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## The Crystal and Molecular Structure of 2-Methylpseudourea Hydrochloride, $[(\text{NH}_2)_2\text{COCH}_3]^+\text{Cl}^-$

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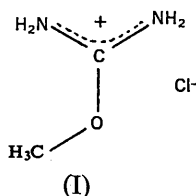
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The crystal structure of 2-methylpseudourea hydrochloride,  $[(\text{NH}_2)_2\text{COCH}_3]^+\text{Cl}^-$ , has been determined by the heavy-atom method and refined by the least-squares procedure to a final  $R$  value of 0.107. The space group is  $P2_12_12_1$  and the cell dimensions are  $a=9.43$ ,  $b=11.16$ ,  $c=5.00$  Å. A total of 681 unique intensities were obtained from visually estimated photographic data collected about two axes. Corrected bond lengths of 1.32 Å for C–O and 1.32, 1.35 Å (all  $\pm 0.01$  Å) for C–N were deduced. The cations are approximately planar and are linked *via* the chloride ions to form a three-dimensional hydrogen-bonded network, with N–H...Cl distances of 3.17, 3.22, 3.24 and 3.40 Å.

### Introduction

The structure of 2-methylpseudourea hydrochloride (I)



has been determined as part of an investigation of amide and amide-like cations. The position of the mobile hydrogen atom in these cations was vigorously disputed in the chemical literature for over a decade; almost all the physico-chemical techniques that could be applied to the problem were used, and conflicting conclusions were drawn from much of the resulting information (see the review by Jones & Katritzky, 1961). Finally low-temperature nuclear magnetic resonance studies provided conclusive evidence for protonation at the oxygen atom rather than at the nitrogen atom (Gillespie & Birchall, 1963), and thus established the struc-

tures in principle but not in detail. To provide more precise information on the structures of these cations, a series of structures of amide and related cations is being determined. The crystal structures of urea nitrate and 2-hydroxypyridinium chloride have also been solved.

### Experimental

The method of Brown & Hoerger (1954) was used to obtain methylisourea picrate which was then suspended in benzene, and the mixture shaken with concentrated hydrochloric acid. The aqueous phase was then evaporated, and the resulting solid 2-methylpseudourea hydrochloride was recrystallized from an ethanol/acetone mixture. Analysis showed C=21.53, H=6.33, N=25.01, Cl=32.9%. Calculated values for  $\text{C}_2\text{H}_7\text{N}_2\text{OCl}$  are C=21.72, H=6.38, N=25.35, Cl=32.12%.

The crystals obtained were needles belonging to the orthorhombic system, and elongated along the  $c$  axis. Systematic absences on Weissenberg photographs were  $h00$  for  $h$  odd,  $0k0$  for  $k$  odd, and  $00l$  for  $l$  odd, indicating uniquely the space-group  $P2_12_12_1$ . The axial lengths, determined from Pt-calibrated Weissenberg photographs, are  $a=9.43$  (0.02),  $b=11.16$  (0.02),  $c=5.00$  (0.03) Å. The error estimates given are probably

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high. The density determined by flotation in an acetone - CCl<sub>4</sub> mixture is 1.37 g.cm<sup>-3</sup>; the calculated value for Z=4 is 1.394 g.cm<sup>-3</sup>.

**Intensity determination**

Two needle-shaped crystals of cross-section about 0.2 × 0.2 mm were used, so that absorption errors should be small though not insignificant ( $\mu=47\text{ cm}^{-1}$ ). The crystals were mounted on glass fibers and coated with several layers of cellulose acetate, since they decompose slowly on exposure to moisture. Equi-inclination integrated Weissenberg photographs using Cu K $\alpha$  radiation (Ni filtered) were taken for layers  $hk0$  to  $hk3$  and  $0kl$  to  $6kl$  using up to 7 films per layer. Visual estimation by comparison with a calibration slip yielded about 1000 intensities which were corrected for the Lorentz and polarization factors and brought to a single arbitrary scale using common reflexions.

A Wilson plot (Wilson, 1942) for the  $hk0$  data gave an approximate scale factor. The 681 resulting reflexions, of which 58 were unobservably weak, represent about 88% of those available in the Cu K $\alpha$  reflexion sphere.

