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TIME-AVERAGED SOLUTION GEOMETRIES FOR LIGAND-EUROPIUM COMPLEXES: THE SIGNIFICANCE OF FUNCTIONAL GROUP ROTATION, BASICITY, AND STERIC ENVIRONMENT

By P. V. Demarco*, B. J. Cerimele, R. W. Crane and A. L. Thakkar

The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46206

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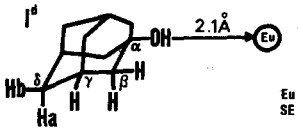
Considerable evidence now exists to support the contention that chemical shifts induced in the pmr spectra of organic aliphatic ligands by paramagnetic lanthanide ions are predominantly pseudocontact in origin.[1-4] Accordingly, lanthanide induced shifts ($\Delta\delta$-values[2]) can be calculated using the McConnell-Robertson expression[5] for the pseudocontact shift, i.e., $\Delta\delta = K(3\cos^2\theta-1)/r^3$. In this expression, r is the distance from the metal atom to the proton in question, θ is the angle made by this vector and the principal magnetic axis of the complex and K is a constant characteristic of the magnetic susceptibility of the metal.

Previous attempts to use this expression quantitatively[2,6-8] were somewhat hampered by uncertainties in the precise metal ion location within the complex. These uncertainties led earlier workers to arbitrarily measure r from the functional group heteroatom or some assumed lanthanide ion location.[1,2,7,8] The lack of X-ray structural information on such complexes and knowledge of the effect on complex geometry of ligand steric effects at the coordination site, functional group basicity, and preferred functional group orientation (in ligands possessing freely rotating functionalities eg., OH, NH_2 etc.) have been the major origins of these uncertainties. To assess the relative importance on such factors, we have attempted to determine approximate, time-averaged, solution geometries for complexes formed by the interaction of both $Eu(fod)_3$ and $Eu(dpm)_3$ with model ligands I-XI (See Table).

The approach taken to estimate ligand-metal complex geometries was similar to previously reported analytical methods[3,9,10,11] involving a

Table: Measured[a] and Predicted Europium Induced Shifts[b] for Ligands I-XI.

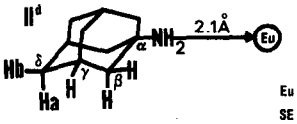
I[d]



Proton	R[c]	θ[c]	Δδobs	Δδcalc
β	4.3	30	16.4	15.8
γ	6.5	22	5.0	5.8
δ_a	6.3	23	5.5	6.3
δ_b	7.4	11	4.0	4.8

Eu coordinates 2.1, 0.0, 0.0
SE = 0.70, $^d_{Ed\text{-}O}$ = 2.1Å, θ = 180°

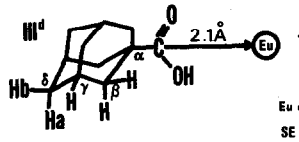
II[d]



β	4.3	30	15.4	14.9
γ	6.5	22	4.6	5.5
δ_a	6.3	23	5.0	5.9
δ_b	7.4	11	3.7	4.6

Eu coordinates, 2.1, 0.0, 0.0
SE = 0.78, $^d_{Eu\text{-}N}$ = 2.1Å, θ = 180°

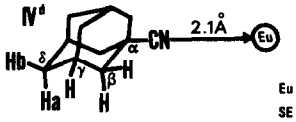
III[d]



β	4.3	30	7.2	7.2
γ	6.5	22	2.6	2.6
δ_a	6.3	23	2.8	2.8
δ_b	7.4	12	2.1	2.2

Eu coordinates 2.1, 0.0, 0.0
SE = 0.04, $^d_{Eu\text{-}C}$ = 2.1Å, θ = 180°

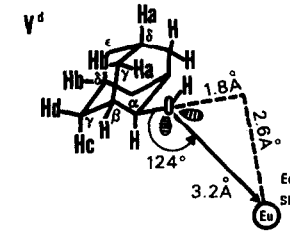
IV[d]



β	5.4	24	5.3	53
γ	7.8	19	2.1	2.1
δ_a	7.4	20	2.2	2.2
δ_b	8.6	10	1.6	1.6

Eu coordinates 2.1, 0.0, 0.0
SE = 0.01, $^d_{Eu\text{-}N}$ = 2.1Å, θ = 180°

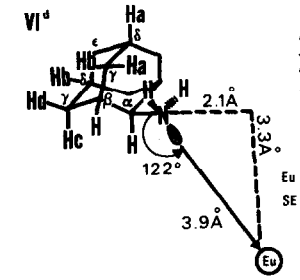
V[d]



