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The Bifurcated Hydrogen Bond in 4-Chloropyridinium Hexachlorostannate(IV). Confirmation via Neutron Powder Diffraction

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Although hydrogen bonding is recognized as a significant factor contributing to the structures displayed by crystalline compounds [1], the interaction described as 'bifurcated' is usually accepted to be an uncommon one, especially in inorganic compounds. This is despite the fact that examples keep being unearthed [2, 3] to add to those others (such as the hydrates of magnesium sulfate and barium chloride [4], ammonium sulfate [5] and potassium tetrachlorostannate(II)monohydrate [6]) which have been documented previously.

Another interesting example was provided by Brill and co-workers [7] who postulated that the proton on the N atom of the heterocyclic group in 4-chloropyridinium hexachlorostannate(IV) was almost equidistant (2.408 and 2.583 Å) from two crystallographically equivalent Cl atoms located on separate, markedly distorted $SnCl_6^{2-}$ moieties. In order to deduce this result from their X-ray data, the authors assumed that all the hydrogen atoms were located 1.08 Å from the ring atoms to which they were bonded.We report here the result of a structure determination on this compound obtained using the powder neutron method.

Experimental

The compound was prepared by evaporation of an HCl solution of $SnCl_4 \cdot 5H_2O$ containing an excess of 4-chloropyridine hydrochloride [8]. *Anal.** Calcd. for $C_{10}H_{10}N_2Cl_8Sn$: C, 21.43; H, 1.80; Cl, 50.6%. Found: C, 21.38; H, 1.87; Cl, 50.77%.

A finely-powdered sample (11.42 g) packed in a 16 mm diameter thin-walled vanadium can was rotated about the axis of the high resolution neutron powder diffractometer on the 6HB takeoff of the HIFAR reactor at Lucas Heights [9]. (This instrument is now fitted with a bank of eight counters). Irradiation was performed using neutrons with λ = 1.893 Å. Peak profile analysis based on the reported space group $P2_1/C$ was carried out on 775 reflections between 10 and 116° using the program devised by Wiles and Young [10], the asymmetric profiles being fitted by a sum of five Gaussians [11]. The background and H(1) positional parameters were refined using the other atom positional and anisotropic thermal parameters fixed at the values reported by Brill *et al.* [7]. A small correction, however, was applied to the positional coordinates of H(6) [set at x = 0.0707, y = 0.2928, z = −0.0420] to bring it into the plane of the pyridinium ring. All the C–H bond distances were left fixed at 1.08 Å. Close convergence to the expected R value was obtained by refining only H(1) and the refinement was not improved significantly by the inclusion of more parameters.

Results and Discussion

Refinement of the neutron data led to the coordinates of the hydrogen bonded proton H(1) of x = 0.1388(44), y = 0.4261(21), z = 0.0709(54) which compare with those deduced by Brill *et al.* of 0.1384, 0.4272 and 0.0639 respectively. These coordinates result in a N–H(1) bond distance of 1.06(6) Å. Thus, the neutron data confirm the previous X-ray crystal structure determination and the authors' suggestion of a bifurcated hydrogen bond in this system. The bifurcation is not completely symmetrical, as appears also to be the case in the salt hydrates mentioned above [4].

It should be noted that in this relatively complex structure ten of the thirty-one atoms are hydrogen which produces a high background due to spin incoherent scattering. Despite the extra scattering of hydrogen relative to carbon, a good refinement of the model (R_w = 0.023) was obtained with the hydrogens in their positions. This reflects the quality of the original X-ray data.

It is clear that the distortions observed in the $SnCl_6^{2-}$ octahedra indeed arise from the hydrogen bonding interactions. These distortions, which are sufficiently large to cause considerable splitting in the ^{35}Cl NQR signals [8] are all the more remarkable because N–H·····Cl hydrogen bonding is generally regarded as one of the weaker interactions. In this case, however, despite the openness of the structure, no phase changes were observed in a DTA scan between −140 and *ca.* 150 °C, after which multiple events occur, including sublimation. In con-

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*Microanalyses by Malissa and Reuter, Engelskirchen, F.R.G.

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trast, pyridinium chloride which has a normal weak N–H·····Cl hydrogen bond, undergoes a solid-solid phase transition at 72 °C [12].

Since the ^{35}Cl NQR signal for the $SnCl_6^{2-}$ unit is not appreciably split in the unsubstituted pyridinium analog [8] and also since the H(1) proton is not abnormally close to the Cl atoms (in fact the H(1)–Cl(3) distances are longer than those found, for example, in pyridoxinium chloride, 2.082 Å [13] or 1,4-butanediyldiammonium tetrachloromanganate(II), *ca.* 2.2 Å [14]) it would appear that the difference in distortion in the two cases must arise mainly in the nett positive charge residing on H(1). Since 4-chloropyridine (p*K*, *ca.* 3.8) is a weaker base than pyridine itself (p*K*, *ca.* 5.25) [15], a higher partial charge is not unexpected.

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