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Predictions and Assignments of NMR Spectra for Strongly Paramagnetic Supramolecular Lanthanide Complexes: The Effect of the "Gadolinium Break"

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Although the assignment of NMR signals for strongly paramagnetic lanthanide complexes (Ln = Tb−Er) is crucial for the analysis of their electronic and geometrical structures in solution,[1] classical crystal-field dependent techniques fail to predict and rationalize ^{1}H NMR spectra for the axial triple-helical lanthanide complexes $[\mathrm{LnCoL_3}]^{6+}$ (Ln = Tb−Er, Co(III) is low spin and diamagnetic) in acetonitrile because drastic deviations of eq 1 from linearity occur near the middle of the lanthanide series.[2] Such breaks have been generally ascribed to structural changes associated with the well-known lanthanide contraction,[1] but the recent use of a crystal-field independent method (eq 2)[3] unambiguously establishes the existence of an isostructural series for $[\mathrm{LnCoL_3}]^{6+}$ (Ln = Ce−Yb).[2] This communication shows that satisfying predictions for ^{1}H NMR spectra of strongly paramagnetic complexes $[\mathrm{LnCoL_3}]^{6+}$ (Ln = Tb−Er) are only accessible with this latter technique, thus leading to reliable assignments which (i) significantly improve the quality of the structural and electronic analyses and (ii) indicate that an abrupt and concomitant variation of the crystal-field parameter $A_2^0\langle r^2\rangle$ and hyperfine coupling constants F_i occurs near the middle of the lanthanide series, in line with specific electronic effects associated with the "gadolinium break".[4] The isotropic paramagnetic shift of a nucleus i in an axial complex of lanthanide j (Δ_{ij}) is given by eq 1 (F_i is proportional to the Fermi hyperfine coupling constant, G_i is the geometric factor containing the structural information, $\langle S_z\rangle_j$ and C_j are magnetic constants peculiar to each lanthanide, $A_2^0\langle r^2\rangle$ is the crystal-field parameter, and temperature dependence is included in $F_i(T^{-1})$ and $G_i(T^{-2})$).[5,6]

$$\Delta_{ij}^{\mathrm{para}} = \Delta_{ij}^{\mathrm{contact}} + \Delta_{ij}^{\mathrm{pseudo-contact}} = F_i\cdot\langle S_z\rangle_j + G_i\cdot A_2^{0}\langle r^2\rangle\cdot C_j \qquad (1)$$

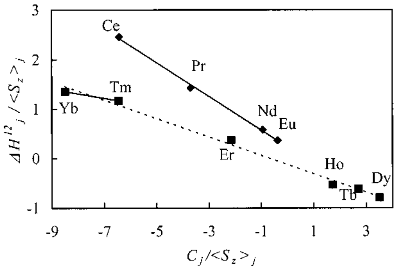

Figure 1. Plot of a linear form of eq 1 for $\mathrm{H^{12}}$ in $[\mathrm{LnCoL_3}]^{6+}$ (acetonitrile, 298 K). Full lines represent inital plots obtained for Ln = Ce−Eu and Ln = Tm−Yb. The dotted line represents the final plot obtained for the second series Ln = Tb−Yb after the assignment of strongly paramagnetic complexes (Ln = Tb−Er).

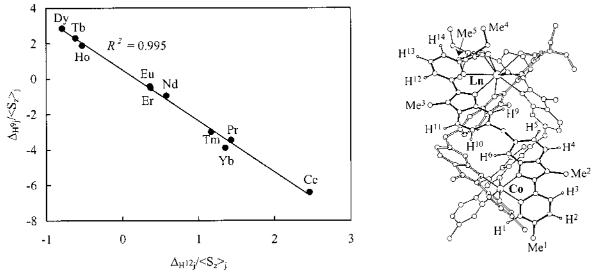

Figure 2. Plot of $\Delta_{ij}/\langle S_z\rangle_j$ vs $\Delta_{kj}/\langle S_z\rangle_j$ according to eq 2 for $\mathrm{H^9}$−$\mathrm{H^{12}}$ in $[\mathrm{LnCoL_3}]^{6+}$ (acetonitrile, 298 K).

