Solution Conformation of Aqueous Lanthanide(III)–Antipyrine† Complexes

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The conformations of lanthanide(III)–antipyrine complexes in aqueous medium have been studied by analysis of their ^1H and ^{13}C n.m.r. spectra. The 1 : 1 Ln^{3+}–antipyrine complexes are proposed to be isostructural (Ln = Pr, Eu, Tb, Dy, Ho, Er, Tm, or Yb). The potentially monodentate ligand does not co-ordinate to the metal *via* the ketone oxygen atom as is expected for a classical co-ordination compound. Instead, one antipyrine ligand is proposed to be weakly bonded to the hydrated Ln^{3+} ion *via* a second co-ordination sphere interaction with the ligand in a non-classical 'metallocene' type of orientation. Anomalous Tm^{3+} data are interpreted in terms of the assumption of axial symmetry being invalid; all the other Ln^{3+} complexes are proposed to have effective axial symmetry.

Since the first report of the n.m.r. lanthanide probe method by Hinckley in 1969,[1] the trivalent lanthanide cations have found widespread use as n.m.r. shift and relaxation probes for the determination of conformations of molecules in solution.[2] The lanthanide probe method relies on the measurement of lanthanide induced shifts (l.i.s.) as well as relaxation perturbations of the various nuclei of a molecule under investigation. It is necessary to separate the contact and pseudo-contact contributions to the l.i.s.[3–7] The resulting pseudo-contact shift ratios, together with relaxation ratios, are then compared with those calculated from an appropriate dipolar model. Inherent in the lanthanide probe method are a number of assumptions, *i.e.* effective axial symmetry of the complex, isostructurality along the lanthanide series, and constancy of the hyperfine coupling constant.[3–7] However, l.i.s. studies on some simple carboxylates,[8,9] amino acids,[9,10] ethylenediaminetetra-acetates,[11] and dithiophosphates[4,12] have suggested that these ligands do not form isostructural complexes with all the lanthanide ions. The above studies contrast with those of Reuben and Elgavish[6,7,13] who reported that certain amino acid and carboxylic acid complexes are in fact isostructural along the lanthanide series but that the pseudo-contact shifts contain non-axial components[6] or that the hyperfine coupling constant may vary along the lanthanide series.[13] Lanthanide-ion dependence of the hyperfine coupling constant[12,14] with[12] or without[14] structural changes of the complexes involved as well as non-axial dipolar contributions to the induced shift have also been reported.[14,15] All the lanthanide probe studies mentioned above involved potential polydentate ligands. In this paper we present the results of a study involving a potential monodentate ligand [antipyrine (phenazone), Figure 1] in order that any structural ambiguity in the metal complex should be removed.

Experimental

Antipyrine was obtained from BDH. NaOD, DCl, and D_2O were obtained from Merck. The lanthanide(III) oxides were purchased from Koch-Light. The lanthanide(III) chloride solutions (pH ~ 5) were prepared as previously described.[16]

The ^1H n.m.r. spectra were measured on Varian FT-80A and Bruker WH-300 spectrometers. The ^{13}C n.m.r. spectra were recorded on a 270-MHz Bruker spectrometer operating in the Fourier-transform mode using a Nicolet Technology 1085 computer. Proton shifts are given in p.p.m. with sodium 3-trimethylsilylpropane-1-sulphonate (tps) as internal standard. Carbon-13 shifts are given in p.p.m. using 1,4-dioxane as internal standard. The proton spin-lattice relaxation times (T_1) were measured using pulsed Fourier-transform techniques (180–τ–90° sequence). All spectra were obtained at 303 K.

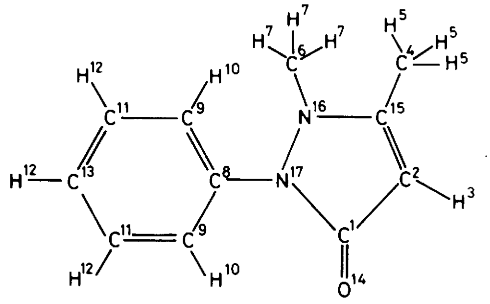

Figure 1. Numbering of atoms in antipyrine

Results

Shift Studies.—The antipyrine proton resonances in the absence of lanthanide ions are not shifted by pH changes over the region 3.0 < pH < 6.5. Final solutions for n.m.r. measurements had pH values between 4.5 and 5.5 in the case of the Ln^{3+}-containing solutions.

