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Conformational Preference and Structural Similarity of the Lanthanide [2.2.1] Cryptates

Sir:

While ligand conformations preferred by d-transition metal chelates have received careful study,[1] no observations of this phenomenon have heretofore been observed for complex ions of f-transiton elements.[2] We now report a 180-MHz ^{1}H NMR examination of the trivalent lanthanide [2.2.1] cryptates, [Ln(2.2.1)]X$_3$ (X = Cl$^-$, NO$_3^-$, ClO$_4^-$), which reveals that these species either show strong *conformational preference* or are structurally rigid within the time frame of the NMR experiment and are, as well, *isostructural* over the entire series.[3] The low-energy barriers known for conformational motion in five-membered chelate rings render the preference of ligand gauche conformations most likely,[1] but our NMR studies cannot distinguish between rigidity or preference of conformation.[1d,4]

Several representative ^{1}H NMR spectra of the title compounds are shown in Figure 1. Of particular interest is that displayed by a CD$_3$CN solution of [La(2.2.1)](NO$_3$)$_3$ wherein signal assignments have been verified by decoupling methods. Geminal methylene protons α to bridgehead nitrogens on the two dioxygen strands may be seen to exhibit an AM doublet (J_{AM} = 13.5 Hz) which is vicinally coupled to the adjacent β-CH$_2$ group denoted as protons H$_X$ and H$_Y$ ($J_{AX} = J_{AY}$ = 3.5, J_{MX} = 9.45, J_{MY} = 6.15 Hz). Observation of a single AMXY pattern for all four *N*-CH$_2$ dioxygen fragments of the molecule implies either that both strands have the same rigid conformation, or that a single conformation is highly favored thermodynamically.[1d,4] The observed variance in vicinal M(X,Y) coupling constants arises from dihedral angle differences as expected from the Karplus equation.[5] The remaining triplet in the *N*-CH$_2$ spectral region is due to the monooxygen strand α-CH$_2$ coupling to symmetry equivalent β-CH$_2$ protons with J_{KL} = 5.25 Hz. The *O*-CH$_2$ spectral region is complicated by extensive resonance overlaps, but the A and B branches of an AA'BB' pattern due to protons H$_E$, H$_F$, H$_{E'}$, and H$_{F'}$ (J_{EF} = 36.5 Hz) may be seen on either side of a complex pattern which is made up of the triplet of the β-CH$_2$ protons of the monooxygen ligand strands (J_{KL} = 5.25 Hz) and the multiplet from the β-CH$_2$ protons of the dioxygen strands. The essential spectral features discussed above are also detected for the salts in D$_2$O, but with less chemical shift separation in the α-CH$_2$ spectral region.

