# The $^1$H N.m.r. Spectra of Diamagnetic and of Paramagnetic Complexes of Rare-earth Salts with an Aromatic Amine

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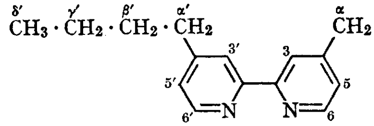
BY an extension of the methods of Frank and Smith[1] and of Badger and Sasse[2] we have synthesised 4,4′-di-n-butyl-2,2′-bipyridyl (I). Compound (I) affords complexes $[L(NO_3)_3dbbp_2]$ (II), where L = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or Y, and dbbp = (I). Satisfactory analyses have been obtained for these complexes and for (I). Infrared spectra (Nujol mulls) show that the nitrate groups are co-ordinated with the metal ion [*e.g.*, for (II; L = La) absorption caused by nitrate appears at 1506 ($\nu_4$), 1266 ($\nu_1$), 1028 ($\nu_2$), and 816 cm.$^{-1}$ ($\nu_6$); there is no absorption at $\sim$ 1380 cm.$^{-1}$]. The complexes are stable in air and fairly stable thermally, melting with decomposition from 252° (La) to 227° (Lu). They are decomposed by water. In contrast to the rather intractable analogous complexes of 2,2′-bipyridyl[3-5] and because of the introduction of the alkyl groups, the complexes are soluble in chloroform, in which they are monomeric.



(I)

The $^1$H n.m.r. spectrum of (I) in $CDCl_3$ solution at 60 Mc./sec. is shown in the Figure. It is of first order with respect to the aromatic protons and $\alpha$-$CH_2$; assignments, resonance positions and coupling constants are stated in the Table. The spectra of the diamagnetic complexes (II; L = La, Lu, or Y) are closely similar to that of (I); resonance positions are stated in the Table, and, except for H-3, differences from the spectrum of (I) are so small to suggest that very little interaction of a covalent nature has taken place between metal ion and ligand. The larger shift of H-3 can probably be related to the conversion of (I) from a preferred *trans*-configuration when uncomplexed into a *cis*-configuration when complexed, with attendant loss or reversal of the deshielding effects, specific to H-3, of the magnetic anisotropy of the N atom in the attached pyridine ring, the van der Waals repulsion of its lone pair and the electric dipole moment of the pyridine ring.[6] However, in the case of 2,2′-bipyridyl, the H-3 resonance shifts to *low* field by 0·56 p.p.m.[6] on passing from a methanolic solution of the free ligand to a methanolic solution of $[Fe(dipy)_3]Cl_2$. The presence of only one set of resonances due to the two ligand molecules in the spectra of the complexes is not necessarily an indication that the ligands are in mutually equivalent positions in the complex but is probably caused by a rapid ligand interchange. This view is supported but not proved by our observation of only one set of resonances in a mixture of (II; L = La) with one molecular proportion of (I).

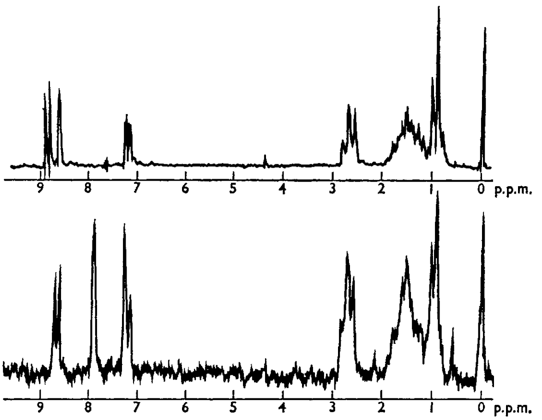


FIGURE. $^1$H *N.m.r. spectra of* (*above*) (I) *and* (*below*) (II; L = La) *at* 60 *Mc./sec. in* $CDCl_3$.