The conformation of the antipyrine complexes was studied by using aqueous Ln^{3+} (Ln = Pr, Eu, Tb, Dy, Ho, Er, Tm, or Yb) as ^1H shift probes, but only Ln = Pr, Eu, or Yb as ^{13}C shift probes. Titrations were performed at a constant antipyrine concentration (60 mmol dm^{-3}), with the lanthanide(III) concentration being increased to up to five times in excess. Addition of the probes causes the various ^1H and ^{13}C resonances of antipyrine to be shifted to different extents. The spectra are sharp for those lanthanides where no appreciable line broadening is expected (Pr^{3+}, Eu^{3+}, or Yb^{3+}), indicating that under all the experimental conditions used the exchange between the free and bound ligand is fast on the n.m.r. time-scale. Aqueous La^{3+} and Lu^{3+} ions were used to make diamagnetic blank corrections to the induced shifts.‡ The near linearity of the

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† 2,3-Dimethyl-1-phenyl-3-pyrazolin-5-one.

‡ The diamagnetic corrections for the proton shifts were less than 10% of the induced shifts in all cases. In two exceptional cases the diamagnetic corrections to the induced carbon shifts were as large as 35% but for all other cases they were less than 15%.

Table 1. Experimental proton shift ratios for antipyrine (relative to C–CH_3 protons) for different lanthanide(III) ions at Ln^{3+}: antipyrine = 1 : 1

	CCH_3 (H^5)	NCH_3 (H^7)	CH (H^3)	*ortho*-H (H^{10})	*meta*- and *para*-H (H^{12})
Pr^{3+}	100 ± 3.0	125.8 ± 3.8	342.3 ± 9.5	164.9 ± 6.9	− 6.2 ± 1.1
Eu^{3+}	100 ± 1.9	150.3 ± 2.4	343.0 ± 4.6	128.2 ± 2.0	−48.0 ± 0.8
Tb^{3+}	100 ± 2.2	101.4 ± 2.4	342.8 ± 6.6	45.7 ± 1.5	−56.8 ± 1.2
Dy^{3+}	100 ± 1.0	124.8 ± 1.1	324.1 ± 3.1	142.2 ± 1.2	−21.4 ± 0.4
Ho^{3+}	100 ± 0.5	120.2 ± 0.6	289.3 ± 1.6	93.7 ± 0.9	−48.5 ± 0.8
Er^{3+}	100 ± 0.7	111.2 ± 0.7	292.2 ± 4.0	59.9 ± 1.0	−70.8 ± 1.5
Yb^{3+}	100 ± 3.9	132.9 ± 5.2	242.8 ± 14.3	119.6 ± 5.1	−68.8 ± 4.1
Tm^{3+}	100 ± 1.1	109.8 ± 1.2	233.4 ± 7.0	−47.0 ± 1.3	−153.6 ± 3.1

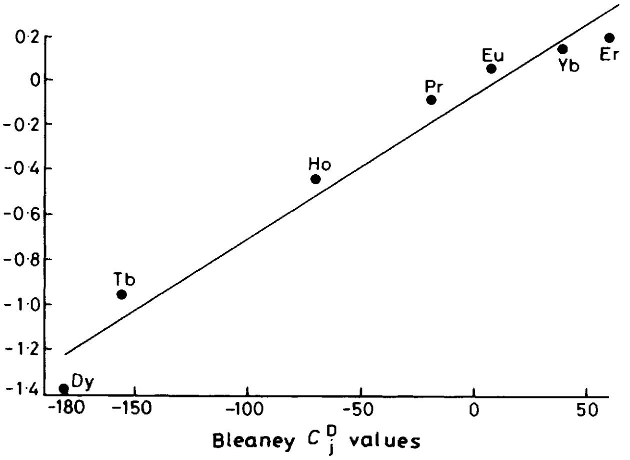

Figure 2. Diamagnetic-corrected shifts of the CCH_3 (H^5) protons induced by different Ln^{3+} ions at a 1 : 1 ratio of antipyrine to cation; [antipyrine] = 60 mmol dm^{-3}

titration curve plots (diamagnetic-corrected induced shifts *vs.* lanthanide concentration) showed that the lanthanide–antipyrine complexes are weak complexes. Also the constancy of the shift ratios makes it extremely probable that only 1 : 1 complexes are present.

