

in behavior are probably related to the distinctly different biological functions of copper and zinc. Other bond angles involving zinc are Zn-N(A)-C(2A): 112.1, Zn-N(B)-C(2B): 111.9, Zn-O(1A)-C(1A): 114.8 and Zn-O(1B)-C(1B): 115.7°.

The hydrogen atoms were located from a difference Fourier synthesis, but their locations were not further refined. The covalent bond distances involving hydrogen vary between 1.02 and 1.16 Å.

The structure contains six hydrogen atoms which can form hydrogen bonds. All six seem to be involved in this type of bonding (Table 7), although only the first three seem to form strong hydrogen bonds. These three are indicated in Fig. 1 by dashed lines. All other intermolecular distances below 3.5 Å are also given in Table 7. The only atom showing considerable anisotropy is O(3A) with a value of 9.35 Å² for the temperature factor along the major axis.

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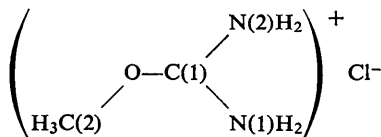
The Crystal and Molecular Structure of *O*-Methylisourea Hydrochloride

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The crystal structure of *O*-methylisourea hydrochloride



has been determined from a single-crystal X-ray study by photographic methods. The space group is $P2_12_12_1$, $a=9.43$ (2), $b=11.16$ (2), $c=5.01$ (1) Å, $Z=4$, $R=0.07$ for 522 observed reflections. Within the cation, bond distances are C(2)-O=1.44 (1), O-C(1)=1.33 (1), C(1)-N(1)=1.29 (1), C(1)-N(2)=1.32 (1) Å; bond angles are C(1)-O-C(2)=117 (1), N(1)-C(1)-O=123 (1), N(2)-C(1)-O=113 (1), N(1)-C(1)-N(2)=124 (1)°; and the angle between planes C(1)-O-C(2) and N(1)-C(1)-N(2)=4 (1)°. The structure is in general agreement with valence theory expectations of multiple bonds between C(1) and the atoms attached to it. The H atoms were located in difference syntheses and refined by least-squares. Each H atom bonded to N is linked in an approximately linear N-H...Cl hydrogen bond, with N...Cl distances of 3.16 (1), 3.23 (1), 3.25 (1) and 3.39 (1) Å.

The molecular structure of the *O*-methylisourea cation has been described (Edsall, 1943) as involving resonance among the bond arrangements

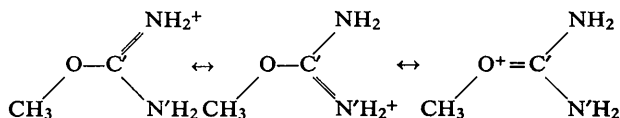


Table 1. *Coordinates and anisotropic temperature factors of CH₃OC(NH₂)₂Cl*

Estimated standard deviations are given in parentheses and apply to the last digits of a number. Values in brackets were assigned.

