Far-infrared Spectra of Aqueous Solutions of Thallium(III) Chloride Complexes

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Summary Transmission spectra below 450 cm^{-1} can be easily obtained from thin films (*ca.* 18 μm) of aqueous solutions with a multiple scan Fourier transform i.r. spectrometer; a study of solutions with Cl: Tl^{III} ratios of 4·1—6·4, combined with interactive spectral substraction techniques, provides evidence for the existence of $[TlCl_5]^{2-}$.

ALTHOUGH the far-infrared spectrum (*i.e.* below 400 cm^{-1}) of water[1] and the effect of simple ionic salts on the profile of the broad bands observed have been reported,[2] water does not appear to have been regarded as a feasible medium for relatively routine far-i.r. studies of complexes. We report that there is no particular difficulty in obtaining transmission spectra from films of aqueous solutions using multiple-scan Fourier-transform (F.t.) infrared spectrometers. For the work reported here conventional i.r. cells with silicon windows (Specac Ltd.) and Melinex spacers were used; a sample thickness of *ca.* 18 μm was found to be appropriate and underlying interference fringes did not appear to have a significant effect on the spectra.

The spectra were obtained with a Nicolet 7199A F.t. i.r. spectrometer with 'Glowbar' source and 6·25 μm Mylar beam-splitter, using a polyethylene-windowed triglycine sulphate detector. The results such as those presented typically employ 1000 superimposed interferograms recorded in *ca.* 3 h. Bands from complex ions are rather broad (width at half maximum absorbance 15—50 cm^{-1}) and a resolution of 4 cm^{-1} is adequate for most purposes.