The diamagnetic-corrected l.i.s. further used in this study are the values corresponding to Ln:antipyrine at 1:1. The approximate linearity of the plots of such shifts against the Bleaney C_j^D values[5,17] (relative calculated pseudo-contact n.m.r. shift values) confirms that the diamagnetic-corrected l.i.s. are predominantly pseudo-contact in character. This is shown in Figure 2 for the CCH_3 (H^5) protons for all the shift probes used with the exception of Tm^{3+} where the observed shifts deviated substantially from this linear relationship. The anomaly in the case of Tm^{3+} is also observed from a comparison of the different shift ratios observed for the various lanthanides; the experimental shift ratios, normalised to the CCH_3 protons (H^5), are approximately constant for all the metal ions with the exception of Tm^{3+} (Table 1).

Separation of the contact and pseudo-contact contributions to the induced shifts of atoms close to the metal ion were effected using all the methods[3–7] mentioned earlier. Similar results were obtained in all cases; the results obtained using the method of Reuben and Elgavish[6] are reported here. Because results for Tm^{3+} were found to be anomalous, they were subsequently not used in the Reuben method for calculating the pseudo-contact shift ratios (to be used in the computerised search procedures). The combined results of all the metals excluding Tm^{3+} thus represent the antipyrine general case (Table 2). All ^{13}C shifts corrected for both diamagnetic and contact contributions were also normalised to the H^5 protons (Table 2).

Table 2. ^1H and ^{13}C dipolar shift ratios for antipyrine [relative to C–CH_3 protons (H^5)]: general case

Nucleus	Shift ratio *
H^5	100 ± 13.7
H^3	329.9 ± 46.1
H^7	120.0 ± 18.9
H^{10}	121.4 ± 31.3
H^{12}	−30.0 ± 9.2
C^1	1 287 ± 372
C^2	543.9 ± 124.5
C^4	128.9 ± 33.5
C^6	160.6 ± 35.8
C^8	345.3 ± 70.5
C^9	309.7 ± 71.5
C^{11}	86.1 ± 62.6
C^{13}	−3.8 ± 28.8

* Shift ratios calculated according to the method of Reuben and Elgavish.[6]

Association Constant Study.—Since the antipyrine–lanthanide complexes are very weak (as deduced from the titration curves), it is assumed that, at most, only 1 : 1 complexes form. The equimolar method as developed by Bouquant and Chuche[18] (and evaluated by Raber and Hardee[19]) was employed to establish the praseodymium–antipyrine association constant, $K_{assoc.}$ = 0.2 ± 0.1. This compares favourably with values of 0.12 ± 0.01 and 0.135 ± 0.0005 reported[20] for the 1 : 1 Nd– and Ho–antipyrine complexes respectively.

Relaxation Studies.—Proton T_1 measurements were carried out in the absence and in the presence of Gd^{3+} and Tm^{3+} ions. Because the effect of Gd^{3+} or Tm^{3+} on tps was almost of the same magnitude as their influence on the antipyrine protons, corrections due to the average change in the relaxation time of the nuclei due to the presence of unbound paramagnetic ions in solution (T_{1b}) could not be made (T'_{1M} = T_{1M} uncorrected for T_{1b}). T'_{1M} values* were calculated according to the method of Barry *et al.*[21] Estimates of T_{2M} values* were obtained by measuring the induced changes in the width at half height of some of the proton resonances. Table 3 shows all the relevant relaxation data expressed as ratios of the $1/T_i$ values. Table 3 shows all the relevant relaxation data expressed as ratios of the $1/T_i$ values of the various nuclei to the $1/T_i$ value of the CCH_3 protons (H^5) for antipyrine.

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* T_{1M} and T_{2M} are the spin-lattice and spin-spin relaxation times, respectively, with the lanthanide in a bound site.