**Structure solution and refinement**

Consistent coordinates for the chlorine atom were deduced from the Harker sections of the Patterson synthesis. A set of structure factors based on these coordinates gave an  $R$  value of 0.408

$$(R = \sum D / \sum |F_o|, \text{ where } D = ||F_o| - |F_c||),$$

and the corresponding difference Fourier synthesis with Fourier coefficients ( $F_o - F_c$ ) revealed the positions of the other five non-hydrogen atoms. After including the six atoms in the structure-factor calculations  $R$  was 0.265. After three cycles of full-matrix least-squares refinement with individual isotropic tem-

Table 1. Observed and calculated structure amplitudes

Scale 10 × absolute. E and \* signify extinction-affected and unobserved reflexions respectively.

H	K	L	IOFC	LOFC	H	K	L	IOFC	LOFC	H	K	L	IOFC	LOFC	H	K	L	IOFC	LOFC		
0	0	2	197	225	1	4	0	0	1	2	6	3	44	36	3	10	0	79	71		
0	0	4	129	122	1	4	1	163	173	2	6	4	62	61	3	10	1	36	41		
0	0	6	79	89	1	4	2	190	164	2	6	4	95	64	3	10	2	46	46		
0	0	1	1	1	1	4	3	122	110	2	7	0	95	74	3	10	3	76	69		
0	0	1	2	313	384	1	4	4	36	39	2	7	1	117	115	3	10	4	24	24	
0	0	2	3	153	162	1	4	5	119	125	2	7	2	106	95	3	11	2	19	13	
0	0	1	4	31	26	1	4	6	0	5	2	7	3	132	119	3	11	1	32	42	
0	0	1	5	15	4	1	4	7	5	46	49	2	7	4	60	49	3	11	2	55	23
0	0	1	6	36	39	1	5	1	35	33	2	7	5	15	20	3	11	3	58	60	
0	0	2	0	45	44	1	5	2	273	261	2	8	0	E	252	261	3	12	0	18	11
0	0	2	1	E	418	412	1	5	3	172	172	2	8	1	110	104	3	12	1	66	63
0	0	2	2	24	20	1	5	4	167	140	2	8	2	111	104	3	12	2	42	39	
0	0	2	3	59	59	1	5	5	96	69	2	8	3	35	49	3	12	3	19	13	
0	0	2	4	48	43	1	6	0	212	227	2	8	4	53	48	3	13	0	28	24	
0	0	2	5	76	65	1	6	1	111	103	2	8	5	12	8	3	13	1	31	40	
0	0	2	6	8	35	0	6	2	29	38	2	9	0	E	122	99	3	13	2	31	36
0	0	3	1	E	419	603	1	6	3	116	106	2	9	1	63	55	4	0	0	124	129
0	0	3	2	30	34	1	6	4	123	118	2	9	2	100	91	4	0	1	28	40	
0	0	3	3	140	135	1	6	5	13	15	2	9	3	75	49	4	0	2	180	127	
0	0	3	4	92	86	1	7	0	61	49	2	9	4	69	46	4	0	3	140	129	
0	0	3	5	91	88	1	7	1	145	157	2	10	0	100	86	4	0	4	67	56	
0	0	3	6	42	38	1	7	2	133	128	2	10	1	138	143	4	0	5	43	34	
0	0	3	7	E	558	600	1	7	3	205	200	2	10	2	70	66	4	0	6	86	83
0	0	4	1	53	53	1	7	4	85	87	2	10	3	26	25	4	1	0	E	294	358
0	0	4	2	262	361	1	7	5	52	46	2	10	4	13	8	4	1	1	177	240	
0	0	4	3	96	90	1	8	0	16	9	2	11	0	21	4	4	1	1	130	116	
0	0	4	4	2	76	75	1	8	1	135	140	2	11	1	61	58	4	1	1	111	97
0	0	4	5	33	33	1	8	2	107	97	2	11	2	19	13	4	1	1	130	116	
0	0	4	6	51	45	1	8	3	83	78	2	11	3	5	14	4	1	1	5	48	48
0	0	5	1	11	6	1	8	4	49	51	2	12	0	100	104	1	1	6	33	48	
0	0	5	2	318	421	1	8	5	62	71	2	12	1	97	49	2	1	7	4	67	56
0	0	5	3	81	74	1	9	0	36	48	2	12	2	53	46	2	1	8	98	109	
0	0	5	4	1	1	1	9	1	2	205	200	2	12	3	26	25	2	1	9	111	121
