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A [^{205}Tl]-THALLIUM NMR STUDY OF THALLIUM(I) AND THALLIUM(III) FLUOROMETALATES IN ACETONITRILE

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SUMMARY

The concentration-dependent behaviour observed for ^{205}Tl n.m.r. resonances from thallium(I) fluorometalates, PF_6^-, WF_7^-, MoF_6^- and UF_6^-, in acetonitrile indicates that some degree of ion-pairing is present in these solutions. The paramagnetic anion, UF_6^-, has a pronounced effect on ^{205}Tl resonance in the Tl^+ salt, but its effect on Tl^{3+} is very small. It is suggested that Tl^{3+} is effectively solvated by MeCN and that direct ion-pairing is unimportant. The ^{205}Tl shielding of Tl^{3+} is decreased by the presence of Tl^+ in solution, possibly as a result of the increase in asymmetry of the Tl^{3+} environment.

INTRODUCTION

Although complex fluorometalate anions are very weak bases and are often regarded as non-coordinating, there is considerable evidence that weak coordination to a cation can occur, at least in the solid state. For example X-ray crystallographic examination of the compounds $Ni(4\text{-methylpyridine})_4(PF_6)_2$ and $Ag(2,4,6\text{-}Bu^t_3C_6H_2NC)_2(PF_6)$ indicates that the PF_6^- anion behaves as a mono- and a bi-dentate ligand respectively [1]. A matrix isolation i.r. study of $CsNbF_6$ has shown that tridentate, facial (C_{3v}) or bidentate, edge (C_{2v}) $Cs^+NbF_6^-$ ion-pair interactions exist depending on the identity of the host and similar observations have been made for other Cs^+ hexafluorometalates [2].

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The situation in solution is less clear-cut since information about the nature of cation-anion interactions is normally obtained indirectly, for example by measurement of ^{75}As nuclear magnetic spin-lattice relaxation times for solutions of potassium hexafluoroarsenate in various organic solvents [3]. Many solvated cation, fluorometalate salts have been prepared in this Department using acetonitrile as solvent [4], and it is possible to envisage a situation in which coordinated MeCN is replaced by an MF_6^- anion. However, experiments in which the effect of a paramagnetic ion, $[Cu(NCMe)_6]^{2+}$ or MoF_6^-, on the n.m.r. spectrum of a diamagnetic counter-ion, PF_6^- or $[Ag(pyridine)_4]^{3+}$, has been examined, have provided no evidence for this situation [5]. In view of the great sensitivity of the ^{205}Tl nucleus to its environment [6,7] we have used ^{205}Tl n.m.r. as a more sensitive probe for cation-fluorometalate interactions in MeCN, studying the behaviour of both Tl^{I} and Tl^{III} fluorometalates.

RESULTS

Thallium(I) salts

The thallium(I) salts, Tl^+X^-, X = PF_6, MoF_6 and UF_6, were freely soluble in MeCN without decomposition. Thallium(I) heptafluorotungstate(V) decomposed in MeCN to a very small extent and gave a small quantity of insoluble material, presumed to be TlF. The latter redissolved on adding a trace of WF_6 to the solution.

All salts showed non-linear ^{205}Tl chemical shift versus concentration behaviour but the magnitude and direction of the effect depended on whether the anion was diamagnetic or paramagnetic, Fig. 1. Increased concentration of $TlPF_6$ or $TlWF_7$ resulted in a small increase in ^{205}Tl shielding, 5 p.p.m. over the range 0.04 - 0.14 mol dm^{-3}. Signal widths at half-height, $\Delta\nu$, were in the range 30 - 40 Hz. The ^{205}Tl shielding in $TlUF_6$ and $TlMoF_6$ solutions however decreased with increasing concentration, 81.5 p.p.m. over the range 0.045 - 0.34 mol dm^{-3} for $TlUF_6$ and 31 p.p.m. over the range 0.04 - 0.14 mol dm^{-3} for $TlMoF_6$. The ^{205}Tl signals were relatively broad, $\Delta\nu$ being 180 - 620 Hz for $TlUF_6$ solutions and 1900 - 570 Hz for $TlMoF_6$ solutions.