α	4.0	31	20.0	20.2
β	4.9	30	11.6	10.9
γ_a	5.5	17	11.2	11.2
γ_b	6.8	18	5.6	5.6
γ_c	6.3	35	4.3	4.3
γ_d	7.2	27	3.3	3.9
δ_a	7.5	7	4.2	4.9
δ_b	8.1	24	2.8	3.0
ϵ	8.3	10	3.2	3.5

Eu coordinates 1.8, 0.0, 2.6
SE = 0.38, $^d_{Eu\text{-}O}$ = 3.2Å, θ = 124°

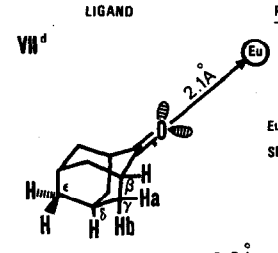
VI[d]



α	4.5	27	19.3	19.7
β	5.6	27	12.2	10.9
γ_a	6.2	14	10.1	10.3
γ_b	7.5	17	5.2	5.6
γ_c	6.8	33	4.5	4.7
γ_d	7.8	26	3.4	4.0
δ_a	8.2	48	4.5	4.8
δ_b	8.7	24	2.9	3.1
ϵ	8.9	11	3.1	3.5

Eu coordinates 2.1, 0.0, 3.3
SE = 0.58, $^d_{Eu\text{-}N}$ = 3.9Å, θ = 122°

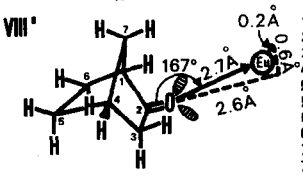
VII[d]



Proton	R[c]	θ[c]	Δδobs	Δδcalc
β	4.1	32	14.3	13.8
γ_a	5.1	30	7.5	7.7
γ_b	6.2	24	4.8	5.0
δ	6.9	18	4.0	4.1
ϵ	7.5	7	3.4	3.7

Eu coordinates 2.1, 0.0, 0.0
SE = 0.36, $^d_{Eu\text{-}O}$ = 2.0Å, θ = 180°

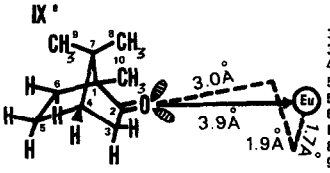
VIII[e]



1	5.3	16	12.4	11.6
3exo	4.6	31	12.3	11.9
3endo	5.0	23	12.1	11.9
4	6.1	35	4.3	4.3
5exo	7.4	22	3.5	3.8
5endo	6.4	27	4.6	5.1
6exo	7.1	6	4.3	5.2
6endo	4.8	37	8.2	7.9
7syn	6.1	15	6.7	7.7
7anti	6.9	18	4.6	5.0

Eu coordinates 2.6, 0.6, −0.2
SE = 0.59, $^d_{Eu\text{-}O}$ = 2.7Å, θ = 167°

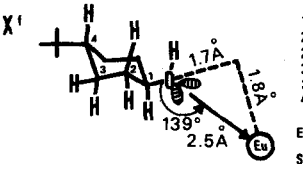
IX[e]



3exo	5.3	32	11.9	12.0
3endo	5.9	23	11.3	11.2
4	7.6	27	4.3	4.7
5exo	8.8	12	3.7	4.2
5endo	8.0	12	5.6	5.6
6exo	8.0	11	5.6	5.5
6endo	7.0	6	8.5	8.5
8-CH_3	6.0	39	5.6	5.5
9-CH_3	8.4	26	3.6	3.5
10-CH_3	5.9	29	9.7	9.4

Eu coordinates 3.0, −1.9, 1.7
SE = 0.20, $^d_{Eu\text{-}O}$ = 3.9Å, θ = 147°

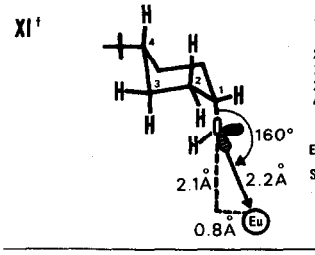
X[f]



1	3.6	34	21.7	22.0
2ax	4.9	15	14.7	14.7
2eq	4.4	32	13.6	13.1
3ax	5.9	32	5.4	5.3
3eq	6.6	24	4.4	4.9
4	6.9	8	5.4	5.7