0	0	5	5	16	12	1	9	2	167	172	2	13	0	15	14	4	2	1	10	9	5
0	0	6	0	50	42	1	9	3	91	86	2	13	1	32	36	4	2	1	101	86	
0	0	6	1	E	249	315	1	10	0	85	80	2	13	2	40	45	4	2	1	130	116
0	0	6	2	142	141	1	10	1	136	140	2	14	0	27	25	4	2	1	104	157	
0	0	6	3	130	122	1	10	2	43	36	3	14	1	215	217	4	3	0	140	157	
0	0	6	4	69	70	1	10	3	67	35	3	14	2	205	219	4	3	1	172	205	
0	0	6	5	91	92	1	10	4	66	61	3	14	3	135	140	4	3	2	120	96	
0	0	7	1	118	118	1	10	5	65	65	3	14	4	107	110	4	3	3	130	116	
0	0	7	2	47	41	1	11	0	33	29	3	15	0	84	56	4	3	4	105	98	
0	0	7	3	100	84	1	11	1	86	87	3	15	1	12	0	4	3	5	185	186	
0	0	7	4	68	60	1	11	2	83	83	3	15	2	180	207	4	3	4	111	124	
0	0	7	5	23	15	1	11	3	92	97	3	15	3	1	267	394	4	4	2	88	70
0	0	7	6	203	215	1	11	4	44	38	3	15	4	12	89	44	4	4	3	126	119
0	0	8	1	58	49	1	12	1	74	77	3	15	5	186	196	4	4	5	82	65	
0	0	8	2	180	186	1	12	2	37	30	3	15	6	136	125	4	5	2	134	122	
0	0	8	3	128	128	1	12	3	20	18	3	15	7	107	110	4	5	3	203	210	
0	0	8	4	29	26	1	13	0	12	9	3	15	8	11	35	4	5	1	134	145	
0	0	8	5	19	19	1	13	1	40	42	3	15	9	433	604	5	2	2	93	85	
0	0	9	1	16	12	1	13	2	44	71	3	15	10	163	187	4	5	3	120	103	
0	0	9	2	50	39	1	14	0	59	65	3	15	11	67	56	4	5	4	133	124	
0	0	9	3	67	61	1	14	1	19	27	3	15	12	189	185	4	5	5	57	59	
0	0	9	4	74	69	2	14	2	193	462	3	15	13	129	126	4	6	0	109	113	
0	0	9	5	48	53	2	14	3	180	229	3	15	14	56	40	4	6	1	140	152	
0	0	10	1	137	142	2	14	4	285	383	2	15	15	36	35	4	6	2	149	137	
0	0	10	2	95	96	2	14	5	101	96	3	15	16	152	159	4	6	3	73	59	
0	0	10	3	56	41	2	14	6	56	49	3	15	17	126	143	4	6	4	86	68	
0	0	10	4	9	11	2	14	7	0	0	3	15	18	172	176	4	6	5	90	50	
0	0	11	1	11	12	2	14	8	70	86	3	15	19	61	53	4	7	0	81	87	
0	0	11	2	61	58	2	14	9	167	213	3	15	20	82	72	4	7	1	123	121	
0	0	11	3	35	43	2	14	10	107	119	3	15	21	115	102	4	7	2	131	126	
0	0	11	4	102	109	2	14	11	115	112	3	15	22	156	180	4	7	3	140	154	
0	0	11	5	76	80	2	14	12	97	92	3	15	23	108	209	4	7	4	146	156	
0	0	12	1	58	55	2	14	13	91	89	3	15	24	85	55	4	7	5	154	76	
0	0	12	2	19	14	2	14	14	36	42	3	15	25	110	94	4	7	6	160	79	
0	0	12	3	122	128	2	14	15	62	50	3	15	26	95	81	4	7	7	176	175	
0	0	12	4	19	18	2	14	16	362	379	3	15	27	124	116	4	7	8	183	79	
0	0	12	5	63	79	2	14	17	115	119	3	15	28	262	282	4	7	9	190	98	
0	0	13	1	101	76	2	14	18	136	117	3	15	29	182	182	4	7	10	202	297	
0	0	13	2	17	14	2	14	19	62	58	3	15	30	109	96	4	7	11	211	91	
0	0	13	3	52	55	2	14	20	94	103	3	15	31	109	95	4	7	12	219	216	
0	0	13	4	66	51	2	14	21	13	10	3	15	32	34	32	4	7	13	227	227	
0	0	13	5	158	167	2	14	22	190	263	3	15	33	77	92	4	7	14	235	235	
0	0	13	6	11	2	2	14	23	79	80	3	15	34	126	132	4	7	15	243	243	
0	0	13	7	150	154	2	14	24	154	167	3	15	35	105	99	4	7	16	251	251	
0	0	13	8	129	148	2	1														

