Tetraphenylarsonium Hydrogen Dithiocyanate

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THERE have been a number of recent additions to the range of hydrogen dihalide anions which may be stabilised in the presence of large cations.[1] However, there are no recorded examples of hydrogen-bonded thiocyanate anions, although it is well established that isothiocyanic acid interacts with a wide range of organic Lewis bases.[2] This communication describes the preparation of tetraphenylarsonium hydrogen dithiocyanate, $Ph_4AsH(NCS)_2$.

Tetraphenylarsonium hydrogen dichloride dihydrate and potassium thiocyanate, in a 1 : 2 molar ratio, were dissolved in liquid sulphur dioxide, potassium chloride being gradually precipitated from the resulting solution. The acid thiocyanate salt was extracted from the residue, after the removal of the sulphur dioxide, with dichloromethane. The solvent was evaporated to dryness at room temperature leaving a pink crystalline salt (the pink coloration is probably due to traces of ferric iron in the hydrated acid chloride) (Found: C, 62·6; H, 4·1; N, 5·2; S, 12·0. Calc. for $C_{26}H_{21}AsN_2S_2$: C, 62·4; H, 4·2; N, 5·6; S, 12·8%.) The salt imparted an acid reaction to water and slowly decomposed when left in contact with moist air.

The *X*-ray powder photographs of the acid thiocyanate and tetraphenylarsonium thiocyanate were apparently unrelated: the melting points of the two thiocyanates were 136° (decomp.) and 276°,

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[1] T. C. Waddington, *J.*, 1958, 1708; D. G. Tuck and E. J. Woodhouse, *Proc. Chem. Soc.*, 1963, 53; T. C. Waddington and J. A. White, *J.*, 1963, 2701; D. H. McDaniel and R. E. Vallée, *Inorg. Chem.*, 1963, **2**, 997; J. A. Salthouse and T. C. Waddington, *J.*, 1964, 4664.

[2] T. M. Barakat, N. Legge and A. D. E. Pullin, *Trans. Faraday Soc.*, 1963, **59**, 1773.

respectively.[3] Proton magnetic resonance spectra of both compounds in dichloromethane showed signals due to the phenyl protons; only the acid thiocyanate gave a concentration-dependent signal below $\tau = 0$.

Infrared spectra (both in KBr discs and in solutions in dichloromethane) showed that ν_{CN} is broader for the acid thiocyanate and that new absorption bands appeared at 2400 br, 1000 vbr, 801 sh and 600 br cm.$^{-1}$. The interpretation of the spectra is not complete at present but the 801 cm.$^{-1}$ band is taken as an indication that the thiocyanate groups are bonded through the nitrogen atoms[4] to the hydrogen in the $H(NCS)_2^-$ anion. The other bands are broad as expected for a hydrogen-bonded structure.

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[3] D. R. Lyon and F. G. Mann, *J.*, 1942, 666.

[4] J. Lewis, R. S. Nyholm and P. W. Smith, *J.*, 1961, 4590.