , whose relative magnitude has been assessed by measuring the separation of the two $\Delta J = 1$ europium emission bands for each of the axially symmetric complexes, is shown to determine the dipolar NMR shift, for complexes of both Yb and Eu (and by extrapolation, the other Ln ions) adopting a common coordination number and coordination geometry. This vindication of Bleaney's theory of magnetic anisotropy should assist in future NMR spectral analyses. In addition, the prominent role of the 'axial' ligand field has been defined: the more polarisable the axial donor (e.g. HMPA > DMSO > DMF > ROH), the smaller the dipolar NMR shift—and the greater the affinity of that axial donor for the lanthanide ion.

This work has also led to the establishment of an order of lanthanide ion donor preference that may be readily assessed spectroscopically in the model series by either measuring $\Delta J = 2/\Delta J = 1$ band intensity ratios or even by comparing the dipolar NMR shift of a common shifted resonance.

Experimental

The lanthanide complexes used in this study were prepared as described elsewhere.^{4,6,10,16,22,46} Luminescence spectra were recorded at 295 K using an Instruments s.a. Fluorolog-3 spectrometer with excitation wavelengths of 397 or 255 nm, using a 375 nm cut-off filter as needed, with excitation and emission slits set at 0.5 and 0.1 nm, respectively. Points were recorded at 0.1 nm intervals with a 1 s integration time. For Eu emission spectra, corrected spectra were obtained, allowing for the response characteristics of the Hamamatsu R928 in the range 650–750 nm.

Absorbance spectra were measured using a Unicam UV2–100 spectrometer. For the CD studies, the complex solution was contained in 1 cm quartz cells. To the complex solution (5 mM) in dry acetonitrile was added an excess (50 equivalents) of the dry donor solvent. Spectra were recorded in four successive scans using a Jasco J-810 spectropolarimeter at 295 K.

^1H (499.824 MHz) and ^{31}P (202.332 MHz) NMR spectra were recorded using a Varian Inova 500 instrument (11.8 Tesla), a Varian Mercury 200 (199.975 MHz), a Varian Unity 300 (299.91 MHz) or a Varian VXR 400 (399.968 MHz) at 295 K in D_2O (99.8% D from Sigma Chem. Co.) or CD_3CN solutions. For the ^1H NMR spectra, added *tert*-butanol was used as internal reference, set at $\delta = 0$ ppm. TOCSY spectra were acquired employing standard VNMR software.

Acknowledgements

We thank EPSRC and the Royal Society (R. S. D.) for support and Professor Jim Riehl (University of Minnesota, Duluth) for assistance in measuring some of the Eu emission spectra.