perature factors the value of  $R$  was 0.182. (The quantity minimized was  $\sum wD^2$ .) At this stage individual anisotropic temperature factors were introduced, and seven reflexions apparently affected by extinction were given zero weight. In two further least-squares iterations  $R$  dropped to 0.126. Throughout the calculations the scattering curves used were from *International Tables for X-ray Crystallography* (1962).

As difference Fourier syntheses had failed to locate clearly any hydrogen atoms, the four amino hydrogen atoms were included in the calculations at their expected positions in the molecular plane. Diffuse positive regions interpreted as the methyl hydrogen atoms were found in a difference Fourier synthesis from which all unobserved reflexions and about 20 of the strongest reflexions as well as those with  $\sin \theta$  greater than 0.6 were omitted. Coordinates for the three methyl hydrogen atoms were assigned, consistent with these Fourier peaks and with normal bonding requirements. Attempts to refine positional coordinates for all hydrogen atoms were only partly successful, one of the three methyl hydrogen atoms and two of the four amino H atoms moving to unlikely positions. Thus the H positions listed in Table 2 are tentative only. The isotropic temperature factors of 3.0 were assumed.

Several methods of weighting the observations were examined during the course of the refinement. That finally judged most appropriate was:

for 45 terms with  $F_o$  between 18 and 24,  $w=0.200$   
for 420 terms with  $F_o$  between 4.5 and 18,  $w=0.752$   
for 188 terms with  $F_o$  less than 4.5,  $w=3.386/F_o$

The reflexions with  $F_o$  larger than 24 were omitted as

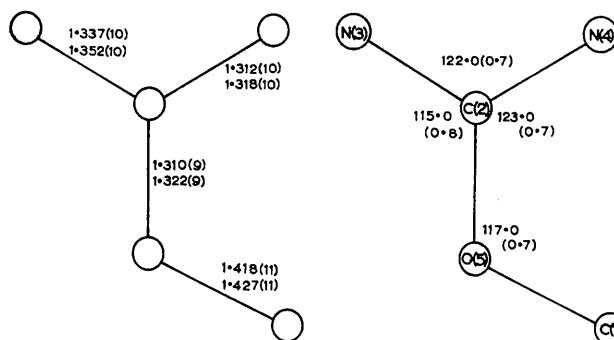


Fig. 1. Bond lengths and angles in  $[(\text{NH}_2)_2\text{COCH}_3]^+$ , with standard deviations in brackets. The lower bond lengths have been corrected for thermal motion.

Table 2. Final atomic fractional coordinates and anisotropic temperature factors

The temperature factor is in the form  $\exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - 2b_{12}hk - 2b_{13}hl - 2b_{23}kl)$ .  
The figures in brackets are standard deviations.