Eu coordinates 1.7, 0.0, 1.8
SE = 0.35, $^d_{Eu\text{-}O}$ = 2.5Å, θ = 134°

XI[f]



1	3.9	24	24.7	24.7
2eq	4.4	29	14.9	14.7
3ax	4.1	36	13.6	13.8
3eq	5.6	30	6.7	6.7
4	6.3	18	6.5	6.7

Eu coordinates 2.1, 0.0, 0.8
SE = 0.13, $^d_{Eu\text{-}O}$ = 2.2Å, θ = 160°

a For shifts induced by Eu (fod)$_3$, $\Delta\delta = \delta_{lim} - \delta_o$, i.e. the difference in shift for a given solute proton when totally complexed to Eu (fod)$_3$ from that when Eu (fod)$_3$ is absent; for shifts induced by Eu (dpm)$_3$, $\Delta\delta = \delta_{n=1} - \delta_o$, i.e. the difference in shift for a given solute proton when an equimolar amount of Eu (dpm)$_3$ is present to that when Eu (dpm)$_3$ is absent.

b In ppm.

c R and θ are in angstroms and degrees respectively. Values reported are for complexes giving the smallest root mean squared error between $\Delta\delta_{obs}$ and $\Delta\delta_{calc}$.

d $\Delta\delta_{obs}$ values reported are for shifts induced by Eu (fod)$_3$ in $CDCl_3$.

e $\Delta\delta_{obs}$ values reported are for shifts induced by Eu (dpm)$_3$ in CCl_4.

f $\Delta\delta_{obs}$ values taken from previously reported results.[3]

computerized sequential-search, model-fit optimization procedure. Input into the program were cartesian coordinates for the various ligand protons, calculated by the Westheimer method,[12] and the empirical $\Delta\delta$ values. In our approach to the problem, metal ion locations within the different complexes were determined through minimization of the standard error (SE) of fit expression shown below

$$SE = \{(\Sigma\Delta\delta_{calc} - \Delta\delta_{obs})^2/M\}^{\frac{1}{2}}$$

where M is the number of ligand protons employed in each calculation. The metal ion location which gives the smallest root mean squared error between $\Delta\delta_{obs}$ and $\Delta\delta_{calc}$ is taken as the correct ion location within the complex.

Structural results recorded for complexes involved ligands I-XI are presented in the Table. Most obvious is (1) the observed invariance of d_{Eu-X}, the Eu...X-C distance, to either the basicity or the nature of the functionality involved in coordination and (2) the sensitivity of d_{Eu-X} to steric variation at the ligand coordination site. Accordingly, in ligands I-IV,* where steric effects at the coordination site are similar, d_{Eu-X} remains invariant at approximately 2.1Å. In contrast, d_{Eu-X} appears to be quite sensitive to steric variation as evidenced by the recorded increases in this value upon increasing the steric crowding at the coordination site. Thus, d_{Eu-X} increases from 2.1Å in adamantanone (VII)* to 2.7Å in norcamphor (VIII) to 3.9Å in camphor (IX). Similar increases in d_{Eu-X} are also noted upon proceeding from the symmetrically substituted 1-adamantane derivatives I (2.1Å) and II (2.1Å) to the corresponding sterically more hindered, unsymmetrically substituted 2-adamantane derivatives V (3.2Å) and VI (3.9Å).

Since metal ion coordination occurs through the agency of the lone

* The observed colinearity of the C-X-Eu europium bonds in compounds I, II, III and VII is an obvious computational artifact introduced by the inherent symmetry of these molecules. In reality C-X-Eu bonds are bent with angles of ca. 130°.

pair electrons, 'a priori' assessment of Eu^{3+} ion location in complexes possessing freely rotating functionalities is difficult owing to uncertainties in the preferred directionality, if any, of lone pair electrons in such systems and to the effect of steric factors on metal ion sampling of the lone pair electrons. Recorded data for ligands V-XI clearly show that the Eu^{3+} ion coordinates in a time-averaged cis configuration to the functional group's vicinal methine proton. Thus, in the presence of europium, rotating functionalities either adopt preferred conformations with their lone pairs oriented cis to the adjacent vicinal methine proton or Eu^{3+} binds to the ligand only when the lone pair is oriented in this direction. This observation contradicts the earlier, more qualitative, finding of Hinckley[8] (i.e., that Eu^{3+} binds in a trans configuration to the hydroxyl vicinal proton) derived on the basis of the $1/r^3$ model.

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