| | x | y | z | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|------------------|-------------|-------------|--------------------|--------------------|--------------------|--------------|--------------|--------------|
| Cl | (a)* 0.4663 (2) | 0.1275 (2) | 0.3356 (5) | 0.0074 (2) | 0.0075 (1) | 0.0408 (11) | -0.0005 (2) | 0.0005 (4) | 0.0005 (4) |
| | (b)† 0.4663 (2) | 0.1276 (2) | 0.3363 (2) | 0.0073 (2) | 0.0079 (1) | 0.0416 (10) | -0.0006 (1) | 0.0005 (3) | 0.0005 (4) |
| O | (a) -0.0597 (5) | 0.1422 (5) | 0.1948 (16) | 0.0092 (6) | 0.0081 (5) | 0.0486 (35) | 0.0002 (5) | -0.0016 (13) | 0.0007 (14) |
| | (b) -0.0595 (5) | 0.1428 (5) | 0.1944 (15) | 0.0086 (5) | 0.0092 (4) | 0.0444 (29) | 0.0001 (4) | -0.0016 (10) | 0.0015 (12) |
| N(1) | (a) 0.1396 (8) | 0.0784 (7) | 0.4217 (17) | 0.0084 (8) | 0.0094 (7) | 0.0315 (44) | -0.0005 (6) | -0.0031 (15) | 0.0028 (14) |
| | (b) 0.1394 (7) | 0.0784 (7) | 0.4229 (16) | 0.0079 (6) | 0.0097 (6) | 0.0345 (36) | -0.0005 (5) | -0.0025 (13) | 0.0034 (12) |
| N(2) | (a) 0.1502 (9) | 0.2090 (7) | 0.0637 (18) | 0.0115 (9) | 0.0091 (6) | 0.0376 (45) | 0.0001 (7) | 0.0034 (18) | 0.0058 (14) |
| | (b) 0.1505 (7) | 0.2085 (7) | 0.0657 (17) | 0.0108 (7) | 0.0093 (5) | 0.0386 (37) | 0.0010 (6) | 0.0020 (15) | 0.0066 (12) |
| C(1) | (a) 0.0796 (8) | 0.1413 (7) | 0.2377 (17) | 0.0084 (7) | 0.0067 (6) | 0.0304 (50) | 0.0007 (6) | -0.0002 (16) | -0.0024 (16) |
| | (b) 0.0798 (7) | 0.1410 (6) | 0.2368 (15) | 0.0085 (6) | 0.0069 (5) | 0.0318 (44) | 0.0005 (5) | +0.0001 (14) | -0.0023 (13) |
| C(2) | (a) -0.1464 (11) | 0.0762 (10) | 0.3792 (28) | 0.0089 (9) | 0.0105 (9) | 0.0485 (68) | -0.0007 (8) | 0.0012 (24) | 0.0059 (23) |
| | (b) -0.1464 (9) | 0.0773 (8) | 0.3816 (24) | 0.0091 (8) | 0.0099 (7) | 0.0546 (65) | -0.0009 (6) | -0.0005 (19) | 0.0065 (19) |
| H(11) | (a) 0.236 (13) | 0.091 (9) | 0.413 (27) | [0.0155] | [0.0110] | [0.0548] | | | |
| | (b) 0.242 (13) | 0.084 (9) | 0.433 (27) | As for H(11) | As for H(11) | As for H(11) | | | |
| H(12) | (a) 0.092 (14) | 0.049 (12) | 0.519 (28) | | | | | | |
| | (b) 0.098 (13) | 0.054 (11) | 0.522 (27) | | | | | | |
| H(21) | (a) 0.273 (12) | 0.200 (11) | 0.099 (24) | | | | | | |
| | (b) 0.260 (12) | 0.208 (10) | 0.075 (24) | | | | | | |
| H(22) | (a) 0.082 (12) | 0.242 (11) | -0.085 (24) | | | | | | |
| | (b) 0.099 (13) | 0.237 (11) | -0.062 (25) | | | | | | |
| H(1) | (a) -0.243 (12) | 0.104 (9) | 0.316 (28) | | | | | | |
| | (b) -0.256 (14) | 0.103 (9) | 0.323 (28) | | | | | | |
| H(2) | (a) -0.132 (15) | 0.101 (12) | 0.537 (28) | | | | | | |
| | (b) -0.120 (13) | 0.102 (9) | 0.610 (26) | | | | | | |
| H(3) | (a) -0.120 (13) | -0.010 (11) | 0.368 (28) | | | | | | |
| | (b) -0.129 (13) | 0.006 (11) | 0.368 (28) | | | | | | |

* Least-squares refinements with unit weights.

† Least-squares refinements with weights as follows: $|F_o| > 20$, $w = 0.26$; $20 > |F_o| > 14$, $w = 0.97$; $14 > |F_o| > 9$, $w = 1.75$; $9 > |F_o| > 6$, $w = 1.74$; $6 > |F_o| > 3$, $w = 2.66$; $|F_o| < 3$, $w = 2.05$.

Some points of interest in such a structure are (1) the question of the chemical equivalence of the N and N' groups, (2) the bond distances and the bond angles around the carbon, nitrogen and oxygen atoms in the ion, (3) the orientation of the N-C'-N' plane relative to the C-O-C' plane, and (4) the kind of H-bonding present in the crystal. In order to investigate these points, the structure of *O*-methylisourea hydrochloride has been determined.