	$10^4x$	$10^4y$	$10^4z$		$10^4x$	$10^4y$	$10^4z$
C(1)	6442 (10)	0770 (9)	1162 (22)	H(7)	4231	0257	-0536
C(2)	4232 (8)	1400 (7)	2679 (15)	H(8)	2519	0779	0553
N(3)	3494 (8)	2087 (7)	4367 (16)	H(9)	2393	2103	4233
N(4)	3616 (7)	0781 (7)	0777 (14)	H(10)	4010	2558	5856
O(5)	5610 (6)	1426 (5)	3014 (14)	H(11)	6080	-0170	1250
Cl(6)	0338 (2)	1274 (2)	1640 (4)	H(12)	7580	0931	1850
				H(13)	6330	1130	-0840
	$10^4b_{11}$	$10^4b_{22}$	$10^4b_{33}$	$10^4b_{12}$	$10^4b_{13}$	$10^4b_{23}$	
C(1)	83 (9)	92 (8)	386 (39)	7 (7)	-30 (20)	-64 (17)	
C(2)	58 (7)	59 (5)	278 (28)	2 (5)	11 (14)	-12 (13)	
N(3)	105 (9)	85 (6)	324 (28)	0 (7)	20 (16)	-58 (13)	
N(4)	62 (7)	83 (6)	267 (26)	-1 (5)	5 (13)	-18 (11)	
O(5)	62 (5)	77 (5)	410 (25)	-9 (4)	-23 (12)	-19 (12)	
Cl(6)	72 (2)	69 (2)	316 (8)	6 (1)	2 (3)	13 (3)	

Table 3. Significant intermolecular distances in  $[(\text{NH}_2)_2\text{COCH}_3]^+\text{Cl}^-$

An asterisk indicates a hydrogen bond.

In plane			Out of plane				
Cl(6) $\cdots$ N(3)*		3.40 Å	C(1) $\cdots$ C(1) (iv)		3.63 Å		
Cl(6) $\cdots$ N(4)*		3.17	N(4) $\cdots$ N(4) (v)		3.71		
N(3) $\cdots$ Cl(6) (i)*		3.22	N(3) $\cdots$ N(4) (v)		3.83		
O(5) $\cdots$ Cl(6) (i)		3.72	Cl(6) $\cdots$ C(1) (v)		3.63		
Cl(6) $\cdots$ C(1) (ii)		3.73	Cl(6) $\cdots$ N(4) (v)*		3.24		
N(3) $\cdots$ O(5) (iii)		3.45	N(4) $\cdots$ N(3) (vi)		3.53		
N(3) $\cdots$ C(1) (iii)		3.80	O(5) $\cdots$ Cl(6) (vii)		3.47		
			C(2) $\cdots$ Cl(6) (vii)		3.53		
Key:			(iv)	$\frac{3}{2}-x,$	$-y,$	$\frac{1}{2}+z$	
(i)	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	$1-z$	(v)	$\frac{1}{2}-x,$	$-y,$	$\frac{1}{2}+z$
(ii)	$x-1,$	$y,$	$z$	(vi)	$x,$	$y,$	$z-1$
(iii)	$x-\frac{1}{2},$	$\frac{1}{2}-y,$	$1-z$	(vii)	$\frac{1}{2}+x,$	$\frac{1}{2}-y,$	$-z$

they were clearly subject to some systematic error, possibly extinction (28 out of 29 reflexions had  $F_o$  less than  $F_c$ ). Refinement was deemed complete when all suggested parameter changes were less than one-tenth of the corresponding estimated standard deviations. The final list of observed and calculated structure amplitudes is presented in Table 1, with  $F_o$  values on an absolute scale.

The final positional and thermal parameters are presented in Table 2.

The final agreement indices are  $R=0.107$  ( $R'=0.127$ ) for the set of 653 terms used in the refinement,  $R=0.103$  ( $R'=0.121$ ) when the unobserved terms are omitted from this set, and  $R=0.113$  ( $R'=0.140$ ) when the

seven hydrogen atoms are omitted from the structure factor calculations. Here  $R' = (\sum wD^2 / \sum w|F_o|^2)^{1/2}$ .

A difference Fourier synthesis showed no significant spurious peaks – the largest background peaks were associated with the chlorine atom.

### Discussion

The interatomic distances and angles shown in Table 3 and in Figs. 1 and 2 were derived from the atomic parameters given in Table 2. Thermal corrections for covalent bond lengths were obtained assuming the riding mode for the outer atoms, and should thus represent the lower limits to the real corrections. The fact that the methyl group has the greatest thermal motion, and that the directions of greatest vibration for all atoms except the chloride ion are inclined at a large angle to the molecular plane (average  $76^\circ$ ), suggests that the thermal parameters have some reliability.

