

## Distortion of the Tetrachlorogallate Ion in Solution

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THE dipole moments of benzene solutions of trialkylammonium benzoates have been interpreted as indicating the existence of hydrogen bonding between the anion and the cation.<sup>1</sup> We report that far-infrared spectroscopy indicates strong association between incompletely substituted

alkylammonium cations and the tetrachlorogallate ion in non-dissociating solvents such as *cis*-1,2-dichloroethylene. Tetra-*n*-propylammonium tetrachlorogallate shows in this solvent the single infrared-active Ga-Cl stretching band at 374 cm.<sup>-1</sup>\* expected for a  $T_d$  symmetry anion.<sup>2</sup> However,

\* All the spectra show a weak band about 340 cm.<sup>-1</sup> which we do not consider to be a Ga-Cl stretching band but for which we can not give a definite assignment.

triethylammonium tetrachlorogallate in  $C_2H_2Cl_2$  shows three Ga-Cl stretching features  $359\text{ cm}^{-1}$ ,  $383\text{ cm}^{-1}$ , and a shoulder at  $390\text{ cm}^{-1}$ . This observation is consistent with the symmetry of the anion being degraded from  $T_d$  to  $C_{3v}$ , and probably arises from the association of the proton on the cation with one of the chlorine atoms of the anion. The behaviour of  $Pr^{\text{III}}_3NH^+GaCl_4^-$  and of  $Bu^{\text{III}}_3NH^+GaCl_4^-$  is identical with that of  $Et_3NH^+GaCl_4^-$ . Di-n-propylammonium tetrachlorogallate also shows three features,  $392$ ,  $381$ , and  $359\text{ cm}^{-1}$ , but in this case the two highest frequency features are resolved. In this case, the  $GaCl_4^-$  ion may be displaying  $C_{3v}$  symmetry with the fourth infrared-active Ga-Cl stretching mode obscured by one of the other three. The spectra are shown in the Figure.

In nitromethane solution, all of the compounds display only a single Ga-Cl absorption at  $372\text{ cm}^{-1}$ , suggesting that the cation is separated from the anion by solvation in this solvent.

The simple interpretation of the results offered here is equally applicable to similar systems containing  $CoCl_4^{2-}$ ,  $MnCl_4^{2-}$ , and  $AuCl_4^-$  ions which we have studied, except that in the case of doubly

charged anions the effect of two cations must be considered.

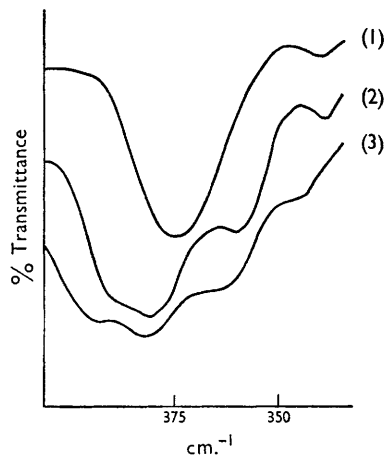


FIGURE. Spectra of (1)  $Pr^{\text{III}}_4NGaCl_4$ , (2)  $Et_3NHGaCl_4$ , (3)  $Pr^{\text{III}}_2NH_2GaCl_4$  solutions in *cis*-1,2-dichloroethylene.

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<sup>1</sup> K. Bauge and J. W. Smith, *J. Chem. Soc. (A)*, 1966, 616.

<sup>2</sup> L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 1956, 3721.