Nuclear Magnetic Resonance Study of Ligand Exchange on the Hexakis(trimethyl phosphate)scandium(III) Ion

By Dino L. Pisaniello, Stephen F. Lincoln,* and Evan H. Williams

(*Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia* 5001)

Summary ^{1}H and ^{31}P N.m.r. studies of scandium(III)–trimethyl phosphate (TMP) solutions show that $[Sc(TMP)_6]^{3+}$ [$J(^{45}Sc–^{31}P)$ *ca.* 35 Hz] is the greatly predominant scandium(III) species in solution, and that its lability towards ligand exchange is intermediate between that of the analogous aluminium(III) and magnesium(II) species.

The scandium(III) ion has been shown to be unexpectedly labile towards ligand substitution in aqueous solution, and it has been proposed that this is because the aqua-scandium(III) species has a co-ordination number greater than six.[1,2] Whereas either six or eight[3] oxygen donor atoms have been shown to occupy the first co-ordination sphere of scandium(III) in the solid state, only 5·1 aqua ligands have been directly detected in the first co-ordination sphere of scandium(III) in solution, probably as a consequence of the displacement of aqua ligands by anionic ligands.[4] Thus there exists a degree of uncertainty in the present understanding of the dynamics of ligand substitution upon scandium(III), and also a paucity of data in this area. Accordingly a preliminary study of the exchange of trimethyl phosphate (TMP) upon $[Sc(TMP)_6]^{3+}$ is now reported.

When the crystalline complex† $[Sc(TMP)_6][ClO_4]_3$ (0·110 mol dm^{-3}) and TMP (0·693 mol dm^{-3}) are dissolved together, under anhydrous conditions, in CD_3CN the ^{1}H (90 MHz) n.m.r. doublet [$J(^{31}P–^1H)$ 11·4 Hz] of co-ordinated TMP is observed 20·3 Hz downfield (246 K) from that of free TMP [$J(^{31}P–^1H)$ 11·0 Hz], and a comparison of the integrated areas of these doublets reveals that $[Sc(TMP)_6]^{3+}$ is the greatly predominant scandium(III) species in solution. This result is typical of those obtained for both CD_3CN and tetrachloroethane‡ solutions embracing a total TMP concentration range of 0·0134—1·353 mol dm^{-3}. Similarly, proton decoupled ^{31}P (36·4 MHz) spectra of the CD_3CN solutions, which provide a rare example of ^{45}Sc–^{31}P coupling [$J(^{45}Sc–^{31}P)$ *ca.* 35 Hz] in the broad octuplet (^{45}Sc, I 7/2) arising from the co-ordinated TMP (Figure), are also consistent with $[Sc(TMP)_6]^{3+}$ being the greatly predominant scandium(III) species.

A complete line shape analysis[5] of the coalescence of the two ^{1}H doublets as TMP exchanges between free and co-ordinated sites in a CD_3CN solution, in which $[Sc(TMP)_6{}^{3+}]$ and [TMP] were 0·110 and 0·693 mol dm^{-3} respectively, yielded the following kinetic parameters for the exchange process: $k_{ex}(300\ K) = 65{\cdot}7 \pm 2{\cdot}6\ s^{-1}$, $\Delta H^{\ddagger} = 29{\cdot}8 \pm 0{\cdot}4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -110{\cdot}9 \pm 1{\cdot}5$ J mol^{-1} K^{-1} where k_{ex} = exchange rate × $\{6[Sc(TMP)_6{}^{3+}]\}^{-1}$. These data, which appear to be the first reported for direct unidentate ligand exchange upon a scandium(III) species, may be compared with[6] $k_{ex}(298\ K) = 0{\cdot}36\ s^{-1}$, $\Delta H^{\ddagger} = 87$ kJ mol^{-1} and $\Delta S^{\ddagger} = 35$ J mol^{-1} K^{-1} for $[Al(TMP)_6]^{3+}$ (nitromethane solution), and[7] $k_{ex}(225\ K) = 683\ s^{-1}$, $\Delta H^{\ddagger} = 51{\cdot}3$ kJ mol^{-1} and $\Delta S^{\ddagger} = 39{\cdot}5$ J mol^{-1} K^{-1} for $[Mg(TMP)_6]^{2+}$ (CD_2Cl_2 solution). This comparison indicates that $[Sc(TMP)_6]^{3+}$ is not an especially labile species in comparison with its aluminium(III) and magnesium(II) analogues under the conditions of this study. It remains possible, however, that the variation of co-ordination number observed in