In Table 4 bond lengths and bond angles for 2-methylpseudourea hydrochloride are compared with those for related compounds. The difference in C–N bond lengths, while only possibly significant in this structure, is observed in urea nitrate also (White & Mason, 1969), where it has greater statistical significance.

The C–O bond, in the cation structures in which it occurs, is intermediate in length between the accepted single and double bond values, and is longer than the corresponding bond in urea. Another notable common feature is the significant difference between the two N–C–X angles, where X represents O or NH, in all but the neutral urea group.

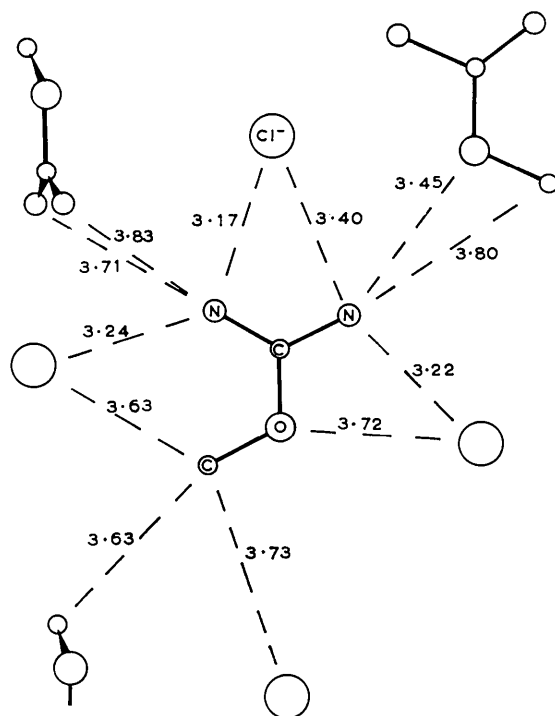


Fig. 2. In-plane intermolecular contacts.

### Planarity of the pseudourea residue

The mean plane through atoms C(1), N(3), N(4), and O(5) (*i.e.* the 'urea' part of the molecule) was calculated by the method of Blow (1960). In the normal form it is,

$$0.0748X + 0.7767Y - 0.6254Z = 0.6846,$$

where  $X, Y, Z$  are coordinates in Å referred to the crys-

Table 4. Bond lengths (Å) and angles (degrees), with standard deviations, for 2-methylpseudourea hydrochloride and related compounds

Distances corrected for thermal motion are also given where available.

	(NH <sub>2</sub> ) <sub>2</sub> COCH <sub>3</sub> <sup>+</sup> Cl <sup>-</sup>	Urea nitrate <sup>a</sup>	Methyl guanidinium ion <sup>b</sup>	Urea <sup>c</sup>
C–N	1.312 (10), 1.337 (10)	1.297 (3), 1.310 (3)	1.326 (7), 1.323 (7)	1.326 (6)
C–N (corr)	1.318 (10), 1.352 (10)	1.311 (3), 1.325 (3)	—	1.356 (6)
C–O	1.310 (9)	1.306 (3)	—	1.268 (7)
C–O (corr)	1.322 (9)	1.320 (3)	—	1.276 (8)
N–C–N	122.0 (7)	122.4 (2)	120.5 (5)	117.9 (6)
N–C–X <sup>d</sup>	123.0 (8), 115.0 (8)	121.7 (2), 115.9 (2)	122.0 (5), 117.5 (5)	121.0 (3)
C–X–C	117.0 (7)	—	123.2 (5)	—

<sup>a</sup> White & Mason 1969.

<sup>b</sup> Curtis & Pasternak (1955), Mendel & Hodgkin (1954).

<sup>c</sup> Caron & Donohue (1964).