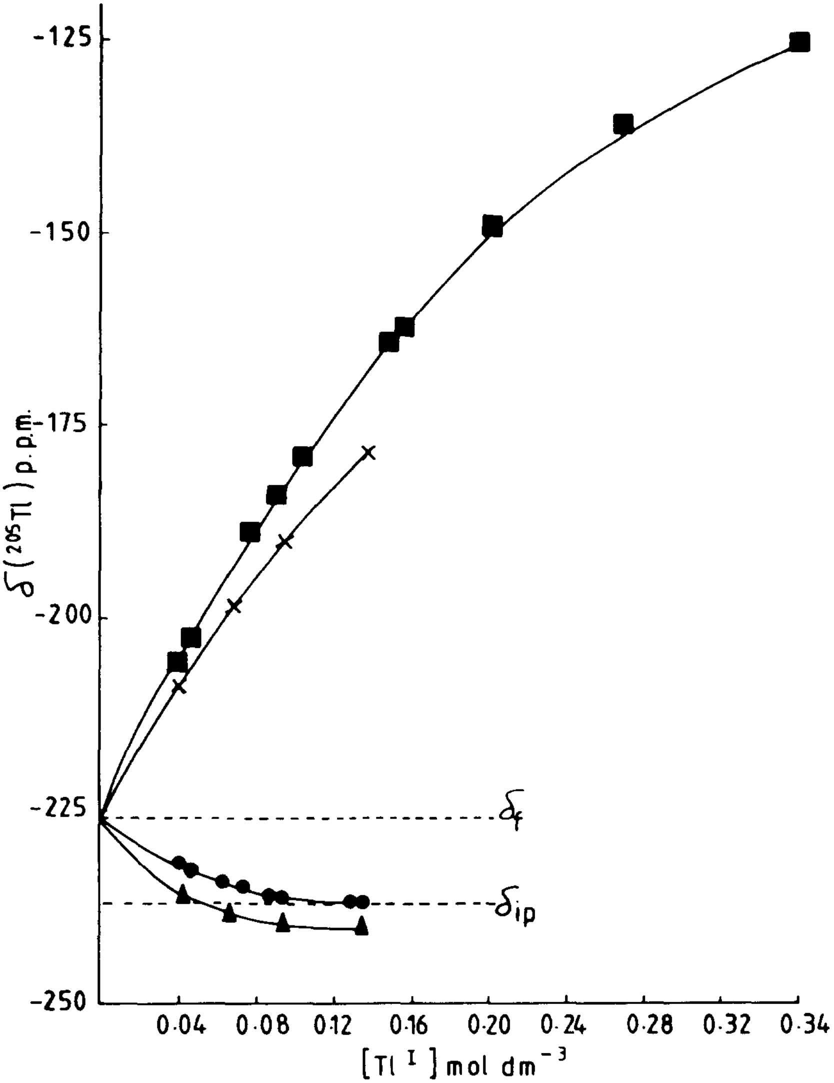

Fig. 1. Variation of ^{205}Tl chemical shift (w.r.t Tl^{+}_{aq}) with concentration in MeCN. $TlPF_6$, ●; $TlWF_7$, ▲; $TlUF_6$, ■; $TlMoF_6$, ✗. δ_f = 'Free ion' chemical shift of Tl^+ in MeCN. δ_{ip} = chemical shift of the $Tl^+PF_6^-$ ion pair.

Each set of ^{205}Tl chemical shift data was extrapolated to infinite dilution from a second degree least-squares analysis using a curve-fitting computer programme. The infinite dilution chemical shifts, which correspond to ^{205}Tl resonance in the absence of any effect due to ion-pairing [6], so obtained were -226.0 (PF_6^-), -225.5 (UF_6^-), -226.5 (MoF_6^-) and -228.0 p.p.m. (WF_7^-). Using the first three values the chemical shift of the 'free' Tl^+ ion in MeCN, δ_f, was determined as -226 ± 1 p.p.m. with respect to that in water.

