Solvation Numbers for Lanthanide Shift Reagent Systems

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Summary Solvation numbers have been determined for a number of lanthanide shift reagents with three substances, using low-temperature ^{1}H n.m.r. spectroscopy under conditions where chemical exchange is slow.

ALTHOUGH lanthanide shift reagents have been extensively used in n.m.r. spectroscopy,[1] there is a lack of information concerning the number of moles of substrate co-ordinated per mole of shift reagent.[2] If the chemical exchange between free and complexed substrate (which is normally rapid on an n.m.r. time scale) can be slowed down, then it is possible to determine unambiguously the solvation number of the shift reagent. This has previously been done for the Eu(fod)$_3$–Me$_2$SO system,[3] and in the Table we present additional data for a variety of shift reagents with three substrates. This method is restricted to strongly co-ordinating substrates, and equilibrium constants for complex formation (which normally will be very large) cannot be determined. The solvation numbers reported were found to be integral values to within experimental error (± 10%). However, in the Yb(fod)$_3$–HMP system the solvation number was solvent dependent. In the CCl$_4$–CDCl$_3$–C$_6$D$_5$-CD$_3$ solvent, or in CDCl$_3$–C$_6$D$_5$CD$_3$ mixtures contaning more than *ca.* 30% v/v of CDCl$_3$, the solvation number was 1 ± 0·1, but in pure C$_6$D$_5$CD$_3$ at — 30°, a solvation number of 2 ± 0·2 was observed. This is presumably due, at least

TABLE

Solvation numbers and 'bound' chemical shifts δ *for* Ln(R^{1}COCHCOR^2)$_3$ *complexes with different substrates. Unless otherwise stated, the solvent is* CCl$_4$: CDCl$_3$: C$_6$D$_5$CD$_3$ (1·5 : 1·8 : 1 v/v)

Shift reagent[a]	Substrate[b]	Solvation number	Shift δ	Temp./°C
Pr(fod)$_3$	HMP	2	+ 2·71[c]	−40
Pr(fod)$_3$	Me$_2$SO	2	+20·5[d]	−80
			+25·2	−92
Pr(fod)$_3$	Et$_3$N[e]	1	CH$_2$, +46·6; CH$_3$ +17·9	−60
Nd(fod)$_3$	HMP	2	+ 3·24	−60
Nd(fod)$_3$	Me$_2$SO	2	+ 6·75	−92
Eu(fod)$_3$	HMP	2	− 2·71[c]	−42
Eu(fod)$_3$	Me$_2$SO	2	− 3·48	−92
Eu(fod)$_3$	Et$_3$N[e]	1	CH$_2$, −30·5; CH$_3$, −7·5	−60
Tb(fod)$_3$	HMP	2	—[c]	−40
Er(fod)$_3$	HMP	1	− 9·33	−40
Yb(fod)$_3$	HMP	1	−11·33	−40
Yb(fod)$_3$	Me$_2$SO	2	—	−90
Pr(dpm)$_3$	HMP	1	+12·71	−60
Eu(dpm)$_3$	HMP	1	− 7·64	−64
Pr(fhd)$_3$	HMP	2	—[c]	−80
Eu(fhd)$_3$	HMP	2	− 2·80[c]	−76
Pr(tta)$_3$	HMP	2	+ 2·26	−80
Eu(hfac)$_3$	HMP	2	+ 0·87	−30

[a] fod, R^1 = n-C$_3$F$_7$, R^2 = C(CD$_3$)$_3$, dpm, R^1 = R^2 = Bu^t; fhd, R^1 = Me, R^2 = n-C$_3$F$_7$; tta, R^1 = CF$_3$, R^2 = thenoyl; hfac, R^1 R^2 = CF$_3$. [b] HMP = hexamethylphosphoramide. [c] At lower temperatures, the complexed HMP peak broadens and splits, presumably due to an intramolecular exchange process being slowed down. [d] δ is very dependent upon the temperature. [e] Solvent is C$_6$D$_5$CD$_3$.

in part, to comparatively strong deuterium bonding between HMP and $CDCl_3$. For $CDCl_3$–$C_6D_5CD_3$ mixtures with less $CDCl_3$, both 1:1 and 2:1 complexes could be detected in the proton resonance spectrum, indicating that there is a considerable potential energy barrier in the reaction $Yb(fod)_3HMP + HMP \rightleftharpoons Yb(fod)_3 (HMP)_2$.

The results in the Table can be rationalized in terms of the acceptor properties of the shift reagent, the donor properties of the substrate, and, in particular, steric repulsions in an actual or hypothetical eight-co-ordinate 2:1 complex. These steric repulsions will increase with increasing size of the β-diketone and of the substrate, and with decreasing radius of the lanthanide ion.

The observed shifts δ caused by co-ordination of the substrate are also given in the Table. For a given substrate and lanthanide, the values of δ are dependent upon the nature of the β-diketone ligand. This conclusion, which will not be greatly affected by the variations in temperature, is consistent with previous room temperature data.[1,4] Two factors which may be involved are the differing stoicheiometry of the complexes, and, for a given stoicheiometry, differences in the co-ordination polyhedron adopted. Also, as suggested by Horrocks and Sipe,[5] with a small β-diketone ligand such as hexafluoroacetylacetonate, a number of complexes with different geometries may coexist, which would tend to lead to small shifts.

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