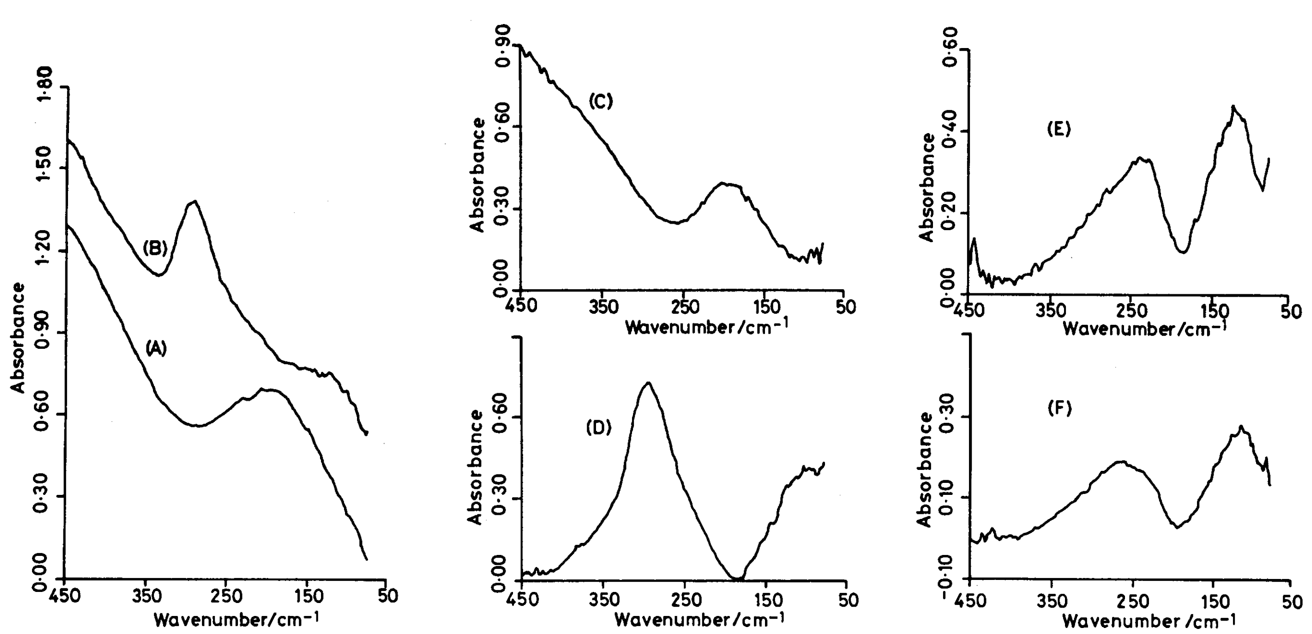

FIGURE. Far-i.r. spectra of *ca.* 18 μm films of (A) water; (B) 2·6 M $Li_{1\cdot1}TlCl_{4\cdot1}$; (C) *ca.* 12 M LiCl after weighted subtraction of spectrum (A); (D) 2·6 M $Li_{1\cdot1}TlCl_{4\cdot1}$ after weighted subtraction of spectra (A) and (C); (E) 2·6 M $Li_{3\cdot4}TlCl_{6\cdot4}$ after weighted subtraction of spectra (A) and (C); (F) 2·5 M $Li_{2\cdot0}TlCl_{5\cdot0}$ after weighted subtraction of spectra (A), C), and (D).

We illustrate the application of these measurements with results for the thallium(III)–chloride system. Figure (A) shows the spectrum of a water film and (B) is that of a 2·6 M solution of $Li_{1\cdot1}TlCl_{4\cdot1}$.

Aqueous LiCl gives a spectrum which differs significantly from that of water, and the result of subtracting a spectrum of pure water from that of a 12 M LiCl solution leaves a residue, shown in Figure (C); it must be appreciated that this interactive subtraction process is somewhat subjective because of the lack of sharp bands in the water spectrum. Combined subtraction of the water and 'LiCl' spectra gives spectrum (D)† for $Li_{1\cdot1}TlCl_{4\cdot1}$, the two bands 293 and 96 cm^{-1} corresponding closely to the maxima of $[TlCl_4]^-$ in $CDCl_3$ solution.[3] The spread of the higher frequency band on the high and low wavenumber sides is doubtless due to the species with more and less than four chlorides, respectively, on thallium in the equilibrium mixture. Treatment of the spectrum of $Li_{3\cdot4}TlCl_{6\cdot4}$ in a similar way gives spectrum (E) with a TlCl stretching band maximum at 230 cm^{-1}, for which we believe $[TlCl_6]^{3-}$ is the predominant species.

Raman spectra show that a species higher in chloride content than $[TlCl_4]^-$ can be formed in water[4] but it has not been possible to demonstrate whether this is $[TlCl_5]^{2-}$ or $[TlCl_6]^{3-}$ and if the latter whether $[TlCl_5]^{2-}$ is a significant intermediate. By recording the spectrum of $Li_{2\cdot0}TlCl_{5\cdot0}$, and subtracting spectra due to solvent *etc.* and part of the spectrum from $Li_{1\cdot1}TlCl_{4\cdot1}$, a residue (Figure F) is left with a TlCl stretching band maximum at *ca.* 262 cm^{-1} which is clearly not due to $[TlCl_6]^{3-}$; treatment of the spectrum of $Li_{3\cdot0}TlCl_{6\cdot0}$ by subtracting 0·42 × spectrum (E) from it gives a virtually identical result. This information is sufficient to demonstrate the existence of $[TlCl_5]^{2-}$ but does not differentiate between square pyramidal (or monohydrated octahedral) and trigonal bipyramidal structures.

Far-i.r. spectroscopy should prove a valuable complement to Raman spectroscopy in the study of aqueous solutions and is of course applicable to densely coloured compounds for which Raman measurements are not possible.

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† We do not use (for example) 2·6 M LiCl to subtract from 2·6 M $Li_{1\cdot1}TlCl_{4\cdot1}$ because the free H_2O concentrations would be different in the two solutions. Although it would be possible to determine what concentration of LiCl solution had the correct Li : H_2O ratio, measure such a solution, and then carry out an appropriate weighted subtraction, this seems an unnecessarily cumbersome procedure, which in any case would not be any more valid since we know that aqueous solution spectra of alkali halides are not totally independent of the anion.

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