The Crystal Structure of Ethylenediammonium Chloride

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Ethylenediamine, as a ligand of the coordination compounds, has been studied by several authors[1-4]. In these crystals, ethylenediamine usually has a gauche-configuration. However, ethylenediamine in other types of compounds has not been sufficiently investigated. In the structure of ethylenediammonium sulfate[5], for instance, though it has not been fully studied, the ethylenediammonium ion has been reported to have a gauche-configuration. On the other hand, in ethylenediammonium adipate, of which only the crystallographic data have been reported[6], a planar and a trans-configuration can be expected on the basis of the data, because the ethylenediammonium ion seems to have a center of symmetry. Thus, the ethylenediammonium ion seems to have either a trans- or a gauche-configuration. Ethylenediammonium chloride was chosen to be investigated in order to add to the data on the trans- and gauche-stereoisomerism of the ethylenediammonium ion. The results of the investigation will be given here.

Recently, tetramethylenediammonium chloride has also been investigated by the present authors from a similar view-point. These results will be published later.

Experimental

The crystals of ethylenediammonium chloride, $H_3N(CH_2)_2NH_3Cl_2$, were grown from an ethylalcohol-water solution. Most of the crystals were obtained as needles elongated along the c axis, while others were obtained as plates, the main face of which was (0 0 1). This difference may be due to slight changes in the conditions of the recrystallizations. A marked cleavage was found perpendicularly to the c axis, as had been reported by Groth[7]. The crystals belong to the monoclinic system. The unit cell dimensions were obtained from the Weissenberg photographs of $(h\,0\,l)$ and $(h\,k\,0)$ by overlapping the powder patterns of aluminum as a standard on the same films; they are;

$$a=9.95\pm0.01 \qquad b=6.89\pm0.01$$
$$c=4.42\pm0.01\text{Å} \qquad \beta=90.7\pm0.3^\circ$$

and

$$a:b:c=1.449:1:0.642$$

The axial ratios of the present investigation agree with the values given by Groth[7] to within the stated range of experimental error, though the β-angles differ a little from one other. The values given by Groth are:

$$a:b:c=1.4439:1:0.6439$$

and

$$\beta=91^\circ35'$$

The space group of the crystal was found to be $P2_1/a$ from the systematic absences of the $(0\,k\,0)$ spectrum for $k=2n+1$ and the $(h\,0\,l)$ spectrum for $h=2n+1$. The density, 1.46 g. cm^{-3}, observed by the floatation method corresponds to two formula units in a unit cell; the calculated density is 1.46 g. cm^{-3}.

Weissenberg photographs were taken around the b and c axes, using Cu$K\alpha$ radiation. The multiple-film technique was used, and the intensities of the $(h\,0\,l)$, $(h\,k\,0)$ and a part of the $(h\,k\,1)$ reflections were estimated visually, comparing them with a standard scale made by the same crystal. The corrections for polarization and Lorentz factors were made. No absorption corrections were made because the shapes of the crystals used were irregular; they should have been made, however, because the linear absorption coefficient for Cu$K\alpha$ radiation is rather large ($\mu=85.0\,\text{cm}^{-1}$).

Structure Determination

Since the crystal belongs to the $P2_1/a$ space group and the number of formula units in a unit cell is two, the ethylenediammonium ion has to occupy a center of symmetry. The position of the chloride ion was determined from the projections of the Patterson function along the b and c axes. The projections of the electron-density functions along the two principal axes were synthesized using the structure factors whose phases were assigned by the coordinates of the chloride ion. The maps thus obtained showed the positions of the carbon and the nitrogen atoms. The coordinates of the atoms thus obtained were, then, refined by successive (F_o-F_c) syntheses. In these procedures, it was found that the