Experimental

CH₃OCN₂H₃.HCl is deliquescent. A needle-shaped 0.3 mm diameter single crystal of the compound sealed in a thin-walled glass capillary was supplied us by Dr Norman Heitkamp and used for the X-ray study. A preliminary examination of the crystal with the Buerger precession camera, and Zr-filtered Mo radiation ($\lambda=0.7107$ Å) showed that it was orthorhombic, space group $P2_12_12_1$, $a=9.43(2)$, $b=11.16(2)$, $c=5.01(1)$ Å. For $Z=4$, $d_{\text{calc}}=1.39$ g.cm⁻³, $d_{\text{meas}}=1.35(10)$ g.cm⁻³ (from Dr Heitkamp). Precession data for $h0l$, $0kl$ and hhl zones were collected photographically by means of timed exposures with Zr-filtered Mo radiation. The crystal was transferred to the Weissenberg camera and $hk0$, $hk1$, $hk2$, and $hk3$ multiple-film pack, equi-inclination data were collected with Ni-filtered Cu radiation ($\lambda=1.5418$ Å). Of the 530 reflections observed, 8 were too intense to be measured accurately: 021, 031,

040, 131, 200, 221, 240 and 320. The intensities of the 522 reflections that remained were measured manually with a Welch Densichron Model I densitometer (0.012 inch Al aperture). Lorentz and polarization corrections were applied to all data and an absorption correction was applied to the Weissenberg data. For the absorption correction, the crystal was treated as a cylinder, $R=0.015$ cm, and $\mu R(\text{Cu})=0.58$. For the precession data, $\mu R(\text{Mo})=0.06$, and no absorption correction was necessary.

Trial coordinates for the Cl atom were obtained by the examination of Patterson syntheses calculated with the program of Sly, Shoemaker & van den Hende (1962). Fourier syntheses of the electron density with phases calculated from the Cl parameters were examined next, and revealed the O, N and C atoms. Least-squares refinement of the parameters of all atoms (except H) with anisotropic temperature factors was carried out by means of the program of Busing, Martin & Levy (1962). The function minimized was $\sum(|F_o| - |F_c|)^2$.

Next, difference Fourier syntheses were calculated in an attempt to locate the H atoms. Four H atoms appeared clearly, but the atoms labelled H(12), H(22), and H(2) were located only with difficulty. In these latter cases, the z coordinate of the H atom is considerably different from that of the C or N atom to which it is bonded, and the resolution in the z direction is apparently not as good as it is in the x and y directions. For the final refinement, each reflection was

Table 2. *Interatomic distances and angles in CH₃OC(NH₂)₂Cl*

Uncertainties are given in parentheses and apply to the last digits of a number. (a) calculated from values of Table 1(a), (b) calculated from values of Table 1(b).

| Distance | (a) | | (b) | | |
|------------|--------------|--------------|------------------|------------|------------|
| | (a) | (b) | (a) | (b) | |
| C(2)—O | 1.437 (13) Å | 1.444 (12) Å | C(2)—O—C(1) | 117.0 (8)° | 116.6 (7)° |
| O—C(1) | 1.332 (9) | 1.331 (9) | O—C(1)—N(1) | 123.5 (9) | 123.5 (7) |
| C(1)—N(1) | 1.289 (11) | 1.294 (11) | O—C(1)—N(2) | 112.6 (8) | 112.7 (8) |
| C(1)—N(2) | 1.331 (10) | 1.321 (10) | N(1)—C(1)—N(2) | 123.9 (8) | 123.8 (7) |
| C(2)—H(1) | 1.00 (13) | 1.11 (14) | C(1)—N(1)—H(11) | 109 (8) | 116 (8) |
| C(2)—H(2) | 0.85 (13) | 1.20 (14) | C(1)—N(1)—H(12) | 117 (11) | 119 (11) |
| C(2)—H(3) | 0.99 (12) | 0.82 (13) | H(11)—N(1)—H(12) | 134 (14) | 123 (14) |
| N(1)—H(11) | 0.92 (12) | 0.97 (13) | C(1)—N(2)—H(21) | 110 (6) | 118 (7) |
| N(1)—H(12) | 0.74 (13) | 0.69 (14) | C(1)—N(2)—H(22) | 111 (6) | 114 (8) |
| N(2)—H(21) | 1.18 (11) | 1.03 (11) | H(21)—N(2)—H(22) | 138 (9) | 127 (11) |
| N(2)—H(22) | 1.05 (12) | 0.86 (14) | H(1)—C(2)—O | 99 (7) | 103 (7) |
| N(1)—C' | 3.159 (10) | 3.161 (9) | H(2)—C(2)—O | 110 (9) | 113 (6) |
| N(1)—Cl' | 3.253 (10) | 3.250 (9) | H(3)—C(2)—O | 108 (7) | 109 (10) |
| N(2)—Cl | 3.401 (10) | 3.394 (10) | H(1)—C(2)—H(2) | 110 (12) | 113 (9) |
| N(2)—Cl'' | 3.216 (10) | 3.228 (9) | H(2)—C(2)—H(3) | 109 (12) | 105 (11) |
| H(11)—Cl | 2.25 (12) | 2.23 (13) | H(3)—C(2)—H(1) | 121 (9) | 115 (10) |
| H(12)—Cl' | 2.59 (14) | 2.63 (14) | N(1)—H(11)—Cl | 172 (12) | 162 (11) |
| H(21)—Cl | 2.32 (12) | 2.51 (12) | N(2)—H(21)—Cl | 151 (8) | 143 (9) |
| H(22)—Cl'' | 2.21 (13) | 2.40 (14) | N(1)—H(12)—Cl' | 150 (13) | 150 (13) |
| N(1)—C(2) | 2.706 (15) | 2.703 (13) | N(2)—H(22)—Cl'' | 159 (9) | 162 (11) |
| H(2)—H(12) | 2.19 (21) | 2.17 (19) | | | |
| | | | Dihedral angle | | |
| | | | N(2)—C(1)—N(1) | | |
| | | | H(21)—N(2)—H(22) | 14 (12)° | 12 (12)° |
| | | | N(2)—C(1)—N(1) | | |
| | | | H(11)—N(1)—H(12) | 10 (16) | 13 (13) |
| | | | H(21)—N(2)—H(22) | | |
| | | | H(11)—N(1)—H(12) | 8 (12) | 4 (11) |
| | | | N(2)—C(1)—N(1) | | |
| | | | C(1)—O—C(2) | 4.2 (11) | 4.0 (8) |