Table 3. Proton relaxation ratios [relative to CCH_3 protons (H^5)] for antipyrine

Nuclei	T_1 Relaxation experiments Gd^{3+a}	 Tm^{3+b}	Line-broadening measurements[c]
CCH_3 (H^5)	100.0 ± 6.3	100.0 ± 5.0	100
NCH_3 (H^7)	81.8 ± 5.0	78.3 ± 4.0	86 ± 12
CH (H^3)	454.6 ± 16.6	718.5 ± 51.4	905 ± 377
ortho-H (H^{10})	277.3 ± 10.5	322.9 ± 18.8	—
meta- and *para*-H (H^{12})	68.2 ± 3.7	135.7 ± 7.2	—

[a] $[Gd^{3+}] = 2.95 \times 10^{-5}$ and 5.8×10^{-5} mol dm^{-3}, [antipyrine] = 300 mmol dm^{-3}. [b] $[Tm^{3+}]$ = 37.9, 75.5, and 125.0 mmol dm^{-3}, [antipyrine] = 62.5 mmol dm^{-3}. [c] Mean taken for Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+} from l.i.s. experiments.

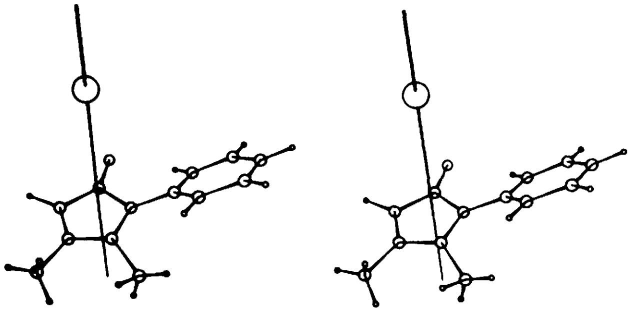


Figure 3. Stereoscopic view of the Ln^{3+}–antipyrine complex in aqueous solution. The symmetry axis is also indicated

Table 4. Experimental and calculated dipolar shift and relaxation ratios for the solution conformation of Ln^{3+}–antipyrine complexes (Ln = Pr, Eu, Tb, Dy, Ho, Er, or Yb).

Nucleus	Dipolar shift ratio Exptl.	 Calc.	Relaxation ratio Exptl.	 Calc.	Metal–Nuclei (Å)
H^5	100	100	100	100	5.3 (weighted)
H^3	329.9	326.3	454.6	455.2	4.5
H^7	120.0	130.8	81.8	72.6	6.6 (weighted)
H^{10}	121.4	160.3	277.3	281.6	5.1 (weighted)
H^{12}	−30.0	−27.6	68.2	71.1	6.2 (weighted)
C^1	1 287	817.0	—	994.7	4.0
C^2	543.9	530.0	—	565.2	4.35
C^4	128.9	134.0	—	100.3	5.8
C^6	160.6	165.8	—	93.6	5.9
C^8	345.3	375.6	—	519.9	4.4
C^9	309.7	170.8	—	319.2	4.9 (weighted)
C^{11}	86.1	12.2	—	143.0	5.6 (weighted)
C^{13}	−3.8	−18.2	—	101.5	5.8
O^{14}	—	—	—	—	4.0
C^{15}	—	367.3	—	313.7	4.8
N^{16}	—	402.4	—	348.6	4.7
N^{17}	—	626.6	—	640.6	4.35

Computerised Search Program.—Two procedures were used to arrive at the most probable solution conformation of the lanthanide(III)–antipyrine complex, *i.e.* METALSEARCH[22] and BURLESK.[21] Both use the *X*-ray crystal co-ordinates of the ligand molecule as a starting point. The computer looks at all possible conformations relative to the metal by adjusting metal–nucleus distances and/or bond angles (where rotation is possible) by an incremental scanning technique. The computer then generates both shift and relaxation data for each conformation and symmetry axis orientation. All those single solutions which agree with the experimental shift and relaxation data within given tolerances were printed and the corresponding structures were subsequently drawn by making use of the CRISTEP program.[23] The position and orientation of the principal symmetry axis of the perturbing lanthanide cation can be described in terms of spherical polar co-ordinates r, φ, ψ, α, and β. These five unknowns, together with the interplanar angle θ_{phenyl}, were solved for using 18 experimental parameters, *i.e.* five proton shifts, five proton relaxations, and eight carbon shifts. Table 4 shows the relevant data of the 'best' solution found for the antipyrine general case. Figure 3 is a stereoscopic view of the general lanthanide–antipyrine complex, together with the principal symmetry axis of the complexed lanthanide ion; $\theta_{phenyl} = 22°$.

