Neutron-Diffraction Determination of the Structure of $CH_3CN \cdot 2HCl$

Sir:

Numerous reports[1-6] of experimental studies of the bichloride ion have appeared recently. Although the existence of this anionic species $(Cl-H-Cl)^-$ in both solution and the solid state appears to be well established, conclusive structure determinations on solid phases by diffraction methods have been lacking.

Among the many reported examples of compounds possibly containing the bichloride ion, $CH_3CN \cdot 2HCl$ is one of the simplest and most interesting. Both Hantzsch,[7] who made an early study of this material,

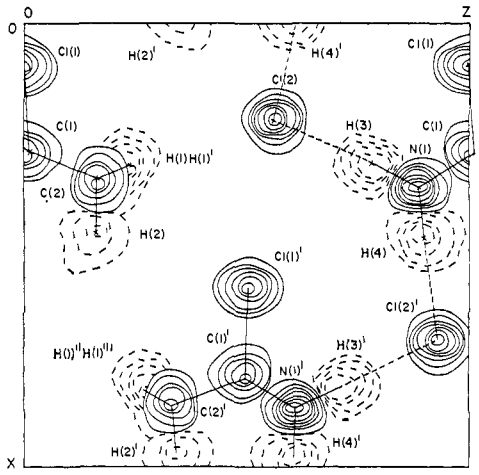


Figure 1. Fourier section at $y = 1/4$ in the unit cell: dashed circles (negative contours) in intervals of 300; positive contours in intervals of 500. The atoms in the asymmetric unit are Cl(1), C(1), C(2), H(1)', H(2), N(1), H(3), H(4), and Cl(2). The out-of-plane methyl hydrogen atoms [H(1), H(1)', H(1)'', and H(1)'''] have been projected onto the plane, and final positional parameters obtained from a full-matrix anisotropic least-squares refinement are indicated on the section with crosses (×). Bonded atoms in the acetimino group are connected by light solid lines. Dashed lines indicate hydrogen-bonding interactions.

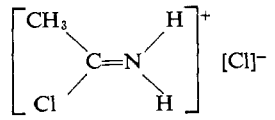
and Janz and Danyluk,[8] who unexpectedly obtained the crystalline solid during conductivity studies of acetonitrile–hydrogen chloride, postulated that the structure was that of a nitrilium salt $[CH_3CNH^+(HCl_2)^-]$. The latter workers based their structure hypothesis largely on the similarity of the infrared spectrum of this compound in solution to that independently observed[2,9] for solid $(CN_3)_4NCl \cdot HCl$, which is assumed (with strong support) to contain the bichloride ion. However, it should be noted that Janz and Danyluk interpreted the spectrum of solid $CH_3CN \cdot 2HBr$ as indicative of an imino hydrohalide structure $[CH_3C(Br)=NH \cdot HBr]$, and they did not rule out the possibility of a similar structure for solid $CH_3CN \cdot 2HCl$.

(1) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, 76, 4046 (1954).
(2) T. C. Waddington, *J. Chem. Soc.*, 1708 (1958).
(3) D. W. A. Sharp, *ibid.*, 2558 (1958).
(4) R. E. Vallee and D. H. McDaniel, *J. Inorg. Nucl. Chem.*, 24, 1017 (1962).
(5) S. Chang and E. F. Westrum, Jr., *J. Chem. Phys.*, 36, 2571 (1962).
(6) J. C. Evans and G. Y-S. Lo, *J. Phys. Chem.*, 70, 11 (1966).
(7) A. Hantzsch, *Ber.*, 64, 667 (1931).
(8) G. J. Janz and S. S. Danyluk, *J. Am. Chem. Soc.*, 81, 3850 (1959).
(9) N. L. Zutty, Ph.D. Thesis, Rensselaer Polytechnic Institute, 1958. Available on microfilm through University Microfilms, Inc., Ann Arbor, Mich.

Another related compound, the hexachloroantimoniate(V) complex $[CH_3CN \cdot 2HCl, SbCl_5]$, has been recently the subject of a detailed infrared study.[10] The molecular structure resulting was found to be consistent with the imino hydrohalide model similar to the case of $CH_3CN \cdot 2HBr$. In view of the above uncertainties we have chosen to investigate the structure of $CH_3CN \cdot 2HCl$ by single-crystal neutron-diffraction methods.

Single crystals suitable for neutron diffraction were grown from anhydrous acetonitrile–hydrogen chloride solutions at −16° under dry nitrogen. Analysis of single-crystal material established the formula to be $CH_3CN \cdot 1.96HCl$. Crystals sealed in glass capillaries were examined by standard X-ray techniques. The orthorhombic cell with $a = 8.72 \pm 0.01$, $b = 6.93 \pm 0.01$, and $c = 8.63 \pm 0.01$ A contains four molecules. The diffraction symbol is mmmPn·a indicating Pnma and $Pn2_1a$ as possible space groups. A statistical test indicated the presence of a center of symmetry establishing the former space group.

Essentially complete three-dimensional neutron-diffraction data (511 independent reflections) were collected at −5° with λ 1.08 A. The structure was solved from the three-dimensional neutron Patterson function with some assistance from an X-ray projection. All atoms except two methyl hydrogens lie in mirror planes. The basic molecular structure is that of the imino hydrohalide model



as is evident from the Fourier section shown in Figure 1. The Cl^- ion is involved as an acceptor in two hydrogen bonds which lie in the molecular plane and which serve to tie together the planar acetimino groups. Bonding between planes is very weak in agreement with the physical properties of the crystal. Although this crystal is rather unstable toward loss of HCl, the bond lengths and angles appear normal. After two cycles of full matrix anisotropic least-squares refinement[11] the weighted $R = [\Sigma w(F_o - F_c)^2]^{1/2}/[\Sigma w F_o^2]^{1/2}$ was 0.085 for all reflections. A full report will appear later.

Acknowledgment. We wish to acknowledge the support of the U. S. Atomic Energy Commission.[12]

(10) E. Allenstein and A. Schmidt, *Spectrochim. Acta*, 20, 1451 (1964).
(11) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.
(12) The present report is assigned Serial No. RLO-1778-3 for indexing purposes.

(13) Metallurgy Division, Argonne National Laboratory, Argonne, Ill.

S. W. Peterson, Jack M. Williams[13]
Department of Chemistry, Washington State University
Pullman, Washington

Received February 4, 1966

New Aspects of the Mechanism of Sulfenyl Chloride Additions to Olefins

Sir:

The addition of alkane- and arenesulfenyl chlorides to unsaturated systems has received considerable at-