1) A. Nakahara, Y. Saito and H. Kuroya, This Bulletin, 25, 331 (1952).
2) Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Cryst.*, 8, 729 (1955).
3) H. Scouloudi, ibid., 6, 651 (1953).
4) M. R. Truter and E. G. Cox, *J. Chem. Soc.*, 1956, 948.
5) Y. Okaya and I. Nitta, *Acta Cryst.*, 5, 564 (1952).
6) S. Hirokawa, T. Ohashi and I. Nitta, ibid., 7, 87 (1954).
7) P. Groth, "Chemische Krystallographie", Vol. III, Engelman, Leipzig (1910), p. 52.

contributions of the hydrogen atoms to the structure factors were not negligible (the electrons which belong to the hydrogen atoms amount to 14% of the total number of electrons in the crystal). Therefore, the coordinates of all the hydrogen atoms were calculated geometrically, using the coordinates of the heavier atoms, and the presences of these hydrogen atoms were confirmed on the $(\rho_o - \rho_c)$ maps. They were included in the calculations of the structure factors, which were used in the further refinements of the structure, whereupon the R factors of two zones decreased by about 0.02. The final $(\rho_o - \rho_c)$ maps of $(h\,0\,l)$ are shown in Fig. 1, where significant changes due to the inclusion or exclusion of the hydrogen atoms are observed not only at the positions of the hydrogen atoms but also almost everywhere. The final atomic coordinates of the heavier atoms are listed in Table I. The isotropic temperature factors assigned for the atoms are: 2.66 for all the atoms for $F(h\,0\,l)$, and 1.40, 0.86, 0.91 and 1.00 for C, N, Cl^- and H's respectively for $F(h\,k\,0)$. Each absolute value of these temperature factors may not have significance, because no absorption corrections for the intensities were made. The observed and the calculated structure factors are compared in Table II. The final

Table I. Final atomic coordinates

	x	y	z
C	0.026	0.072	0.118
N	0.083	0.241	0.954
Cl^-	0.1703	0.5803	0.4058

Table II. Observed and calculated structure factors

In each column, the left hand column is the h index, the middle column the observed structure factor, and the right hand column, the calculated structure factor. All structure factors have been multiplied by ten.

$(h\,0\,l)$			−10	174	158	$(h\,k\,0)$			11	87	96	5	89	80
$h\,0\,0$			−12	42	47	$h\,0\,0$			12	39	36	6	0	− 16
2	24	42	$h\,0\,3$			2	40	42	$h\,3\,0$			7	40	40
4	178	−174	0	40	57	4	187	−193	1	0	10	8	111	110
6	241	241	2	196	−213	6	245	275	2*	272	441	9	181	−162
8	160	−151	4	139	144	8	200	−210	3	52	50	10	95	− 87
10	21	− 24	6	61	− 68	10	38	− 43	4	255	−264	$h\,6\,0$		
12	142	116	8	203	−189	12	211	219	5	0	6	0	316	−382
$h\,0\,1$			10	68	58	$h\,1\,0$			6	0	− 6	1	49	− 48
0	75	− 73	− 2	138	133	1	57	− 41	7	18	11	2	52	59
2	220	224	− 4	271	−278	2	33	− 29	8	101	87	3	34	− 34
4	299	297	− 6	33	36	3*	304	564	9	22	14	4	96	96
6	321	−326	− 8	116	117	4*	260	−356	10	308	−297	5	0	− 6
8	12	− 29	−10	53	− 56	5	173	−151	11	0	− 18	6	183	−185
10	102	98	$h\,0\,4$			6	0	2	12	9	16	7	28	− 29
12	111	− 88	0	141	−154	7	91	− 82	$h\,4\,0$			8	147	142
− 2	724	693	2	156	175	8	156	146	0	67	− 57	9	0	6
− 4	58	− 52	4	59	− 60	9	202	223	1	274	−274	$h\,7\,0$		
− 6	246	−232	6	108	−112	10	85	− 74	2	122	117	1	33	34
− 8	220	220	8	61	62	11	141	−135	3	0	5	2	21	− 24
−10	0	9	− 2	93	−101	12	0	11	4	20	− 2	3	230	−245
−12	35	− 28	− 4	78	79	$h\,2\,0$			5	186	172	4	119	121
$h\,0\,2$			− 6	131	−135	0	136	164	6	220	−201	5	104	104
0	249	243	− 8	0	5	1*	191	−425	7	250	−267	6	0	− 10
2	272	282	$h\,0\,5$			2	162	−156	8	29	32	7	50	63
4	313	−335	0	82	96	3	16	− 15	9	17	− 17	$h\,8\,0$		
6	32	19	2	80	− 68	4	45	27	10	60	51	0	123	−115
8	0	1	4	0	− 13	5	221	195	11	75	77	1	156	151
10	170	−158	− 2	90	− 94	6	264	282	$h\,5\,0$			2	56	56
− 2	364	−339	− 4	121	−109	7	245	−280	1	91	96	3	23	21
− 4	152	173				8	62	− 49	2	60	57	4	0	2
− 6	41	47	− 6	61	64	9	0	11	3	272	−283	5	86	− 89
− 8	123	−126				10	55	− 67	4	237	−242			