TABLE

| Compound | H-3[a] | H-5 | H-6 | $H_\alpha$ | $H_{\beta,\gamma}$[b] | $H_\delta$ |
|---|---|---|---|---|---|---|
| (I)[c] | 8·60 | 7·25 | 8·84 | 2·72 | 1·55 | 0·92 |
| (II; L = La) | 7·91 | 7·24 | 8·71 | 2·75 | 1·55 | 0·96 |
| Lu | 7·95 | 7·23 | 8·60 | 2·77 | 1·58 | 0·97 |
| Y | 7·83 | 7·10 | 8·45 | 2·67 | 1·52 | 0·93 |
| Ce | | 9·07, 6·27 | | 2·67 | 1·58 | 0·95 |
| Pr | | 9·70, 5·70 | | 2·25 | 1·45 | 0·86 |
| Nd | | 9·03, 7·43 | | 2·27 | 1·45 | 0·87 |
| Sm | | 7·88, 6·95 | | 2·78 | 1·56 | 0·97 |
| Eu | | 8·63, 5·95, 5·50 | | 3·61 | 1·67 | 1·05 |

[a] Resonance positions in p.p.m. to low field from $Me_4Si$.
[b] Centre peak of multiple peak.
[c] Coupling constants for (I) (c./sec.): $J_{3,5}$ = 1·75, $J_{3,6}$ = 0·70, $J_{5,6}$ = 4·9.

The paramagnetic complexes (II; L = Ce, Pr, Nd, Sm or Eu) gave spectra whose parameters are stated in the Table. The aromatic proton resonances are broadened and show no coupling. In the case of Eu, which has a diamagnetic $^7F_0$ ground state, all three aromatic proton resonances are present, but only two of these are obtained where L = Ce, Pr, Nd, or Sm. The heavier paramagnetic lanthanides gave no spectra except Yb which showed broadened n-butyl resonances only. Previous studies of lanthanide complexes[7] are limited to $L(acac)_3(H_2O)_3$ (L = Eu and Tb) and shifts relative to $Me_4Si$ at 60 Mc./sec. of $Eu_{CH_3}$, −421; $Eu_H$, −360; $Tb_{CH_3}$, −2829; $Tb_H$, −8647 c./sec. were attributed to pseudo-contact interaction. We attribute the much smaller shifts relative to the diamagnetic complexes shown in these studies to true contact interactions for reasons briefly as follows. The Table shows an almost complete attenuation of shift, relative to a corresponding diamagnetic complex, along the butyl chain. This is characteristic of an effect transmitted inductively from the aromatic ring to $C_\alpha$ and to $C_\beta$, the unpaired spin being delocalised, very feebly in comparison with effects observed[7–9] for *d*-transition metals, from a metal *f*-orbital into an antibonding bipyridyl molecular orbital. A pseudo-contact effect should vary as $r^{-3}$, where $r$ is the metal–proton internuclear distance.[7] Calculation and molecular models show that, due to free rotation of the butyl groups the metal–$H_\alpha$ and metal–$H_\beta$ distances are about 7·2 and 7·5 Å respectively, which would not lead to the large attenuation shown.

These observations indicate that there is only minimal electronic interaction between lanthanide ions and the bipyridyl system in these complexes even though on general grounds this system ought to be a favourable one for the generation of covalent character in a lanthanide–ligand bond.

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[1] R. L. Frank and P. V. Smith, *Org. Synth*, 1947, **27**, 38.
[2] G. M. Badger and W. H. F. Sasse, *J. Chem. Soc.*, 1956, 618.
[3] N. I. Lobanov and V. A. Smirnova, *Zhur. neorg. Khim.*, 1963, **9**, 2208.
[4] S. P. Sinha, *Spectrochim. Acta*, 1964, **20**, 879.
[5] F. A. Hart and F. P. Laming, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1825.
[6] S. Castellano, H. Gunther, and S. Ebersole. *J. Phys. Chem.*, 1965, **69**, 4166.
[7] D. R. Eaton, *J. Amer. Chem. Soc.*, 1965, **87**, 3097.
[8] E. W. Randall and D. Shaw, *Mol. Phys.*, 1965, **10**, 41.
[9] B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 4597.