19. Schwartz, M. E. & Switalski, J. D., *J. chem. Phys.*, **57** (1972), 4125.
20. Frost, A. A., *J. chem. Phys.*, **47** (1967), 3707.
21. Christoffersen, R. E., Spangler, D., Hall, G. G. & Maggiora, G. M., *J. Am. chem. Soc.*, **95** (1973), 8526.
22. Obtained from QCPE, Chemistry Department, Indiana University, Bloomington, Indiana 47401, USA.
23. Amos, A. T. & Yoffe, J. A., *Chem. Phys. Lett.*, **31** (1975), 57.
24. Amos, A. T. & Yoffe, J. A., *Chem. Phys. Lett.*, **31** (1975), 53.
25. Chu, S. Y. & Frost, A. A., *J. chem. Phys.*, **54** (1971), 760.
26. Frost, A. A. & Rouse, R. A., *J. Am. chem. Soc.*, **90** (1968), 1965.
27. Pauling, L., *The nature of the chemical bond* (Cornell University Press), 1960.
28. Moccia, R., *J. chem. Phys.*, **40** (1964), 2164, 2176, 2186.

Strong Solvent Dependence of Phosphorus Chemical Shift in Lanthanide Complexes $[(CH_3)_2PS_2]_3Ln$

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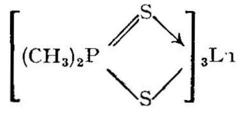
The ^1H and $^1H(^{31}P)$ NMR spectra of the paramagnetic complexes LnL_3 [Ln=Pr(III), Nd(III), Eu(III), L=$(CH_3)_2PS_2$] are found to be strongly solvent dependent. Solutions in acetone-d_6 exhibit greater half-widths in P-CH_3 doublet and larger δ_P values than the corresponding solutions in methanol-d_4.

Reactions between stoichiometric amounts of lanthanide ions and the sodium salt of dimethyldithiophosphinic acid $(CH_3)_2P(S)SNa.2H_2O$ in ethanol medium gave the octahedral complexes of the type (I)[1].



I

Ln=La(III), Pr(III), Nd(III), Eu(III), Sm(III)

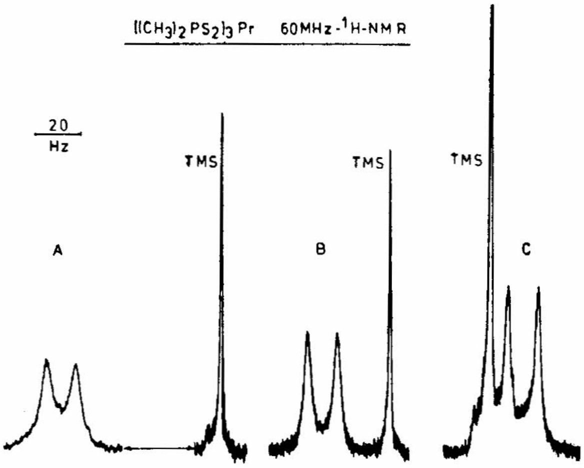


Fig. 1 — 60 MHz NMR spectrum for protons in $[(CH_3)_2PS_2)]_3Pr$ [40 mg complex dissolved in 0·4 ml of solvents: CD_3COCD_3 = A; CD_3COCD_3/CD_3OD (1 : 1) = B; and CD_3OD=C]

It is found that the 60 MHz ^1H and $^1H(^{31}P)$ NMR spectra of the paramagnetic Pr(III), Nd(III) and Eu(III) complexes are strongly solvent dependent. Solutions of I in acetone-d_6 exhibited greater half-widths in P-CH_3 doublet lines and larger δ_P values than in methanol-d_4 (see Fig. 1). An unusual strong sensitivity of δ_P in I towards change of the solvent is observed. δ_P values were observed in the wide range of about 100 ppm widths (see Table 1). As we were able to prepare well-defined di-adducts, $LnL_3.2B$ of some complexes (I) (e.g. Ln= Pr(III); L=$(CH_3)_2PS_2$; B=CH_3OH, C_5H_5N) as stable solid compounds, we assume that the coordination number six in I is expanded to eight in the solutions of the above-mentioned solvents. We suggest that the magnitude of the extremely strong shift in δ_P and the change in the spectral half-widths may be in correlation with the solvent donor properties. Therefore, we intend to use the paramagnetic complexes (I) in particular $[(CH_3)_2PS_2]_3Pr$ for systematic studies of their interactions with a wide variety of donor solvents.

References

1. Mohan Das, P. N., Kuchen, W., Keck, H. & Hägele, G., *J. inorg. nucl. Chem.*, (in press).

Table 1—Solvent Dependent Chemical Shifts of Phosphorus, Proton and Spectral Half-widths of P-CH_3 Doublets

Compound	CD_3COCD_3			CD_3OD		
	δ_P	δ_H	$\Delta\nu_{1/2}$	δ_P	δ_H	$\Delta\nu_{1/2}$
LH	—	2·117	0·5	+50·9	2·083	0·5
LaL_3	—	—	—	+52·2	2·000	1
PrL_3	+19·2	1·167	10	−51·4	**−0·242**	3
NdL_3	−26·7	2·767	15	−58·4	1·558	1
SmL_3	+57·6	1·783	10	+53·7	1·792	6
EuL_3	+51·2	**−0·222**	3·5	−24·3	1·735	1·5

δ_P= phosphorus chemical shift calc. vs H_3PO_4 85% (ppm).
δ_H= proton chemical shift vs TMS (ppm).
$\Delta\nu_{1/2}$ = spectral half-width of P-CH_3 doublets (Hz).
LH=$(CH_3)_2PS_2H$.