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The crystal structure of hydrazinium chloride, N_2H_5Cl . By KIICHI SAKURAI and YUJIRO TOMIIE,
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The crystal structures of the hydrazonium salts such as $N_2H_5F_2$ (Kronberg & Harker, 1942), $N_2H_6Cl_2$ (Wyckoff, 1923; Donohue & Lipscomb, 1947) and $N_2H_6SO_4$ (Nitta, Sakurai & Tomiie, 1951) have already been investigated by X-ray methods, but none of the structures of the hydrazinium salts which are characterized by the existence of the $N_2H_5^+$ ion has yet been examined. We have thus determined the structure of the hydrazinium chloride, N_2H_5Cl . The crystal of hydrazinium chloride obtained from an alcoholic solution are very fine needles parallel to the c axis and somewhat hygroscopic.

Useful X-ray data were obtained from oscillation and Schiebold-Sauter photographs taken with filtered Cu $K\alpha$ radiation. There are sixteen formula units in the unit cell of the dimensions

$$a = 12.49, b = 21.85, c = 4.41 \text{ \AA},$$

and the space group is C_{2h}^2-Fdd . The intensities of reflexions were measured by means of a microphotometer. The x and y parameters of the atoms were determined by the Patterson and the electron-density maps projected on (001), the termination error being taken into account. The z parameters were first found by the method of trial and error, using the ($h0l$) data together with following special sets of relations:

$$(644) > (424) \ll (264), (662) < (602) \text{ and } (644) \gg (824).$$

They were then confirmed by comparing observed and calculated F values for the ($hk2$) reflexions. The parameter values of the atoms thus determined are given in Table 1. The effect of thermal motion was taken into account by multiplying the calculated F values with temperature factors $\exp[-B(\sin \theta/\lambda)^2]$, where $B = 2.13 \text{ \AA}^2$ for the ($hk0$) reflexions and 1.90 \AA^2 for the ($hk2$) reflexions. The value of $R = \sum ||F_o| - |F_c|| \div \sum |F_o|$ is 0.15 for the ($hk0$) reflexions.

Table 1. Atomic co-ordinates

	x	y	z
Cl	0.0410	0.0835	0.000
N_I	0.1032	0.2363	0.776
N_{II}	0.0687	0.1922	0.549

Table 2. Interatomic distances

N_I-N_{II}	1.45 \AA	$N_I \cdots N_I$	3.52 \AA
$N_{II}H \cdots N_I$	2.95	$N_{II} \cdots N_{II}$	3.77
$N_I \cdots Cl$	3.26, 3.43, 3.49	$Cl \cdots Cl$	3.78, 3.79
$N_{II} \cdots Cl$	3.41, 3.12, 3.12		

The interatomic distances are listed in Table 2. The observed N-N distance in the $N_2H_5^+$ ion is 1.45 \AA, slightly shorter than that of the hydrazine molecule, 1.47 \AA in gaseous state or 1.46 \AA in crystal (Giguère & Schomaker, 1943; Collin & Lipscomb, 1951), and somewhat longer than that of the $N_2H_6^{++}$ ion, 1.40–1.42 \AA in the crystals of $N_2H_6F_2$, $N_2H_6Cl_2$ and $N_2H_6SO_4$. Such shortening of the N-N distance with increasing total charge of the hydrazine group may be attributed to the

'formal charge' effect (Kronberg & Harker, 1942). However, it should be remarked that, as already pointed out (Donohue & Lipscomb, 1947; Nitta *et al.*, 1951), the formal-charge effect alone does not seem sufficient for explaining a shortening as remarkable as that actually observed. Another reason for the observed variation of these N-N bond distances may be as follows. Although, in the ammonia molecule, the contribution of the $s-p$ hybridization of the nitrogen atom is not so great, this becomes quite important in the ammonium ion. Similar relations may exist in the pair of N_2H_4 and $N_2H_6^{++}$, the nitrogen atoms thus being linked together more closely to each other in the latter than in the former. It can naturally be expected that the N-N distance of the $N_2H_5^+$ ion has an intermediate value between those of N_2H_4 and $N_2H_6^{++}$.

Each $N_2H_5^+$ group has eight neighbours, i.e. six chlorine and two nitrogen atoms. The arrangement of the atoms around one $N_2H_5^+$ group resembles that for the $N_2H_6^{++}$ group in $N_2H_6Cl_2$ except the fact that one of the neighbouring chlorine atoms of each nitrogen in the latter is replaced by a nitrogen atom.

In Fig. 1 the environment of one $N_2H_5^+$ group is projected upon two planes parallel and perpendicular to the N_I-N_{II} axis.