Thallium(III) Salts and Solutions Containing Thallium(III) and Thallium(I)

The ^{205}Tl resonances observed from solutions of Tl^{III} hexafluorouranate(V) in MeCN occurred at higher frequencies than those from Tl^I salts. The ^{205}Tl shielding decreased with increasing concentration, Fig. 2, but the effect of UF_6^- was far smaller than in the Tl^I case, being 5.7 p.p.m. over the range 0.045 - 0.34 mol dm^{-3}. Peak widths at half-height were 70 - 100 Hz, and the value of the free Tl^{3+} ion chemical shift, δ_f, determined by computer analysis, was 1991.0 ± 0.5 p.p.m. w.r.t. that in water.

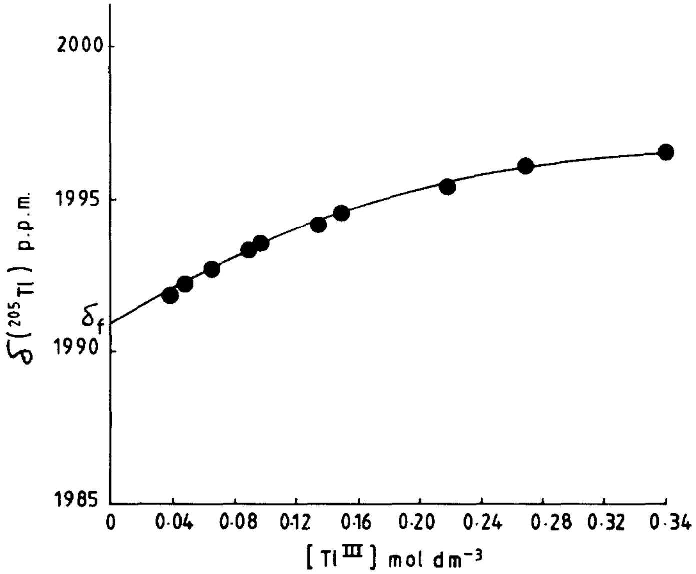

Fig. 2. Variation of ^{205}Tl chemical shift with concentration in Tl^{III} hexafluorouranate(V) solutions. δ_f = 'Free ion' chemical shift of Tl^{3+} in MeCN.

Oxidation of thallium metal by UF_6 or MoF_6 in MeCN can lead to mixtures of Tl^{III} and Tl^{I} hexafluorometalates(V) under some circumstances [8], and the ^{205}Tl n.m.r. spectra of solutions prepared by mixing Tl^{III} and Tl^{I} hexafluorouranates(V) in a 1:1 molar concentration ratio were therefore examined to determine whether there was any evidence for a mutual Tl^{I} - Tl^{III} interaction in solution. The presence of Tl^{I} had a pronounced effect on the ^{205}Tl shielding of Tl^{III} and resulted in a deshielding of Tl^{III}. Thus ^{205}Tl resonances due to Tl^{3+} occurred approximately 195 p.p.m. to lower applied field in the mixed solutions compared with those in which Tl^{+} was absent, Fig. 3.