References

- 1 B. R. Judd, *Phys. Rev.*, 1962, **127**, 750; G. S. Offelt, *J. Chem. Phys.*, 1962, **37**, 511.
- 2 S. F. Mason and G. F. Tranter, *Chem. Phys. Lett.*, 1983, **94**, 29; B. Stewart, *Mol. Phys.*, 1983, **50**, 61; S. F. Mason, R. D. Peacock and B. Stewart, *Mol. Phys.*, 1975, **30**, 1829.
- 3 (a) I. Bertini and C. Luchinat, *Coord. Chem. Rev.*, 1996, **150**, 1; (b) C. N. Reilly, B. W. Good and J. F. Desreux, *Anal. Chem.*, 1975, **47**, 2110; (c) S. Rigault and C. Piguet, *J. Am. Chem. Soc.*, 2000, **122**, 9304; (d) N. Ouali, B. Bocquet, S. Rigault, P.-Y. Morgantini, J. Weber and C. Piguet, *Inorg. Chem.*, 2002, **41**, 1436.
- 4 (a) S. Aime, M. Botta and G. Ermondi, *Inorg. Chem.*, 1992, **31**, 4291; (b) M. P. M. Maquess, C. F. G. C. Geraldes, A. D. Sherry, A. E. Merbach, H. Powell, D. Pubanz, S. Aime and M. Botta, *J. Alloys Compd.*, 1995, **225**, 303; (c) S. Hoeft and K. Roth, *Chem. Ber.*, 1993, **126**, 869.
- 5 J. H. Forsberg, R. M. Delaney, Q. Zhao, G. Harakas and R. Chandran, *Inorg. Chem.*, 1995, **34**, 3705.
- 6 (a) J. Ren and A. D. Sherry, *J. Magn. Reson. Ser. B*, 1996, **111**, 178; (b) C. F. G. C. Geraldes, A. D. Sherry and G. E. Kiefer, *J. Magn. Reson.*, 1992, **97**, 290.
- 7 T. A. Hopkins, J. P. Bolender, D. H. Metcalf and F. S. Richardson, *Inorg. Chem.*, 1996, **35**, 5356; T. A. Hopkins, D. H. Metcalf and F. S. Richardson, *Inorg. Chem.*, 1998, **37**, 1401.
- 8 (a) J. Lisowski, *Magn. Reson. Chem.*, 1999, **37**, 287; (b) J. Lisowski, J. L. Sessler and T. D. Mody, *J. Am. Chem. Soc.*, 1995, **117**, 2273.
- 9 R. S. Dickens, D. Parker, H. Puschmann, C. Crossland and J. A. K. Howard, *Chem. Rev.*, 2002, **102**, 1977.
- 10 M. Woods, S. Aime, M. Botta, J. A. K. Howard, J. M. Moloney, M. Navet, D. Parker, M. Port and O. Rousseaux, *J. Am. Chem. Soc.*, 2000, **122**, 9781.
- 11 S. Aime, M. Botta, D. Parker, K. Senanayake, J. A. G. Williams, A. S. Batsanov and J. A. K. Howard, *Inorg. Chem.*, 1994, **33**, 4696.
- 12 S. Aime, A. S. Batsanov, M. Botta, R. S. Dickens, S. Faulkner, C. E. Foster, A. Harrison, J. A. K. Howard, J. M. Moloney, T. J. Norman, D. Parker, L. Royle and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 3623.
- 13 S. Amin, J. R. Morrow, C. H. Lake and M. R. Churchill, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 773.
- 14 L. L. Chappell, D. A. Voss, W. de W. Horrocks and J. R. Morrow, *Inorg. Chem.*, 1998, **37**, 3989.
- 15 S. Aime, A. Barge, J. I. Bruce, M. Botta, J. A. K. Howard, J. M. Moloney, D. Parker, A. S. de Sousa and M. Woods, *J. Am. Chem. Soc.*, 1999, **121**, 5672; L. Alderighi, A. Bianchi, L. Calabi, P. Dapporto, C. Giorgi, P. Losi, L. Pateari, P. Paoli, P. Rossi, B. Valtancoli and M. Virtuani, *Eur. J. Inorg. Chem.*, 1998, 1581.
- 16 R. S. Dickens, J. A. K. Howard, C. L. Maupin, J. M. Moloney, D. Parker, J. P. Riehl, G. Siligardi and J. A. G. Williams, *Chem. Eur. J.*, 1999, **5**, 1095.
- 17 S. Aime, A. Barge, A. S. Batsanov, M. Botta, D. Delli Castelli, F. Fedeli, A. Mortillaro, D. Parker and H. Puschmann, *Chem. Commun.*, 2002, 1120.
- 18 R. Katakya, K. E. Matthes, P. E. Nicholson, D. Parker and H. J. Buschmann, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1425.
- 19 B. R. McGarvey, *J. Magn. Reson.*, 1979, **33**, 445; V. S. Mironov, Y. G. Galyametdinov, A. Ceulemans, C. Gorlier-Walrand and K. Binneemans, *J. Chem. Phys.*, 2002, **116**, 4673; T. A. Babushkina, V. F. Zolin and L. G. Koreneva, *J. Magn. Reson.*, 1983, **52**, 169.
- 20 J. M. Ren, S. R. Zhang, A. D. Sherry and C. F. G. C. Geraldes, *Inorg. Chim. Acta*, 2002, **339**, 273; J. Ren and A. D. Sherry, *J. Magn. Reson. Ser. B*, 1996, **111**, 178.
- 21 J. I. Bruce, D. Parker and D. J. Tozer, *Chem. Commun.*, 2001, 2250.
- 22 R. S. Dickens, S. Aime, A. S. Batsanov, A. Beeby, M. Botta, J. I. Bruce, J. A. K. Howard, C. S. Love, D. Parker, R. D. Peacock and H. Puschmann, *J. Am. Chem. Soc.*, 2002, **124**, 12697.
- 23 F. S. Richardson, *Inorg. Chem.*, 1980, **19**, 2806.
- 24 L. DiBari, G. Pintacuda, P. Salvadori, R. S. Dickens and D. Parker, *J. Am. Chem. Soc.*, 2000, **122**, 9257.
- 25 M. Asano-Someda and Y. Kaizu, *J. Photochem. Photobiol. A*, 2001, **139**, 161; J. X. Meng, K. F. Li, J. Yuan, L. I. Zhang, W. K. Wang and K. W. Cheah, *Chem. Phys. Lett.*, 2000, **332**, 313.
- 26 F. R. Goncalves e Silva, O. L. Malta, C. Reinhard, H.-U. Gudel, C. Piguet, J. E. Moser and J.-C. G. Bunzli, *J. Phys. Chem. A*, 2002, **106**, 1670.
- 27 A. I. Voloshin, N. M. Shovaleev and V. P. Kozakov, *J. Lumin.*, 2001, **93**, 115.
- 28 L. di Bari, G. Pintacuda and P. Salvadori, *J. Am. Chem. Soc.*, 2000, **122**, 5557.
- 29 B. Bleaney, *J. Magn. Reson.*, 1972, **8**, 91.
- 30 C. L. Maupin, D. Parker, J. A. G. Williams and J. P. Riehl, *J. Am. Chem. Soc.*, 1998, **120**, 10563.
- 31 D. R. Forster and F. S. Richardson, *Inorg. Chem.*, 1983, **22**, 3996; M. F. Reid and F. S. Richardson, *J. Phys. Chem.*, 1984, **88**, 3579; M. F. Reid and F. S. Richardson, *J. Chem. Phys.*, 1983, **79**, 5735; E. M. Stephens, M. F. Reid and F. S. Richardson, *Inorg. Chem.*, 1984, **23**, 4611.
- 32 R. D. Peacock, *Struct. Bonding (Berlin)*, 1975, **22**, 83; D. F. Henrie, R. L. Fellows and G. R. Choppin, *Coord. Chem. Rev.*, 1976, **18**, 199.
- 33 R. D. Amos, I. L. Alberts, J. S. Andrews, A. J. Cohen, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, G. J. Laming, A. M. Lee, P. E. Maslen, C. W. Murray, P. Palmieri, J. E. Rice, E. D. Simandiras, A. J. Stone, M.-D. Su and D. J. Tozer,