Within an isostructural series of complexes possessing identical structural (G_i), crystal-field ($A_2^0\langle r^2\rangle$), and hyperfine coupling (F_i) parameters at a fixed temperature, multi-linear least-squares fits of eq 1 for different lanthanides provide electronic (F_i) and structural ($G_i\cdot A_2^0\langle r^2\rangle$) characteristics for the complexes in solution. Deviations from linearity have been generally ascribed to structural changes along the series (variation of G_i),[1] but changes in the hyperfine coupling[3] or in the crystal-field[5,6] have been recently recognized as valuable alternatives for interpreting NMR data. As a result of the increased nuclear relaxation induced by the coupling of electronic and nuclear magnetic moments in $[\mathrm{LnCoL_3}]^{6+}$, reliable NOE effects and $\{^1\mathrm{H}-^1\mathrm{H}\}$-COSY spectra can be obtained only for Ln = Ce−Eu, Tm, and Yb, which display limited paramagnetism.[7] For the C_3-symmetrical triple-helical complexes $[\mathrm{LnCoL_3}]^{6+}$, we observe an isostructural series for Ln = Ce−Eu according to eq 1, but complexes with Ln = Tm, Yb significantly deviate from this straight line (Figures 1 and S1). Taking the F_i and $G_i\cdot A_2^0\langle r^2\rangle$ parameters found for Ln = Ce−Eu (Table 1) and those obtained for the hypothetical second series Ln = Tm−Yb, the spectra of Ln = Tb−Er can be calculated (Table 1, Figure 3a,b). Comparison with experimental data give satisfying agreements only for Ln = Tb, Dy when the series Ln = Ce−Eu is used as a model, but attempts to predict ^{1}H NMR spectra for Ln = Ho, Er only fail. To overcome this limitation, we have resorted to a recently revisited[3] crystal-field independent method (eq 2) which shows a unique straight line for $\Delta_{ij}/\langle S_z\rangle_j$ vs $\Delta_{kj}/\langle S_z\rangle_j$ for all pairs of protons $\mathrm{H}^{i,k}$ ($i \neq k$) and for all studied lanthanides in $[\mathrm{LnCoL_3}]^{6+}$ (Figure 2), thus firmly establishing the existence of a single and common structure along the complete lanthanide series (Ln = Ce−Yb) in agreement with the similar X-ray crystal structures found for $[\mathrm{LnCoL_3}]^{6+}$ (Ln = La, Lu) in the solid state.[2]

$$\frac{\Delta_{ij}}{\langle S_z\rangle_j} = \left(F_i - F_k\cdot\frac{G_i}{G_k}\right) + \frac{G_i}{G_k}\cdot\frac{\Delta_{kj}}{\langle S_z\rangle_j} \qquad (2)$$

If the NMR signal of one particular proton Δ_{ij} can be assigned for $[\mathrm{LnCoL_3}]^{6+}$ (Ln = Ho, Er), reliable predictions for the remaining protons Δ_{kj} with eq 2 ($i \neq k$) are then straighforward and the use of the easily assignable protons $\mathrm{H^1}$ or $\mathrm{H^2}$ as references leads to simulated spectra ($\mathrm{H^{1-14}}$, $\mathrm{Me^{1-5}}$; Tables 1 and S1) which closely match the experimental data (Figure 3c,d) and allow the reliable assignment of all protons in strongly paramagnetic lanthanide complexes.

The subsequent treatment of the NMR data of $[\mathrm{LnCoL_3}]^{6+}$ (Ln = Ho, Er) according to eq 1 provides a second straight line for the linear forms shown in Figures 1 and S1 which involves Ln = Ho−Yb and demonstrates that the ratios of the magnetic

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Table 1. Experimental and Calculated ^{1}H NMR Shifts (with Respect to TMS) for Some Aromatic Protons in $[LnCoL_3]^{6+}$ (Ln = Ho, Er) Complexes in CD_3CN and Hyperfine Coupling Constants F_i and Structural Parameters $G_i{\cdot}A_2^0\langle r^2\rangle$ Calculated According to Eq 1

compd	method	H^4	H^5	H^6	H^9	H^{10}	H^{11}	H^{12}	H^{13}	H^{14}
$[HoCoL_3]^{6+}$	exp[a]	4.79	4.65	−8.62	−37.4	4.25	6.21	20.6	16.0	13.8
$[HoCoL_3]^{6+}$	calc[b]	4.93	4.73	−7.76	−38.1	3.82	5.80	20.5	16.9	12.6
$[ErCoL_3]^{6+}$	exp[a]	8.52	8.03	7.04	13.00	7.64	6.13	2.91	4.57	4.34
$[ErCoL_3]^{6+}$	calc[b]	8.48	8.00	7.29	13.14	7.51	5.83	3.07	4.83	4.76
F_i	(Ce−Eu)	−0.01(1)	−0.01(1)	−0.05(1)	−0.07(3)	−0.01(1)	0.12(1)	0.24(1)	0.09(2)	0.17(1)
$G_i{\cdot}A_2^0\langle r^2\rangle$	(Ce−Eu)	0.068(1)	0.060(1)	0.29(1)	0.93(3)	0.067(4)	−0.019(6)	−0.33(1)	−0.23(1)	−0.15(1)
F_i	(Tb−Yb)	0.05(1)	0.04(1)	0.22(2)	0.79(4)	0.06(1)	0.09(1)	−0.11(3)	0.06(2)	−0.02(3)
$G_i{\cdot}A_2^0\langle r^2\rangle$	(Tb−Yb)	0.046(1)	0.043(3)	0.177(1)	0.58(1)	0.038(2)	−0.007(3)	−0.20(1)	−0.132(8)	−0.097(9)

[a] Experimental spectrum in CD_3CN at 298 K. [b] Calculated with eq 2.

