Lanthanide-induced Shifts in Inorganic and Organometallic Compounds: A Method for Distinguishing Between *N*- and *S*-Thiocyanato-compounds

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Summary Appreciable lanthanide-induced shifts are observed in the ^1H n.m.r. spectra of organic thiocyanates on addition of tris-(7,7-dimethyl-1,1,1,2,2,3,3-heptafluoro-octane-4,6-dionato)europium(III) [$Eu(fod)_3$], but not in the spectra of isothiocyanates RNCS; a similar distinction in behaviour occurs for inorganic compounds containing *S*- and *N*-thiocyanato-groups and suitable proton-containing ligands, and provides a convenient method for distinguishing between possible isomers.

Although the use of lanthanide shift reagents in organic chemistry has been extensive, recent reviews[1] reveal that relatively few applications to inorganic or organometallic systems have been reported. This may be due to the lack of a suitable Lewis base component in the inorganic system which can co-ordinate to the lanthanide, but this objection does not apply if the compound contains a group with known bridging or ambidentate properties, such as the thiocyanate group.

We have studied the induced chemical shifts caused by the lanthanide shift reagent $Eu(fod)_3$ in the proton resonances of the compounds MeSCN and $PhCH_2SCN$. Assuming the formation of a 1:1 adduct, the bound chemical shifts (ΔB = 8·3 and 7·6 p.p.m. for the methyl and CH_2 protons respectively) and binding constants (K = 11·8 and 11·2 l mol^{-1} at 35° respectively) have been calculated using the

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procedure of Armitage *et al.* No lanthanide-induced shifts were observed for the corresponding organic isothiocyanates,‡ nor for dimethyl sulphide whereas $PhCH_2CN$ gave ΔB = 19·0 p.p.m. for the CH_2 protons and K = 9·3 l mol^{-1} at 35°. These results imply that the terminal atom of the functional group is the potential donor in each case and that when it is nitrogen (in RSCN or RCN) co-ordination occurs and a lanthanide-induced shift is observed, but that when it is sulphur (in RNCS or Me_2S) little or no co-ordination occurs and no shift is observed. Such behaviour is consistent with the known characteristics of a class 'a' metal like europium to co-ordinate readily with nitrogen but reluctantly with sulphur.

TABLE

Lanthanide induced shifts in thiocyanate complexes

S-thiocyanato	$\delta\Delta$	*N*-thiocyanato	$\delta\Delta$
(π-cp) $Fe(CO)_2SCN$	0·6	(π-cp) $Fe(CO)_2NCS$	0·02
$Pd(AsPh_3)_2(SCN)_2$	0·3[a]	$Pd(AsPh_3)_2(NCS)_2$	0·05[b]
$Co(DH)_2py(SCN)$	0·8		
		$Rh(PPh_3)_2(CO)X$	0·00
		X = Cl or NCS	(0·05)[b]
		$Rh(PPh_3)_3NCS$	0·00
		(π-cp)$_2$Ti(NCS)$_2$	0·00

All spectra were recorded in $CDCl_3$ unless otherwise stated. Concentration of substrate = 0·01 M; mole ratio $Eu(fod)_3$: substrate = 0·5 [except for (π-cp)$_2$Ti(NCS)$_2$ which was 0·005 M, and for which mole ratio = 1·0].

[a] Recorded in MeCN; [b] recorded in CS_2.

With these results in mind, it was of interest to determine whether lanthanide-induced shifts could be observed for inorganic *S*- and *N*-thiocyanato-compounds which also contained protons. The results for some linkage isomers and other compounds are presented in the Table as chemical shifts obtained under approximately identical conditions. Because of the low solubility of either the substrate or the shift reagent in each other's presence, and because of the known tendency of some of these linkage isomers to coexist in equilibrium in certain solvents it was not possible to make measurements over a range of concentrations and thus to obtain ΔB and K values except for the complex $Co(DH)_2(py)SCN$ (DH = dimethylglyoximato anion) where K = 11·1 l mol^{-1}; *cf* RSCN. Nevertheless, the same conclusions apply, that *N*-bonded thiocyanates experience only a very small shift whereas *S*-thiocyanates, with a terminal nitrogen available for co-ordination with europium, experience a significant shift. Thus, a convenient method is available for distinguishing between linkage isomers of the thiocyanate group provided that the compounds in question contain some protons, and this method can be used to supplement the sometimes ambiguous infrared evidence that is widely used in this context.[3]

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‡ Very small shifts were observed using CS_2 as a solvent, but they were insufficient to obtain any meaningful results for ΔB and K.

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