Evidence for structural identity of lanthanide [2.2.1] cryptates is deduced from ^{1}H NMR spectra of the paramagnetic ion species in D$_2$O which show eight widely dispersed, equally intense resonances (see Figure 1) which were assigned by considering resonance frequencies and line widths. Lanthanide ion induced chemical shifts obey an equation of the form
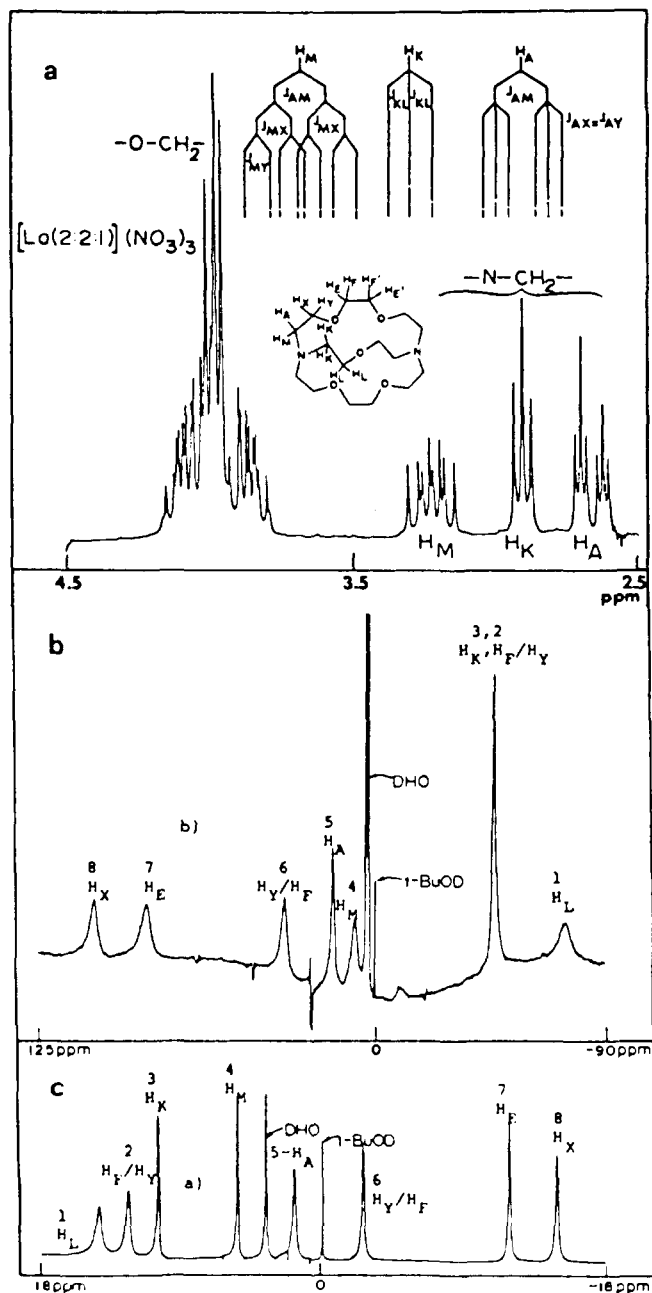
Figure 1. 180-MHz ^{1}H NMR spectra of some lanthanide [2.2.1] cryptates: (a) [La(2.2.1)](NO$_3$)$_3$ in CD$_3$CN solution. Me$_4$Si reference; (b) [Pr(2.2.1)](NO$_3$)$_3$ in D$_2$O; (c) [Er(2.2.1)](NO$_3$)$_3$ in D$_2$O; *t*-BuOD reference in D$_2$O.

$$\delta_i = A_i(S_z) + DG_i \qquad (1)$$

where δ_i is the chemical shift of the *i*th proton measured from the diamagnetic resonance position of the La^{3+} complex, $A_i(S_z)$ is the Fermi contact term, G_i is a geometric factor dependent on the position of the proton relative to the ion, and D is a constant of different value for each lanthanide whose magnitude is determined by temperature and g value anisotropy.[6] Relative proton resonance line widths in lanthanide complexes depend on the radial distance of the proton from the ion[7] as shown in eq 2. By using X-ray structural data, it is therefore possible to calculate metal-proton distances and expected radius and line width ratios.

$$T_2^A/T_2^B = \Delta\nu_{1/2}^B/\Delta\nu_{1/2}^A = r_A^6/r_B^6 \qquad (2)$$

Since no detailed crystal data were available for any lanthanide cryptates, the recently published structure[8] of the

Table I. Radial Distances, Calculated Sixth Power of Relative Distances for Protons in Some [2.2.1] Cryptate Complexes, and Assignments of Their Proton Resonances

	proton[a]							
	H_L	H_F	H_K	H_M	H_A	H_Y	H_E	H_X
r, Å[b]	4.10	4.30	4.04	3.72	4.38	4.28	3.58	3.42
$(r_{IIA}/r_{IIi})^6$	1.49[b]	1.12[b]	1.62[b]	2.66[b]	1.00[b]	1.15[b]	3.35[b]	4.41[b]
resonance (H_i)[a,b]	1	2	3	4	5	6	7	8
assignment[a,b]	H_I	H_F/H_Y	H_K	H_M	H_A	H_Y/H_I	H_E	H_X
theoretical[c]	1.49	1.12/1.15	1.62	2.66	1.00	1.15/1.12	3.35	4.41
Ce			2.2	2.8	1.0			4.2
Pr	1.5	1.2	1.6	2.4	1.0	1.2	3.3	4.0
Nd	1.4	1.2			1.0	1.1	3.3	4.0
Eu	1.5	1.2	1.6	2.4	1.0	1.4	3.2	4.0
Tb	1.5	1.1			1.0	1.6	3.4	4.3
Dy	1.7	1.1	2.0	2.6	1.0			4.1
Ho	1.4	1.3	1.5	2.5	1.0	1.3	2.7	4.0
Er	1.6	1.1	1.8	2.5	1.0			4.0