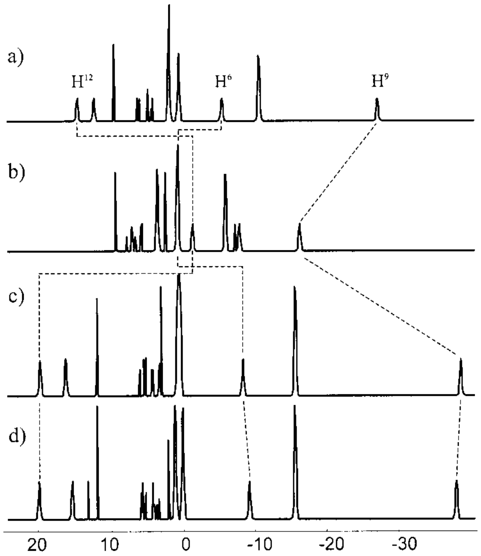

Figure 3. Simulated ^{1}H NMR spectra for $[HoCoL_3]^{6+}$ using (a) eq 1 and the Ln = Ce−Eu series, (b) eq 1 and the Ln = Tm−Yb series, (c) eq 2 with Ln = Ce−Eu, Tm, Yb, and (d) experimental data. Each signal is represented as a broad singlet and the numbering scheme corresponds to the crystal structure of $[LaCoL_3]^{6+}$.[8]

parameters $\langle S_z\rangle_j/C_j$ are too close for the two heavier lanthanides (Tm and Yb) to allow any reliable predictions using eq 1 for neighboring lanthanides. However, the ^{1}H NMR spectra of $[LnCoL_3]^{6+}$ (Ln = Tb, Dy) can be satisfyingly predicted with eq 1 from both series Ln = Ce−Eu and Ho−Yb, but statistical analyses indicate that a significantly better agreement between calculated and observed spectra is obtained for $[DyCoL_3]^{6+}$ when the second series is used. We thus assign $[DyCoL_3]^{6+}$ as a member of the second series while $[TbCoL_3]^{6+}$ corresponds to the meeting point leading to the F_i and $G_i{\cdot}A_2^0\langle r^2\rangle$ parameters for each series Ln = Ce−Eu and Tb−Yb collected in Tables 1 and S1. As G_i values are identical along the isostructural series $[LnCoL_3]^{6+}$ (Ln = Ce−Yb; eq 2, Figure 2),[2] we conclude that the breaks observed according to eq 1 (Figures 1 and S1) result from changes in the crystal-field parameters and/or hyperfine coupling constants. We deduce from the $G_i{\cdot}A_2^0\langle r^2\rangle$ values collected in Table 1 that the average ratio of the crystal-field parameters $A_2^0\langle r^2\rangle_{Ln=Ce-Eu}/A_2^0\langle r^2\rangle_{Ln=Tb-Yb}$ amounts to 1.6(2), thus pointing to significantly larger interactions between the donor atoms of the ligands and Ln(III) in the first series which can be roughly rationalized in term of a larger spatial diffuseness of the 4f electronic orbitals for the lighter lanthanides. A careful examination of absolute F_i values indicates that a concomitant change occurs in the hyperfine coupling constants and significantly larger F_i values are generally found for the second series (except for H^{12} and H^{14}, Tables 1 and S1). Surprisingly, the latter variation has negligible effects on the plots of eq 2 and the calculations of the $F_i - F_k{\cdot}G_i/G_k$ terms show compensation effects leading to similar intercepts, thus demonstrating that the crystal-field independent approach (eq 2) is not very sensitive to minor changes in the hyperfine coupling constants although larger effects remain accessible.[3] These results strongly suggest that the break occurring between Eu and Dy in $[LnCoL_3]^{6+}$ has an electronic origin and is reminiscent of related anomalous physical and/or chemical behaviors occurring near the middle of the lanthanide series sometimes referred to as the "gadolinium break" and resulting from the introduction of supplementary electrons into the half-filled 4f shell.[4] Although it appears difficult to strictly correlate the magnitude of crystal-field parameters with peculiar $4f^n$ electronic structures, Richardson and co-workers[9] recently report related observations for triple-helical complexes $Na_3[Ln(oda)_3]$ in the solid state (oda = oxidiacetate) for which the crystal-field parameters display anomalous behaviors for Ln = Gd and Tb. We finally conclude that (i) the crystal-field independent method[5,6] revisited by Geraldes (eq 2)[3] is a powerful tool for characterizing isostructural series and for accurately assigning NMR spectra of strongly paramagnetic supramolecular lanthanide complexes which allows a significant improvement of the structural analysis in solution and (ii) the break observed along the lanthanide series according to eq 1 for $[LnCoL_3]^{6+}$ reflects changes in crystal-field parameters and hyperfine coupling constant whose origins may be tentatively assigned to peculiar half-filled shell effects.

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Supporting Information Available: A table of experimental and calculated NMR data for H^{1-3} and methyl groups in $[LnCoL_3]^{6+}$ and a figure showing plots for H^{12} according to the second linear form of eq 1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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