<sup>d</sup> X stands for O or NH.

tallographic axes. This portion of the cation is planar to the limits of accuracy of the determination (mean deviation of the four atoms from the plane is  $0.006 \text{ \AA}$ ), but the deviation of the methyl carbon atom from this plane,  $0.07 \text{ \AA}$ , is significant and corresponds to a  $3^\circ$  out-of-plane twist of the  $\text{O}-\text{CH}_3$  bond. This twist may indicate an attempt to reduce the intramolecular steric interaction between the two out-of-plane hydrogen atoms and a hydrogen atom attached to the adjacent nitrogen atom. For these atoms  $\text{H}\cdots\text{H}$  distances are approximately  $2.1 \text{ \AA}$  (*cf.* van der Waals sum of  $2.4 \text{ \AA}$ ). A similar twist out of plane of  $0.06 \text{ \AA}$  was noted in the structure of creatine (Mendel & Hodgkin, 1954) which contains the methylguanidinium grouping, though not in the methylguanidinium cation itself (see Curtis & Pasternak, 1955).

### Molecular packing

A view of the structure along the  $[00\bar{1}]$  direction is shown in Fig. 3; the postulated hydrogen bonding scheme is also indicated. Each chloride ion participates in three approximately coplanar hydrogen bonds of lengths  $3.17$ ,  $3.22$  and  $3.40 \text{ \AA}$ , the last of these being very weak, and in a further strong hydrogen bond of  $3.24 \text{ \AA}$  inclined at about  $80^\circ$  to the plane of the other three. These are the shortest interionic distances and are also oriented most closely to the expected hydrogen-bond directions. Thus, all amino hydrogen atoms are involved in  $\text{N}-\text{H}\cdots\text{Cl}$  hydrogen bonds, linking the 2-methylpseudourea cations and chloride anions into a three-dimensional network.

If viewed along the  $[\bar{1}00]$  direction, the structure may be considered as 'herring-boned'. The mean plane discussed above is inclined at angles of  $4$ ,  $51$  and  $39^\circ$  to the  $a$ ,  $b$  and  $c$  axes respectively; the  $a$ -axis projection (not given) shows that two symmetry-related cations, those in the left half of the unit cell of Fig. 3, are almost coplanar, and make an angle of about  $78^\circ$  with the corresponding symmetry-related units in the right-hand half of Fig. 3.

Most of the important interionic contacts are thus between two coplanar units; these in-plane contacts are shown in Fig. 2. The significant contacts between non-coplanar units are the short  $\text{C}(1)\cdots\text{C}(1(\text{iv}))$  methyl-methyl carbon distance of  $3.63 \text{ \AA}$ , which however involves no  $\text{H}\cdots\text{H}$  contact shorter than  $2.7 \text{ \AA}$ , and several interactions involving the  $\text{Cl}^-$  ion. A number of hydrogen-bonded and non-bonded contacts are shown in Table 3.

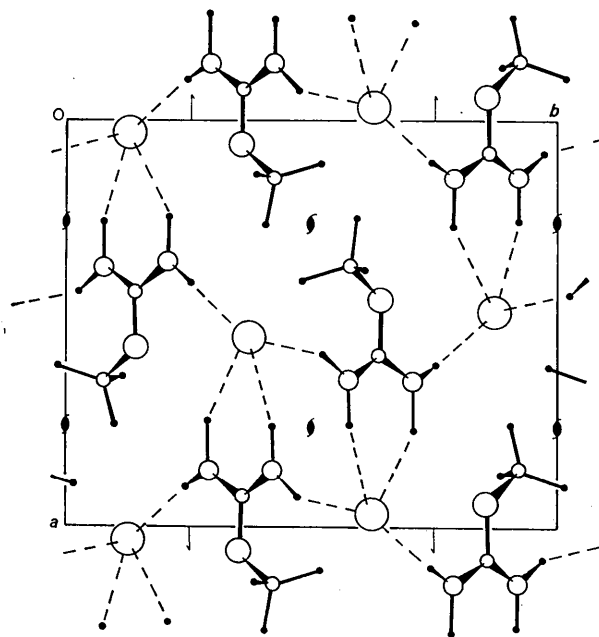


Fig. 3. Projection of the structure down the  $c$  axis.

The programs *ORFLS* for least-squares, and *ORFFE* for crystallographic function and error calculations, by W. R. Busing, K. O. Martin & H. A. Levy, were used throughout. The program *MUFR3* by J. C. B. White was used for Fourier syntheses. One of us (S.A.M.) wishes to acknowledge receipt of a University of Melbourne Research Grant. Thanks are due to Dr B. F. Hoskins for his assistance and encouragement.

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