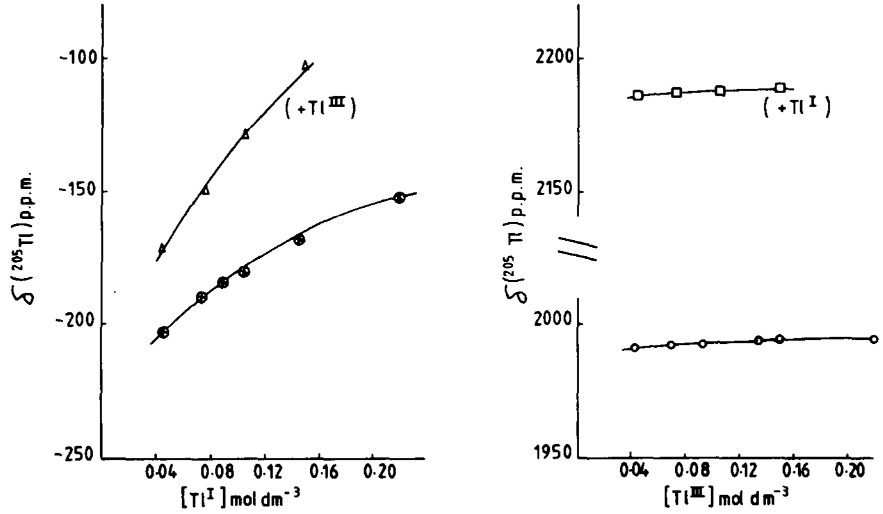

Fig. 3. Variation of ^{205}Tl chemical shifts with concentration for Tl^{I}, Tl^{III} hexafluorouranate(V) mixtures in MeCN. $[Tl^{I}]:[Tl^{III}]$ = 1:1, △ and □; Tl^{I} alone, ⊛ ; Tl^{III} alone, ○.

The ^{205}Tl chemical shifts of Tl^{+} also occurred at lower applied fields than in the absence of Tl^{3+} and the signals were considerably broader, Fig. 3. The ^{205}Tl chemical shift versus concentration behaviour observed for solutions of mixed Tl^{I}, Tl^{III} hexafluoromolybdate(V), prepared by the oxidation of Tl metal with MoF_6 in MeCN [8], was identical to that described above.

DISCUSSION

The chemical shifts of solvated Tl^+ and Tl^{3+} in acetonitrile at infinite dilution are well separated as expected from previous n.m.r. studies of Tl^{I} and Tl^{III} compounds under various conditions [6,7]. The difference in the chemical shifts is far greater than any concentration effect and ^{205}Tl n.m.r. spectroscopy is a reliable method for differentiating between thallium oxidation states, for example in redox reactions [9]

The concentration dependences observed for ^{205}Tl resonances in the four Tl^+ fluorometalates examined, Fig. 1, indicate that anion-cation interaction does exist in solution. The behaviour observed for the diamagnetic salts $TlPF_6$ and $TlWF_7$ is similar to that of $TlNO_3$ or $TlClO_4$ in a number of non-aqueous solvents [10-12] where the observed ^{205}Tl chemical shift behaviour has been explained on the basis of the equilibrium between free $Tl^+$and X^-, $X = ClO_4$, NO_3, etc., ions and the Tl^+X^- ion pair (eqn. 1).

$$Tl^+ + X^- \rightleftharpoons Tl^+X^- \qquad (1)$$

The observed ^{205}Tl shift depends on the chemical shift of the free Tl^+ cation, δ_f, the chemical shift of the ion-paired species Tl^+X^-, δ_{ip}, and the concentrations of Tl^+ and Tl^+X^-. From these data the equilibrium constant, K_{ip}, for eqn. (1) can be derived [6,11].

The value of δ_f for Tl^+ in MeCN determined in the present work is -226 p.p.m. w.r.t. $Tl^+_{(aq)}$ and is a reflection of the strength of the interaction between Tl^+ and the solvent MeCN. In previous work [10] it has been shown that the relationship between δ_f and the donor properties of solvents as measured by the Gutmann donor number [13], is approximately linear. Solvents with higher donor numbers give rise to ^{205}Tl resonances at lower applied fields and the value of δ_f in MeCN is in accord with this relationship. The value of δ_{ip} estimated for the ion-pair $Tl^+PF_6^-$ in MeCN is -236 ± 1 p.p.m., Figure 1, and K_{ip} is estimated to be ca. 120 dm^3mol^{-1}. The value of K_{ip} estimated for $Tl^+WF_7^-$ is 140 dm^3mol^{-1}. The K_{ip} values calculated for $Tl^+NO_3^-$ in dimethyl sulphoxide and in pyrrole are 75 ± 50 and 208 ± 50 dm^3mol^{-1} respectively [11]. The behaviour in all these systems is very comparable and is consistent with the recent suggestion, made on the basis of ^{19}F n.m.r. chemical shift concentration behaviour, that there is some degree of ion pairing between $[Tl(mesitylene)_2]^+$ and $[B(OTeF_5)_4]^-$ in dichloromethane [14].