Discussion

General Case (*Excluding* Tm^{3+}).—When shift ratios of different nuclear resonances are found to be independent of the lanthanide cation, it is reasonable to assume that (*a*) the shifts have their origin in dipolar coupling, (*b*) the geometry of the Ln^{3+} complex is the same along the lanthanide series, and (*c*) to a good approximation, the observed anisotropy of the magnetic susceptibility of the complex has average axial symmetry.[3] In the present case the diamagnetic-corrected shifts do follow Bleaney's predicted pseudo-contact shift values (Figure 2) whilst the observed shift ratios for the various lanthanides are approximately constant (Table 1). It thus follows that the Ln^{3+}–antipyrine complexes are probably isostructural and, further, have axial symmetry.

The nature of the computer search method gives a family of single conformations which fit data from shift and relaxation measurements. A family is composed of a set of conformations related to one another by single step changes in the parameters, namely, distance from the metal, bond angle, and symmetry axis orientation. Depending on the tolerances set (relative weighting of data) specific single conformations are selected on the basis of a goodness of agreement factor (similar to the *R* factor in crystallography). The specific conformation shown in Table 4 and Figure 3 represents the best fit, in our opinion, to the experimental data; variation in the relative weighting of data (tolerances) during the computer search produces other 'best' fits (family of conformations) which in the final analysis do not differ significantly from Figure 3.

It has already been stated that the exchange between free and bound ligand is fast on the n.m.r. time-scale. The n.m.r. data thus may represent some reflection of a conformation ensemble average. It is, however, barely conceivable that both the theoretical and experimental shift and relaxation data would fit the same family of conformations unless for each single conformation (best solution depending on tolerances set) the molecule exists essentially in a similar conformation.

For the symmetry of the bound lanthanide ion to be axial on a static model, a three-fold rotation axis is the minimum requirement. This obviously does not apply to the structure depicted in Figure 3. However, the conformation which was generated by our analyses is not thought to be rigid in the sense used by the crystallographer. The single conformation can only represent an average over related conformations, *e.g.* when the ligand molecule (antipyrine) rotates freely (or *via* three or more equivalent positions) about the symmetry axis shown in Figure 3. Effective axial symmetry thus results.

A crystal structure determination[24] of the neodymium–antipyrine complex in the solid state showed that the Nd^{3+}–O(antipyrine) bond distance varies between 2.339(4) and

Table 5. Metal ion–nuclei distances (Å) for the Ln^{3+}–antipyrine complexes

Nucleus	General case	Tm
H^5	5.3 (weighted)	4.5 (weighted)
H^3	4.5	3.6
H^7	6.6 (weighted)	5.3 (weighted)
H^{10}	5.1 (weighted)	3.9 (weighted)
H^{12}	6.2 (weighted)	5.3 (weighted)
C^1	4.0	2.6
C^2	4.35	3.2
C^4	5.8	4.8
C^6	5.9	4.7
C^8	4.4	3.1
C^9	4.9 (weighted)	3.7 (weighted)
C^{11}	5.6 (weighted)	4.6 (weighted)
C^{13}	5.8	5.0
O^{14}	4.0	2.8
C^{15}	4.8	3.6
N^{16}	4.7	3.4
N^{17}	4.35	2.9

2.354(5) Å. Our present solution structure (Figure 3) has the ketone oxygen 4.0 Å from the lanthanide ion (Table 4). It is clear that the ketone oxygen cannot be directly bonded to the lanthanide ion and neither can any other atom of the antipyrine molecule (Table 4).