* These reflections were not used for the refinements because of their marked extinction effects.

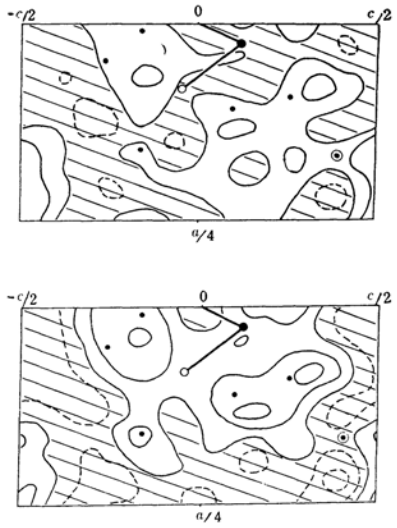

Fig. 1. Final $(\rho_o-\rho_c)$ projected on the (0 1 0). (a) : ρ_c includes all the atoms; (b) : ρ_c does not include any hydrogen atoms. Contours at intervals of 0.4 e. Å^{-3}, broken lines represent negative contours, and negative areas are shaded.
● C ○ N ⊙ Cl • H

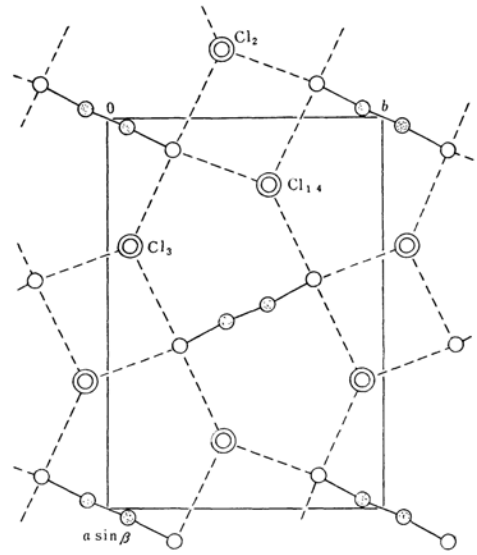

Fig. 2. The structure of ethylenediammonium chloride projected on the (0 0 1). Broken lines represent hydrogen bonds.
◎ C ○ N ◎ Cl

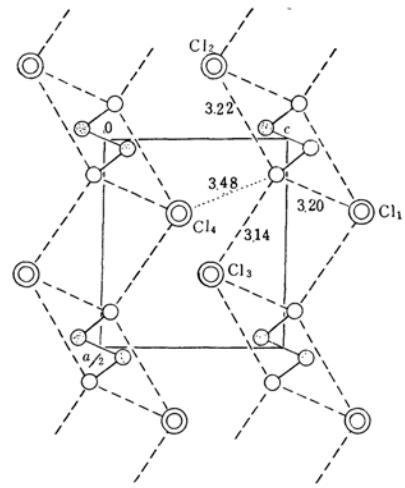

Fig. 3. The structure of ethylenediammonium chloride projected on the (0 1 0). Broken lines represent hydrogen bonds. A dotted line shows another short contact between N and Cl^-.
◎ C ○ N ◎ Cl

R factors are 0.065 for all the observed reflections of $(h\,0\,l)$ and 0.081 for $(k\,k\,0)$, excluding four reflections which showed marked extinction effects (these are shown with asterisks in Table II).