The paramagnetic anions UF_6^- and MoF_6^- have a considerable effect on ^{205}Tl resonance in the Tl^I salts. Their effect on the shielding is evidently in the same sense as the paramagnetic term of the ^{205}Tl shielding equation and thus shifts to lower applied field are observed with increasing concentration. It is reasonable to assume that ion-pairing occurs in these solutions, however the concentration effect is too great for the method used earlier to be applied.

In marked contrast, the UF_6^- anion has a very small effect on ^{205}Tl resonance in Tl^{III} hexafluorouranate(V) solutions, Fig. 2. We infer that direct ion-pairing is far less important for Tl^{3+} in MeCN than it is for Tl^+. This is unexpected if the sole factors determining ion-pairing are free cation size and charge, and it appears that Tl^{3+} is far more effectively solvated by MeCN than is Tl^+. We suggest that the UF_6^- anions are located in the disordered solvent zone of the solution rather than in the primary or secondary solvation shells. Good solvation of Tl^{3+} by MeCN is not too surprising since the cation has a d^{10} electronic configuration and other d^{10} cations, for example Cu^+ and Ag^+, are also effectively solvated by this solvent [15].

The deshielding of Tl^I in the presence of added Tl^{III} hexafluorouranate(I) can be accounted for at least in part by the increase in UF_6^- concentration, but the effect of added $TlUF_6$ on $^{205}Tl^{III}$ resonances cannot be accounted for on this basis. A direct Tl^I - Tl^{III} interaction is a possibility but there is no other spectroscopic evidence for this, for example a low energy band is not observed in the solution electronic spectrum of $Tl(MoF_6)_2$ although the solid is yellow [8]. Our tentative suggestion to account for the $^{205}Tl^{III}$ deshielding is that the added Tl^I results in an increase in the asymmetry of the Tl^{3+} solvation environment which in turn leads to an increase in the ^{205}Tl paramagnetic shielding term. The lower symmetry could be the result of a change in the 'bulk solvent' structure caused by the introduction of solvated Tl^+ and $Tl^+UF_6^-$ ion pairs. The situation is in some ways analogous to the solvation of Tl^+ in mixed solvents, where there is a contribution to the ^{205}Tl shielding from changes in solvent structure [10].

EXPERIMENTAL

All operations were carried out in a Pyrex vacuum system or an N_2-atmosphere box ($H_2O < 5$ p.p.m.). The thallium(I) salts $TlPF_6$ and $TlWF_7$ were prepared from TlF and PF_5 or WF_6 in MeCN [8,16]; $TlMoF_6$ and $TlUF_6$ were prepared by oxidation of Tl metal with the appropriate NO^+ salt in MeCN [9]. The thallium(III) salt, $[Tl(NCMe)_5][UF_6]_3$, and a solid which contained both Tl^{III} and Tl^{I} hexafluoromolybdate(V) were prepared by oxidation of Tl metal with UF_6 or MoF_6 in MeCN [8]. Acetonitrile was purified as previously described [3].

Standard solutions (5 ml) of thallium fluorometalates in MeCN were prepared in Grade B volumeric flasks, salts being contained in frangible glass ampoules. Solutions of different concentrations were prepared by dilution using two microburettes and flamed-out vessels fitted with 5 mm n.m.r. tubes. Solutions were degassed, tipped into the n.m.r. tubes, and the latter were sealed.

[^{205}Tl]-Thallium n.m.r. spectra were obtained at 298 K using a Jeol FX90 spectrometer at 51.62 MHz (Tl^{I}) and 51.74 MHz (Tl^{III}). Signals were referenced to the infinite-dilution resonance frequency of Tl^+ in water, Ξ = 57.683833 MHz [6]; chemical shifts are quoted as positive at lower applied field.

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