-
- CADPAC 6.5, The Cambridge Analytical Derivatives Package, 1998.
- 34 F. A. Hamprecht, A. J. Cohen, D. J. Tozer and N. C. Handy, *J. Chem. Phys.*, 1998, **109**, 6264.
- 35 T. A. Dunning, *J. Chem. Phys.*, 1970, **53**, 2823.
- 36 A. D. Becke, *J. Chem. Phys.*, 1988, **88**, 2547.
- 37 U. Mayer and V. Gutmann, *Struct. Bonding (Berlin)*, 1972, **12**, 113; Y. Marcus, *J. Solution Chem.*, 1984, **13**, 599; I. Persson, *Pure Appl. Chem.*, 1986, **58**, 1153.
- 38 P.-C. Maria and I. F. Gal, *J. Phys. Chem.*, 1985, **89**, 1296.
- 39 G. Muller, R. S. Dickins, D. Parker and J. P. Riehl, *J. Phys. Chem. A*, 2002, **106**, 12349.
- 40 C. C. Bryden and C. N. Reilley, *Anal. Chem.*, 1982, **54**, 610.
- 41 S. Amin, D. A. Voss, W. DeW. Horrocks, C. H. Lake, M. R. Churchill and J. R. Morrow, *Inorg. Chem.*, 1995, **34**, 3294.
- 42 S. Aime, M. Botta, G. Ermondi, E. Terreno, P. L. Anelli, F. Fedeli and F. Uggeri, *Inorg. Chem.*, 1996, **35**, 2726.
- 43 L. DiBari, G. Pintacuda and P. Salvadori, *Eur. J. Inorg. Chem.*, 2000, 75; H. G. Brittain and J. F. Desreux, *Inorg. Chem.*, 1984, **23**, 4459.
- 44 S. T. Frey and W. DeW. Horrocks, *Inorg. Chim. Acta*, 1995, **229**, 383.
- 45 P. Caravan, J. Ellison, T. J. McMurry and R. B. Lauffer, *Chem. Rev.*, 1999, **99**, 2293.
- 46 A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc., Perkin Trans. 2*, 1999, 493.
- 47 R. S. Dickins, D. Parker, H. Puschmann, C. Crossland and J. A. K. Howard, *Chem. Rev.*, 2002, **102**, 1977.
- 48 J. I. Bruce, S. Lopinski, D. Parker and R. D. Peacock, *Chirality*, 2002, **14a**, 562.