assigned unit weight, the H atom temperature factors were fixed at $B=5.5 \text{ \AA}^2$, and a convergence factor (Rollett, 1962) was applied to damp the oscillations in the H atom positions. The final agreement values for 522 observed reflections were $R_1 = \sum |F_o| - |F_c| / \sum |F_o| = 0.073$ and $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2} = 0.076$. Scattering factors for the atoms were taken from *International Tables for X-ray Crystallography* (1962).

Since the structure appeared slightly different from that which had been anticipated, a final Fourier synthesis was calculated and inspected in order to verify the assignment of the heavier atoms. The relative peak heights for the C, N, O, and Cl atoms appeared reasonable (6.0:7.3:7.7:18.1). The final difference Fourier synthesis, calculated without H atoms, revealed some obviously spurious peaks and valleys, especially in the region close to the Cl atoms, but there seemed no reasonable alternative to the H atom positions chosen for refinement.

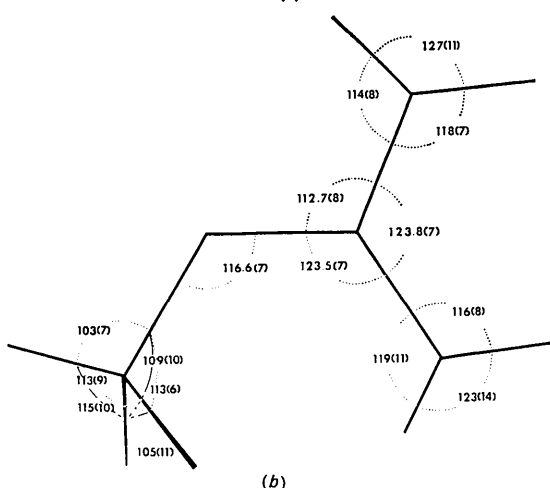
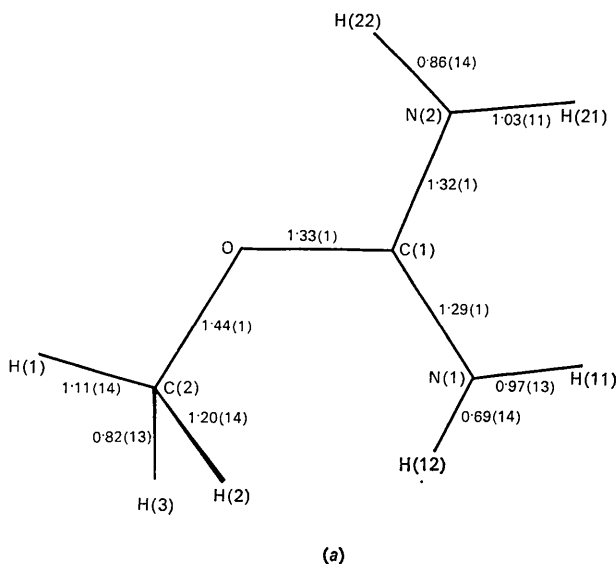


Fig. 1. Structural diagram of $\text{CH}_3\text{OC}(\text{NH}_2)_2^+$ showing (a) bond lengths and (b) bond angles.