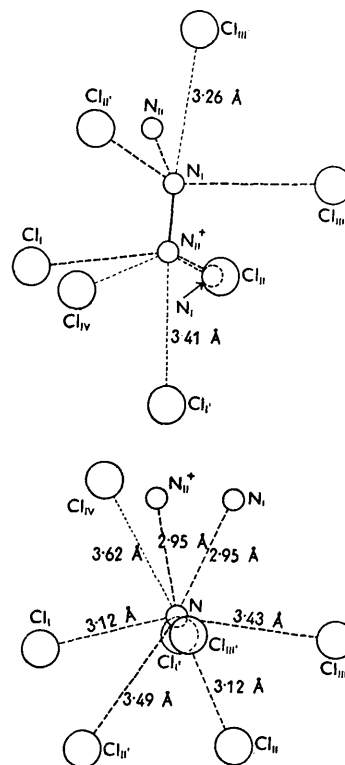


Fig. 1. Environment of one $N_2H_5^+$ group projected upon two planes parallel and perpendicular to the N_I-N_{II} axis. Thick broken lines represent hydrogen bonds.

the N_I-N_{II} axis. The distances $N_{II}\cdots Cl$ are shorter than those of $N_I\cdots Cl$, and this fact suggests that N_I is the $-NH_2$ group and N_{II} the $-NH_3^+$ group. It is a characteristic of this crystal that the cations are linked by the hydrogen bonds of the type $N^+H\cdots N$ with a distance of 2.95 Å and these form infinite spiral chains along the c axis.

Finally, it is interesting to note that in the iso-electronic crystal of hydroxylammonium chloride (Jerslev, 1948) there is no hydrogen bond of the type $N^+H\cdots O$.

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Notes and News

Announcements and other items of crystallographic interest will be published under this heading at the discretion of the Editorial Board. Copy should be sent direct to the British Co-editor (R. C. Evans, Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England).

Advances in Physics

Messrs. Taylor and Francis announce the publication, as from January 1952, of a new quarterly periodical, *Advances in Physics*, which is to appear under the editorship of N. F. Mott as a supplement to the *Philosophical Magazine*. It is the policy of the journal to publish critical review articles covering a wide range of physical subjects, but those in any one part will be confined to a restricted field. The first issue is of particular interest to crystallographers, being devoted to three articles on solid-state physics: 'The Mean Free Path of Electrons in Metals' by E. H. Sondheimer, 'The Generation of Vacancies by Moving Dislocations' by F. Seitz and 'Crystal Growth and Dislocations' by F. C. Frank.

The journal is published in the same format as the *Philosophical Magazine* and the first issue consists of 109 pages. The price is 15s. per part or 55s. per annum.

Charts for X-ray Crystallography

A previous note under this title (*Acta Cryst.* (1950), **3**, 482) listed short descriptions of a number of charts used in X-ray crystallography, and invited comments on their use and on the probable demand for such charts. As a result of replies received the X-ray Analysis Group of the British Institute of Physics has now obtained supplies of the following items and these may be purchased from the Institute at the address given below. For this purpose charts will be known by reference numbers with the prefix PC (the figures in parenthesis following each item below refer to the description of the chart in the previous note).

- PC 1. Equatorial (Wulff) stereographic net (half circle); 5 in. diameter on tracing paper; 2° intervals (1 (1)(a)).
 PC 18. Equatorial (Wulff) stereographic net (whole circle); 5 in. diameter; 2° intervals (1 (2)(a)).
 PC 30. Equatorial (Wulff) stereographic net (whole circle); 30 cm. diameter on thin card; 1° intervals (1 (1)(c)). It is difficult to reproduce a chart of this size with the necessary accuracy

and definition, and differences in length between the two principal diameters of about 0.2% may be found. In addition, in extreme conditions of temperature or humidity further changes of dimensions of about the same order may occur. It is hoped to be able to make a further announcement later about a more accurate reproduction of this chart.

- PC 4. Greninger chart for back-reflexion photographs; 2° intervals; specimen-film distance 3 cm. (C. S. Barrett, *Structure of Metals*, p. 170. New York: McGraw Hill, 1943) (1 (1)(e)).
 PC 14. Bernal ξ , ζ chart for flat film; specimen-film distance 4 cm. (J. D. Bernal, *Proc. Roy. Soc. A*, **113**, 117, 1927) (2 (1)(a)).
 PC 2. Bernal ξ , ζ chart for cylindrical film of diameter 6 cm. (2 (1)(b)).
 PC 5. α , ω , θ (or ρ , φ , θ) chart for cylindrical film of diameter 6 cm., for orientation purposes. Here α (or ρ) is the angle between the axis (A) of oscillation and the normal (N) to the reflecting planes; ω (or φ) is the angle between the plane containing A and N and that containing A and the incident X-ray beam; and θ is the Bragg angle (2 (2)(b)).
 PC 31. Weissenberg chart for cylindrical film of diameter 6 cm.; 9 cm. traverse = 180° (chart to cover 13.5 cm.) (M. J. Buerger, *X-ray Crystallography*, p. 268. New York: Wiley, 1942) (2 (1)(e)).
 PC 32. As PC 31 but for film of diameter 5.73 cm. and with 240° traverse (2 (1)(g) (ii)).
 PC 16. Constant- ρ chart for 6 cm. diameter Weissenberg camera (N. Wooster & W. A. Wooster, *Phil. Mag.* (7), **37**, 262, 1946) (2 (1)(f)).
 PC 17. Constant- θ chart for 6 cm. diameter Weissenberg camera (N. Wooster & W. A. Wooster, *Phil. Mag.* (7), **37**, 262, 1946) (2 (1)(f)).
 PC 34. Cochran chart on a scale of 1 reciprocal unit = 10 cm., for combined correction for Lorentz and polarization factors (including Cox-Shaw-Tunell corrections) for normal-beam Weissen-