It has been proposed[25] that the inner-sphere water co-ordination number of rare-earth ions in aqueous solution decreases from nine to eight with a decrease in ionic radii. The ions La^{3+} through to Nd^{3+} are nine-co-ordinated, those between Nd^{3+} and Tb^{3+} are between nine and eight, and those from Tb^{3+} to Lu^{3+} are eight-co-ordinated. It is also possible to calculate the theoretical size of a hydrated lanthanide ion in cases where there is direct interaction, even if it is weak, with a donor atom lying in the second co-ordination sphere of the metal ion. From *X*-ray diffraction studies of such systems, *e.g.* $[Gd(H_2O)_6Cl_2]Cl$,[26] $[Nd(H_2O)_9][BrO_3]_3$,[27] $[Er(H_2O)_9][(EtO)SO_3]_3$,[28] $[Er(H_2O)_nCl]^{2+}$,[29] and $[Ln(H_2O)_nCl]^{2+}$,[25] a mean $[Ln(H_2O)_n]^{3+}$ radius of 3.11 ± 0.26 Å can be calculated. Should the C, N, and O atoms of the antipyrine molecule lie in the second co-ordination sphere of Ln^{3+}, and also interact with the metal ion, then the Ln^{3+}–X distances would be expected to be approximately 3.9 ± 0.3 Å (X = C, N, or O). From Table 4 and Figure 3 it would appear as if the hydrated Ln^{3+} ion is both symmetrically disposed above, and bonded to, the ketone oxygen and carbon atoms (C^1 and O^{14}, Figure 1) *via* second co-ordination sphere interactions. Interaction with C^2 and N^{17} (Figure 1) may still just be possible (*e.g.* hydrogen bonding between N^{17} and a water of hydration molecule). No other 'bonding' interactions between the hydrated Ln^{3+} ion and the antipyrine molecule are envisaged.

The Tm^{3+} *Case.*—If the l.i.s. due to aqueous Tm^{3+} can also be assumed to be predominantly pseudo-contact in nature, then the diamagnetic-corrected experimental shift ratios can be used directly, together with the Tm^{3+} relaxation data, in computerised search procedures to give an indication of the Tm–antipyrine solution conformation. Axial symmetry is then assumed while Tm^{3+} is also used as an isotropic relaxation probe.

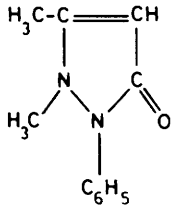
The best solution thus found is completely analogous to the general case (Figure 3) in terms of its overall conformation. However, the Tm^{3+}–nuclei distances are markedly decreased (Table 5). Because the Ln^{3+}–nuclei distances for second co-ordination sphere interactions are expected to be 3.9 ± 0.3 Å (see above) the antipyrine molecule must then necessarily lie in the first co-ordination sphere of the Tm^{3+} ion. This can again only happen if between three and four of the water molecules (of hydration) around Tm^{3+} are displaced by the ligand. The O and two N atoms of antipyrine which may then co-ordinate directly to Tm^{3+} (in place of the displaced H_2O molecules) are then, however, found at distances greater than expected for such direct bonding interactions. The only conclusion we can come to is that such a proposed Tm^{3+}–antipyrine type of structure cannot be a reality. We propose instead that the assumption of axial symmetry for Tm^{3+} is invalid. The use of Tm^{3+} shift data in the computerised search programs is consequently improper. Interestingly, anomalous pseudo-contact shifts for the Tm^{3+} ion, *i.e.* relative to expectation based on Bleaney's predicted pseudo-contact shift values, have also been reported[30] from n.m.r. studies of the water proton shifts of aqueous Ln^{3+} solutions.

The longitudinal relaxation rates (T_1) for L-proline have been studied in the presence of ten different lanthanide cations.[14] If ratios of relaxation data are calculated from the literature values, then the standard deviation of the mean for the various nuclei, expressed as a percentage of the mean, is found to vary between 21% and 50%. Those relaxation-rate data are nevertheless used as a basis for stating[14] that isostructural complexes are formed between proline and all ten lanthanide cations. Similarly the data presented in Table 3 are not incompatible with the postulate that Tm^{3+}, together with all the other lanthanide cations, form isostructural antipyrine complexes in solution. A computer search using the Tm^{3+} relaxation data in conjunction with the general case shift data subsequently produced a best fit which is almost identical with the solution depicted in Figure 3 and summarised in Table 4.