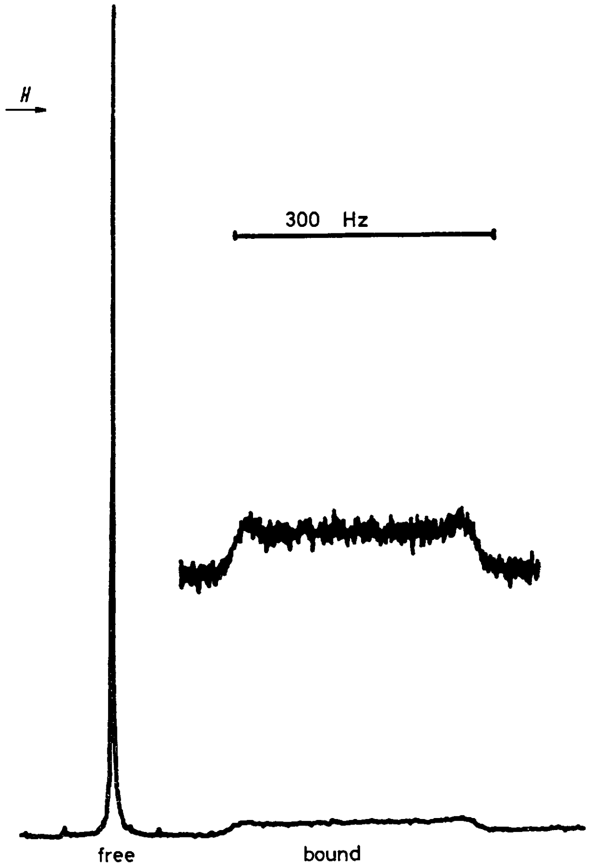

Figure. ^{1}H Decoupled ^{31}P (36·4 MHz) Fourier transform n.m.r. spectrum of a CD_3CN solution of $[Sc(TMP)_6]^{3+}$ (0·110 mol dm^{-3}) and TMP (0·693 mol dm^{-3}) at 235 K. The TMP singlet appears downfield from the broad $[Sc(TMP)_6]^{3+}$ octuplet, which is also displayed at a higher amplitude in the inset.

---

† Good analyses were obtained for this complex and i.r. spectra were consistent with the absence of co-ordinated perchlorate.

‡ No co-ordinated acetonitrile or tetrachloroethane was detected under these conditions.

the solid state[3] also occurs in solution, as the nature of the ligand is changed, and that this is accompanied by a considerable variation in the lability of scandium(III) towards ligand exchange and substitution.

We thank the Australian Research Grants Committee for supporting this work.

(*Received*, 25th *July* 1978; *Com.* 806.)

[1] G. Geier, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 617.
[2] H. Diebler, M. Eigen, G. Ilgenfritz, G. Maas, and R. Winkler, *Pure Appl. Chem.*, 1969, **20**, 93.
[3] T. J. Anderson, M. A. Neuman, and G. A. Melson, *Inorg. Chem.*, 1974, **13**, 158, 1884.
[4] A. Fratiello, R. E. Lee, and R. E. Schuster, *Inorg. Chem.*, 1970, **9**, 391.
[5] S. F. Lincoln, *Progr. Reaction Kinetics*, 1977, **9**, 1.
[6] L. S. Frankel and E. R. Danielson, *Inorg. Chem.*, 1972, **11**, 1964.
[7] D. L. Pisaniello, S. F. Lincoln, and E. H. Williams, *Inorg. Chim. Acta*, in the press.