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Proton Transfer through Hydrogen Bond in Solid Pyridine-Chloroacetic Acid Complexes as Evidenced by ^{35}Cl Nuclear Quadrupole Resonance

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Hydrogen bond formation between dissimilar molecules is a prototype of acid-base interaction. Interesting examples are solid hydrates of acids, *e.g.* $HNO_3 \cdot H_2O$ and $(COOH)_2 \cdot 2H_2O$, in which protons are given up to the water of crystallization by the acid molecule if it is sufficiently strong or retained by the acid if it is weak. In solids, the electrostatic field generally built up in the lattice as a result of the proton transfer can further facilitate such a transfer; thus glycine exists in the form of zwitterions in the α crystal, while it assumes a molecular conformation in an isolated state.[1]

The purpose of the present communication is to

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[1] S. Takagi, H. Chihara, and S. Seki, This Bulletin, **32**, 84 (1959); see also Y. Grenie, J. C. Lassegues, and C. Garrigou-Lagrange, *J. Chem. Phys.*, **53**, 2980 (1970).

present an experimantal evidence that protons have been transferred from chloroacetic acids to pyridine in the solid 1:1 complexes formed between them. The complexes are known in solution state to be in tautomeric equilibrium between the two forms, simple hydrogen bonded pair or ion-pair, as revealed by infrared[2] and the ultraviolet[3] spectral studies. Dielectric study[4] also suggested such possibilities.

TABLE 1. CHLORINE QUADRUPOLE RESONANCE FREQUENCIES AT 77°K (MHz)

$(CCl_3COO)(C_5H_5NH)$ (1:1)	37.8396, 37.9275, 38.0166, 38.0722, 38.3075, 38.4915, 38.5118, 38.5932, 38.6002, 38.6365, 38.7205, 38.7598
$(CHCl_2COO)(C_5H_5NH)$ (1:1)	36.3882 36.6843

We have measured the ^{35}Cl nuclear quadrupole resonance frequencies of pyridine complexes with di- and tri-chloroacetic acids in polycrystalline form. Frequencies measured at 77°K are given in Table 1. The trichloroacetic acid complex gives twelve resonance lines differing at most by 0.9 MHz, whereas the dichloacetic acid complex gives only two; this suggests a relatively simpler crystal structure for the latter. Since the solid state effects are generally small[5] and we are interested in the state of the valence electrons of the chlorine atoms on which the effect of proton transfer is considered to appear, we take mean value ν_m of the observed resonance frequencies for each complex and compare them with those for pure acids and ammonium salts. Such a comparison is shown in Table 2.

We see that (a) in the series of pure acids, ν_m changes monotonously with the number of chlorine atoms contained in them (*i.e.* with the acid strength) and (b) in the series of ammonium salts of mono- and di-chloroacetic acids, ν_m decreases with the number of acidic hydrogen atoms.

It is to be noted that pyridine-dichloroacetic acid has the ν_m value very close to that of $CHCl_2COONH_4$. If pyridine is linked to dichloroacetic acid through the O–H···N hydrogen bond and the proton is moving sufficiently rapidly between the two potential minima along the hydrogen bond, *i.e.* if there is a dynamic equilibrium between the covalent and the ionic forms, O–H···N and O^-···H–N^+, the observed resonance frequency ν_m may be given by $\nu_m = P_i\nu_i + (1-P_i)\,\nu_c$ where P_i is the fractional importance of the ionic form and ν_i and ν_c are the frequencies characteristic of either form. Upon substitution of appropriate figures, $\nu_m =$ 36.54 MHz, $\nu_i = 36.46$ MHz, and $\nu_c = 38.39$ MHz, one obtains $P_i = 0.95$ as compared with $P_i = 0.71$ in a non-dissociative solvent at room temperature.[2] This would mean that in solid pyridine-dichloroacetic acid, the pyridine molecule deprives the acid of its carboxyl hydrogen almost completely, forming an ionic crystal lattice in which cations and anions are bonded by N^+–H···O^- hydrogen bonds. This is a situation locally analogous to that of glycine or other amino acid crystals. Comparison of the ν_m's for the pyridine complexes with di- and tri-chloroacetic acids also indicates that the same would hold for $CCl_3COO \cdot C_5H_5NH$.

TABLE 2. COMPARISON OF MEAN ^{35}Cl RESONANCE FREQUENCIES BETWEEN PURE CHLOROACETIC ACIDS AND THEIR SALTS AND THE SHIFT OF THE FREQUENCY FROM THOSE OF THE PURE ACIDS (MHz)

Substance	Mean Freq. (ν_m)	Shift ($\Delta\nu$)
CCl_3COOH	40.12[a)]	—
$(CCl_3COO)_2HNH_4$	39.49[b)]	0.63
$CCl_3COOH \cdot C_5H_5N$	38.37	1.75
$CHCl_2COOH$	38.39[a)]	—
$(CHCl_2COO)_2HNH_4$	37.63[d)]	0.76
$CHCl_2COONH_4$	36.46[d)]	1.93
$CHCl_2COOH \cdot C_5H_5N$	36.54	1.85
$CH_2ClCOOH$	35.25[c)]	—
$(CH_2ClCOO)_2HNH_4$	33.73[e)]	1.52
$CH_2ClCOONH_4$	33.23[e)]	2.02

a) H. Allen, *J. Phys. Chem.*, **57**, 501 (1953).
b) See Ref. 5.
c) H. Negita, *J. Chem. Phys.*, **23**, 214 (1955)
d) H. Chihara and N. Nakamura, unpublished results.
e) T. Yamamoto, N. Nakamura, and H. Chihara, unpublished results (room temperature values).

Attempts have been made to measure the quadrupole resonances in pyridine-monochloroacetic acid and ammonium trichloroacetate. However, no resonance could be detected for unknown reasons although several specimens prepared by different methods were examined. The dichloroacetic acid complex used in the present study was precipitated from cold pyridine solution of the acid, and the trichloroacetic acid complex was crystallised from an ethyl acetate solution containing an excess of pyridine. Both products were washed with ether and dried.

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[2] G. M. Barrow, *J. Amer. Chem. Soc.*, **78**, 5802 (1956).

[3] J. Nasielski and E. V. Donckt, *Spectrochim. Acta*, **19**, 1989 (1963).

[4] M. Davies and L. Sobczyk, *J. Chem. Soc.*, **1962,** 3000; S. R. Gough and A. H. Price, *J. Phys. Chem.*, **73**, 459 (1969).

[5] D. Biedenkapp and A. Weiss, *Ber. Bunsenges. Phys. Chem.*, **70**, 788 (1966).