Discussion

In Table III, some of the important interatomic distances and bond angles in this crystal are shown. Because the ethylenediammonium ion occupies a center of symmetry, the ion has a trans-configuration and the N–C–C–N chain of the ion is geometrically planar. The equation of the plane is:

$$0.895X-0.448Y-0.020Z=0$$

where $X=ax\sin\beta$, $Y=by$ and $Z=cz+ax\cos\beta$. Thus, in the crystals, the ethylenediammonium ion was found to have either a trans- or a gauche-configuration, depending on the structure of the crystals.

TABLE III. IMPORTANT INTERATOMIC DISTANCES (Å) AND ANGLES (deg.)

C-C	1.53	CCN	109.8
C-N	1.49		
		CNCl(1)	111.5
N-Cl(1)	3.20	CNCl(2)	103.8
N-Cl(2)	3.22	CNCl(3)	106.0
N-Cl(3)	3.14	Cl(1)NCl(2)	103.9
		Cl(1)NCl(3)	111.3
N-Cl(4)	3.48	Cl(2)NCl(3)	120.5
Cl(3)-Cl(4)	3.89		

The crystal structures projected on the (0 1 0) and the (0 0 1) planes are shown in Figs. 2 and 3. The nitrogen atom's three nearest neighbors are chloride ions (Cl(1), Cl(2) and Cl(3), cf. Figs. 2 and 3), the N–Cl distances being 3.20, 3.22 and 3.14 Å respectively. These N–Cl lengths may be compared

to the values 3.11 and 3.24Å found in hexamethylenediammonium chloride[8] and to many others[9]. Thus, these short contacts may be said to be hydrogen bonds, when we consider the $<$CNCl or $<$ClNCl angles shown in Table III and the positions of the hydrogen atoms shown in Fig. 1. One N–Cl contact 3.48Å in length may not have significance, judging from the argument given above, and such a length has also been reported in hexamethylenediammonium chloride[8] (3.37 and 3.58Å). The shortest Cl–Cl distance is 3.88Å, between those chloride ions which are related to each other by a twofold screw axis. Thus, in this crystal, the three N–H···Cl hydrogen bonds binds the organic ions and the chloride ions and make infinite two-dimensional networks perpendicular to the c axis. The forces which combine these layers along the c axis may be van der Waals forces, together with weak electrostatic forces, if any. These facts explain the perfect cleavage along the (0 0 1) plane.

8) W. P. Binnie and J. M. Robertson, *Acta Cryst.*, 2, 180 (1949).

9) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman and Co., San Francisco (1960), p. 290.

Summary

The crystal structure of ethylenediammonium chloride has been determined. The crystal belongs to the monoclinic system with $a=9.95$, $b=6.89$, $c=4.42$Å and $\beta=90.7°$; the space group is $P2_1/a$. The unit cell contains two ethylenediammonium ions and four chloride ions. The ethylenediammonium ion occupies a center of symmetry and takes a transform; thus, the ethylenediammonium ion was found to be either a trans- or a gauche-form in the crystals, depending on the structures of the crystals. The bond distances and angles of the ethylenediammonium ion are: C–C 1.53, C–N 1.49Å and $<$CCN 109.8°. Three N–H···Cl hydrogen bonds (3.20, 3.22 and 3.14Å) make two-dimensional networks of the ions perpendicular to the c axis.

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