Effect of Axial Symmetry.—If lanthanide reagents form strong (rigid) chelates with substrate molecules, then the non-axial term of the magnetic susceptibility may not be averaged out by the internal rotation about the lanthanide–donor bond or by fast chemical exchange among geometrical isomers. A number of examples are known where the contribution of the non-axial term to the pseudo-contact shift cannot be ignored.[6,31,32]

However, lanthanide complexes are generally labile with respect to intramolecular and intermolecular exchange processes. Many complexes thus have effective axial symmetry resulting from rotational averaging and ligand exchange.[2] This is also the case for the Ln–antipyrine complexes under discussion, but with the exception of Tm^{3+}. This anomaly at Tm^{3+} cannot be a matter of radius, steric hindrance, or hydration number only. Williams and co-workers[33] and Dobson and co-workers[15] have concluded that an increased rigidity in Tm complexes (decrease in rate of exchange) effects a smaller extent of averaging of the magnetic susceptibility tensor with the resulting partially averaged tensor then being axially asymmetric. This extra rigidity at Tm^{3+} is associated with the electronic structure of the 4*f* core (ligand-field splitting energies of the Tm^{3+} ion in the complex) rather than with cation size. These authors also concluded that no structural change took place in solution conformation at Tm^{3+}.

Lanthanide(III)*–Antipyrine Solution Structure.*—In aqueous chloride solutions of the lanthanide(III) ions, the chloride ion in $[Ln(H_2O)_nCl]^{2+}$ only lies in the outer co-ordination sphere of the metal ion.[25] Association constants of *ca.* 0.8 ± 0.3 for these chloro complexes[34] thus reflect the poor bonding involved. The association constant of *ca.* 0.2 ± 0.1 for the Pr^{3+}–antipyrine complex is therefore consistent with the antipyrine molecule also lying in the second co-ordination sphere of the metal ion. Additional evidence for an outer-sphere complex is obtained from the shift data; the contact shift contribution to the l.i.s. of all the observed carbon and proton resonances is close to zero



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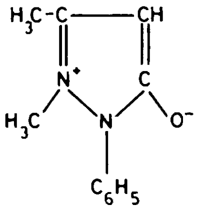

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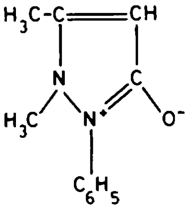

(III)

within the limits of experimental error. The orientation of the molecule towards the metal ion (Figure 3) is, however, intriguing. The dipole moment of antipyrine has been found[35] to be 5.5 D (D = 3.336 × 10^{-30} C m); three resonance structures (**I**), (**II**), and (**III**) were thus proposed to contribute to the observed dipole moment.

The dipole moments for water, methanol, acetone, and urea in contrast are only 1.86, 1.71, 2.88, and 4.56 D respectively. The inability of antipyrine to bond directly to the lanthanide(III) ion is thus surprising. Further, lanthanide(III)–antipyrine complexes can be synthesised from aqueous medium,[36] although the most appropriate synthesis of lanthanide(III)–antipyrine complexes is from non-aqueous (acetone) medium.[37] Interestingly, the association constants for the Nd^{3+}– and Ho^{3+}–antipyrine complexes in ethanolic solutions are 3.35 × 10^4 and 7.45 × 10^5 respectively.[20] In the resulting crystalline neodymium product the Nd^{3+} ion is surrounded by three antipyrine ligands with the Nd–O(antipyrine) bond varying between 2.339(4) and 2.354(5) Å.[24] This distance is as expected for a 'classically' bonded antipyrine molecule. The Nd–O–C(antipyrine) bond angle is *ca.* 156.5°; in Figure 3 the same Ln–O–C bond angle is 78.9°.

The relative contributions of resonance structures (**II**) and (**III**) were also calculated[24] and found to be 30% and 15% respectively. In a number of other M^{2+}–antipyrine complexes (M = Mg, Ca, Co, Cu, Zn, or Pb)[38–40] similar configurations to that of the Nd–antipyrine structure were obtained, indicating that the results of this n.m.r. solution conformation study are in direct contrast to all the solid-state structures.

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