[a] See Figure 1 and text. [b] Distances from ref 8. [c] Calculated by using eq 2; see text.
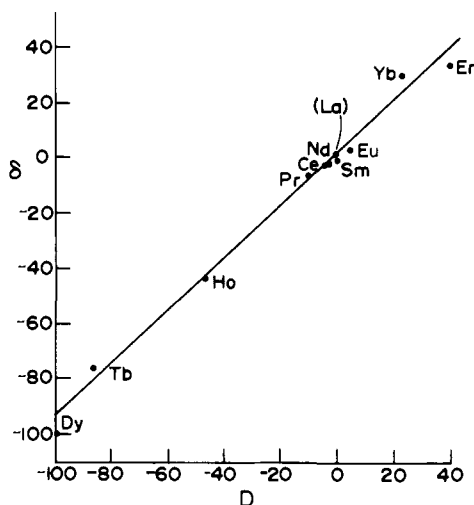

Figure 2. The scaled paramagnetic shifts of proton H_2 at 25 °C in several $[Ln(2.2.1)]^{3+}$ species vs. the Bleany[6] anisotropy constant D (see text).

[Na(2.2.1)]SCN complex was used as an acceptable model since the ionic radius of Na^+ is near that of the lighter trivalent lanthanide ions.[9] The relative distances recorded in the table were obtained therefrom by use of the programs HFINDR and DISTAN.[10] It may be seen in eq 2 that, if the geometry of the paramagnetic lanthanide cryptate is similar to that of the Na^+ complex, then the ratio $(r_{H_A}/r_{H_i})^6$ calculated from the Na^+ complex should be approximately equal to $\Delta\nu_{1/2}{}^i/\Delta\nu_{1/2}{}^A$, where $\Delta\nu_{1/2}{}^A$ is the line width of the narrowest line in the spectrum, when H_A is taken to be the proton farthest from the metal center and H_i any other proton in the molecule. Relative line widths of all protons can thereby be used for signal assignments of paramagnetically shifted resonances. The success of this technique is demonstrated in Table I, which includes data for each of the signals whose line width could be obtained with reasonably accuracy (i.e., the line was unobscured by overlap with another signal, and no residual spin-spin coupling was visible). All resonances except those for H_F and H_Y, which have very similar distances from the metal center, were unambiguously assignable.

Chemical-shift data may also be used to verify this correlation. According to eq 1, a plot of δ_i vs. D for the ith proton of a series of lanthanide complexes with a given ligand should be a straight line passing through the origin, *if contact interactions are negligible and if the geometry of the molecule remains constant*. Figure 2 shows typical plot of this type for one of the eight protons in the paramagnetic $[Ln(2.2.1)]^{3+}$ complexes. Values of D used were taken from the work of

Bleany[6] and scaled to $D = -100$ for $Dy(2.2.1)^{3+}$, as were the measured paramagnetic shifts, i.e., δ_i scaled to $\delta_i(Dy) = -100$ ppm. Chemical shifts were measured from the position of the corresponding signal in the diamagnetic La complex. Taken together, chemical-shift and coupling-constant data for the lanthanide [2.2.1] cryptates therefore suggest both conformational preference and structural similarity across the series. Little change in NMR spectra in D_2O was seen even in mildly basic solution, attesting to the kinetic inertness of the complexes. Similar studies for a few $2_B.2.1$ complexes[12] parallel these results, but no such correlations are observed for the 2.2.2 complexes, although at least the lightest members of that series are kinetically inert to dissociation in aqueous solution.

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