Table 3. Observed and calculated structure factors
Values of $F(\text{obs})$ denoted as V. L. (very large) were too large to measure accurately and were excluded from the least-squares refinement.

| h | k | l | $F(\text{obs})$ | $F(\text{calc})$ | $F(\text{obs})$ | $F(\text{calc})$ | $F(\text{obs})$ | $F(\text{calc})$ | $F(\text{obs})$ | $F(\text{calc})$ | $F(\text{obs})$ | $F(\text{calc})$ | $F(\text{obs})$ | $F(\text{calc})$ |
|----|---|---|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|
| 0 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 4 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 5 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 6 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 7 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 8 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 9 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 10 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 11 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 12 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 13 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 14 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 15 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 16 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 17 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 18 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 19 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 20 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 21 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 22 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 23 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 24 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 25 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 26 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 27 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 28 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 29 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 30 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 31 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 32 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 33 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 34 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 35 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 36 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 37 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 38 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 39 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 40 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 41 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 42 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 43 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 44 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 45 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 46 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 47 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 48 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 49 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 50 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 51 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 52 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 53 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 54 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 55 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 56 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 57 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 58 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 59 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 60 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 61 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 62 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 63 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 64 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 65 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 66 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 67 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 68 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 69 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 70 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 71 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 72 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 73 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 74 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 75 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 76 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 77 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 78 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 79 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 80 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 81 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 82 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 83 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 84 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 85 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 86 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 87 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 88 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 89 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 90 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 91 | 0 | 0 | 100 | 100 | 0 | 0 | 0 | 0 | | | | | | |

the least-squares refinement was repeated two times. The coordinates and temperature factors obtained with these weights as well as those obtained with unit weights are given in Table 1. Interatomic distances and angles calculated (Busing, Martin & Levy, 1964) from coordinates obtained with the use of the earlier (unit) weights and the newer weights are given in Table 2. Table 3 contains observed and calculated structure factors for the 522 reflections that were measured. The coordinates of Table 1(b) were used in the calculations.

As may be observed from Table 2, there is very little difference in the interatomic distances and angles calculated with the different weighting schemes. The six ranges of $|F_o|$ and the relative weights, ω , used in each range were: $|F_o| > 20$, $\omega = 0.26$; $20 > |F_o| > 14$, $\omega = 0.97$; $14 > |F_o| > 9$, $\omega = 1.75$; $9 > |F_o| > 6$, $\omega = 1.74$; $6 > |F_o| > 3$, $\omega = 2.66$; $|F_o| < 3$, $\omega = 2.05$. The values $R_1 = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.073$ and $R_2 = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2} = 0.089$ were obtained. These results are in general agreement with our earlier experiences with various weighting schemes. In his review of the revised manuscript, a referee also expressed his skepticism regarding the weighting scheme used above.

Discussion

An examination of Fig. 1 shows that the positive ion has the general configuration expected (Edsall, 1943). However, the two bond lengths, $C(1)-N(1) = 1.29(1)$ Å, $C(1)-N(2) = 1.32(1)$ or $1.33(1)$ Å appear to differ considerably. Nevertheless, as was pointed out by the referees, the difference is probably not significant. More striking is the difference between the bond angles, $O-C(1)-N(1) = 123.5(7)^\circ$, $O-C(1)-N(2) = 112.7(8)^\circ$. It seems most reasonable to associate these differences with the contacts, $N(1)-C(2) = 2.70(1)$, $H(12)-H(2) = 2.2(2)$, $H(12)-H(3) = 2.3(2)$ and $N(1)-Cl = 3.16(1)$, $H(11)-Cl = 2.2(1)$ Å. The first group of contacts would tend to open the angles $O-C(1)-N(1)$ and $C(2)-O-C(1) = 117.0(7)^\circ$ from their normal values, while the $N(1)-H(12) \cdots Cl$ hydrogen bond would simultaneously become shorter (3.16 Å) than the other principal H bonds within the structure depicted in Fig. 2 (3.23, 3.25 and 3.39 Å). A similar, but more extreme, deformation was observed in nitroguanidine (Bryden, Burkardt, Hughes & Donohue, 1956). $C(1)-N(2)$ is a fairly normal amide distance (Sutton, 1965), while $C(1)-N(1)$ appears slightly shorter than normal. The average C-N

