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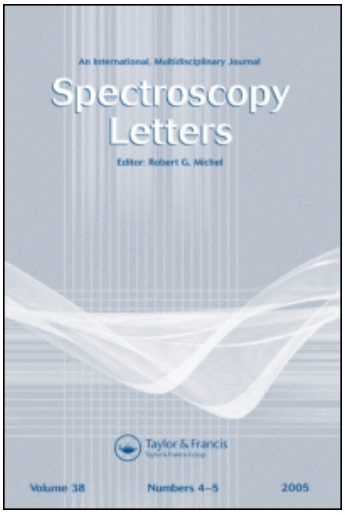


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# N.M.R. Studies of Lanthanide(III) Complexes. High Field Shifts in Complexes of 1,10-Phenanthroline

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SPECTROSCOPY LETTERS 4(12), 399-402 (1971)

# N.M.R. STUDIES OF LANTHANIDE(III) COMPLEXES. HIGH FIELD SHIFTS IN COMPLEXES OF 1,10-PHENANTHROLINE

KEY WORDS: NMR Shifts, Lanthanide Complexes, Phenanthroline

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In continuation of our studies on the complexes of lanthanide(III) ions with N-donor ligands[1,2], especially those of 1,10-phenanthroline (phen)[3,4], we wish to report the proton N.M.R. spectra of several lanthanide(III) complexes of phen in aqueous ($D_2O$) solution at 330 K. Table 1 contains the observed chemical shifts of the four types of protons in phen relative to the methyl resonance of the internal standard 2-methyl-2-propanol. For comparison, the spectrum of an authentic sample of $Nd(phen)_2Cl_3.2H_2O$ complex prepared by the method of Sinha[5] was recorded and the spectrum found to be virtually indistinguishable from that obtained by mixing the individual components in the proper ratio.

In all four cases, the formation of a complex with lanthanide ion results in a high field shift of <u>all</u> the protons in phenanthroline whereas, by contrast, the protonation of the ligand results[6,7] in a low field shift for all the protons. Except in the case of Nd(III) complex, the trend



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TABLE 1

Ligand Proton Chemical Shifts for 1,10-Phenanthroline mixed with Lanthanide Chlorides in $D_2O$ at 330 K

| Hydrated lanthanide trichloride[a] | Chemical Shift, ppm below internal $(CH_3)_3COH$ | | | |
|---|---|---|---|---|
| | 2(9) | 3(8) | 4(7) | 5(6) |
| --[b] | 7.65 | 6.34 | 6.89 | 6.26 |
| Ce | 5.63 | 5.88 | 6.73 | 6.13 |
| Pr | 3.77 | 5.61 | 6.76 | 6.32 |
| Nd | 7.17 | 6.20 | 6.69 | 6.10 |
| Nd[c] | 7.24 | 6.24 | 6.80 | 6.19 |
| $Nd(phen)_2Cl_3.2H_2O$[d] | 7.21 | 6.25 | 6.78 | 6.18 |
| Eu | 5.53 | 5.54 | 6.56 | 6.13 |

a: Ratio of M:phen = 1:2; conc. of phen = 0.4 mol $dm^{-3}$
b: Conc. of phen < 0.2 mol $dm^{-3}$
c: 0.1 mol $dm^{-3}$ in Nd
d: 0.1 mol $dm^{-3}$

in proton shift at this ion:ligand ratio (1:2) is $5(6) < 4(7) < 3(8) < 2(9)$. The Nd(III) complex follows the order $3(8) < 5(6) < 4(7) < 2(9)$. The shift of the 2(9) proton is always the largest in a given complex, with Pr(III) ion producing a shift of 4 ppm.

Contrary to this finding of high field shifts in the lanthanide complexes, Rosenberger[6,7] observed low field shifts of the 3, 4 and 5 protons and a high field shift of 1-1.5 ppm for the 2 proton in the tris-phenanthroline complexes of some d-transition metal ions: Fe(II), Co(III) and Zn(II).



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The 'anomalous' high field shift of the 2 proton in the tris-complexes of the d-transition metals was attributed[7] to a steric factor: the 2 proton, being near and perpendicular to the plane of another ligand moiety, experiences an upfield shift due to the magnetic anisotropy of another ligand. Such a shielding mechanism is probably inoperative for the lanthanide(III)-bis-phenanthroline cation possessing a different symmetry[3,8].

It seems more likely that a combination of contact and pseudocontact interactions of the ligand with the paramagnetic lanthanide(III) ion is responsible for the shifts reported here. A similar situation for the complexes of Pr(III) and Nd(III) with substituted pyridines has recently been reported by Birnbaum and Moeller[9]. They observed shifts of different magnitude resulting from complexation of the different trivalent lanthanides with the substituted pyridines. Their observation of a substantial change of shift upon varying the counter-ion does not affect the validity of the present results since the anion ($Cl^-$) is common to all our systems.

There is, however, a dependence of shift on the relative concentrations of ion and ligand. Although the nature of this dependence is not yet well characterised, it does suggest caution about regarding the shifts herein reported as those of the bis-phenanthroline complexes; apparently the ligands are exchanging rapidly with the 'free' ligands in solution, with a population weighted time-averaged signal being observed.



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