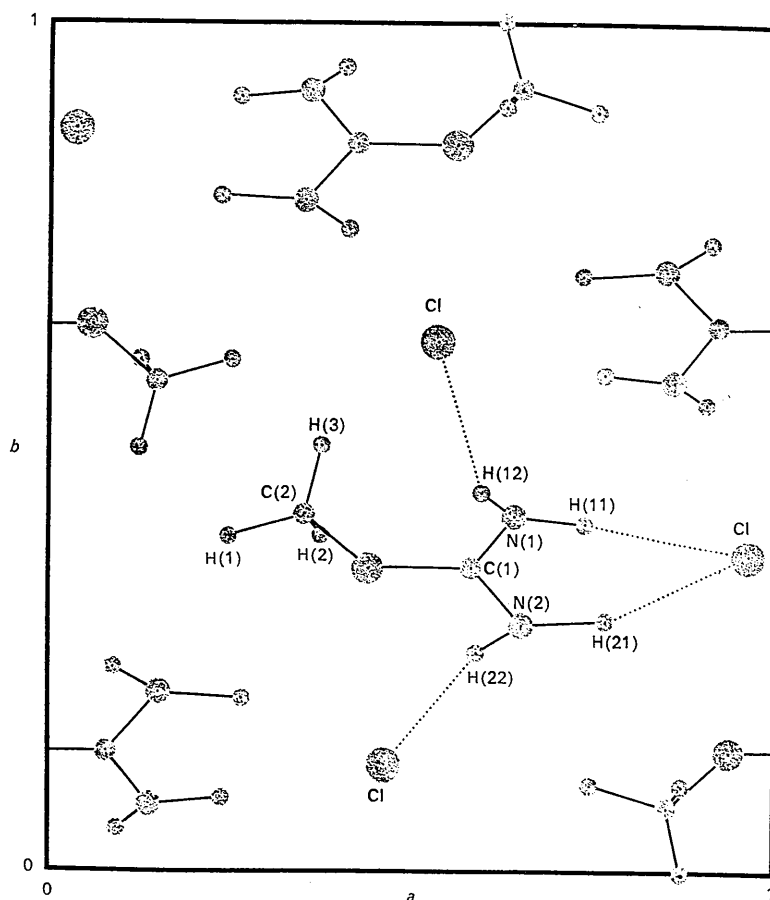


Fig. 2. Projection of the structure along [001]. Hydrogen bonds are indicated by dotted lines.

bond length in some guanidinium structures (Bryden, Burkardt, Hughes & Donohue, 1956; Curtis & Pasternak, 1955; Haas, Harris & Mills, 1965) is 1.33 Å. C(2)–O = 1.44 (1) Å is a normal C–O single bond (Sutton, 1965), while O–C(1) = 1.33 (1) Å is quite short, but similar to C–O bond lengths found in COH groups of carboxylic acids, and in some esters (Sutton, 1965). The planes determined by N(1)–H(12)–H(11), N(2)–H(22)–H(21) and N(1)–C(2)–N(2) are not tilted significantly from one another and the angle between planes N(1)–C(1)–N(2) and C(1)–O–C(2) is only 4 (1)°. Thus it appears that the central carbon atom C(1) forms bonds with considerable multiple-bond character with each of the three atoms attached to it, but steric and H-bonding effects in the crystal cause significant differences in the NH₂ groups attached to the central atom. The 'free' ion may well differ considerably in shape from that observed in the crystal.

The configuration of H bonds in the crystal is shown in Fig. 2. There are four NH...Cl H bonds for each cation. The NH...Cl angles are fairly close to 180°, and the distances 3.23 and 3.25 Å appear normal, while 3.39 Å is longer and 3.16 Å shorter than the value of 3.30 Å for NH...Cl observed in guanidinium chloride (Haas, Harris & Mills, 1965).

Since the cation is H bonded to several different Cl atoms, no adequate thermal motion corrections to bond distances suggested themselves. The 'minimum' correction (Busing & Levy, 1964) for the C(2)–O bond distance is 0.001 Å and for the C(1)–O bond distance is <0.001 Å; the maximum corrections are +0.105 and 0.112 Å respectively.

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Norman Heitkamp first brought this compound to our attention and kindly supplied us with the crystal used for study.

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