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The Crystal and Molecular Structure of Semicarbazide Hydrochloride

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The crystal structure of semicarbazide hydrochloride (space group $P2_12_12_1$) has been solved and refined by three-dimensional Fourier methods. The organic ion is not planar: the $-NH_3^+$ group is 0·44 Å from the plane of the other heavy atoms. The bond configuration in semicarbazide and the hydrogen bonding in the structure as a whole are discussed.

Introduction

The X-ray analysis of the structure of semicarbazide hydrochloride was carried out in this laboratory as part of a study of semicarbazide–metal complexes. The aim of the study is to investigate the possible changes in bond lengths and angles of semicarbazide in the ionic or in the coordinated state. When the work was complete and this paper had already been written the authors read the thesis of Johnson (1960)* in which the same structure was solved and refined by least-squares methods with data taken around [001] ($l=0$, 1, 2, 3,). Nevertheless, it seems interesting to compare the results of the two determinations, especially because different methods were used in the refinement.

Experimental

Semicarbazide hydrochloride crystallizes from aqueous solutions in colourless prisms elongated along [001]. Crystal data, determined from rotation and Weissenberg photographs (Cu $K\alpha$ radiation) with the crystal rotating about the c and a axes, are as follows:

$CO(NH_2)NHNH_3Cl$; $M=111·5$. Orthorhombic.
$a=7·51\pm0·01$, $b=13·13\pm0·01$, $c=4·64\pm0·01$ Å.
$V=457·8$ Å^3, $Z=4$, $D_x=1·618$ g.cm^{-3}.
$\mu=61·8$ cm^{-1} (Cu $K\alpha$).
$F(000)=228$.
Absent spectra: $h00$, $0k0$, $00l$ with odd orders.
Space group: $P2_12_12_1$ (D_2^4).

For the structural analysis the $hk0$, $hk1$, ... $hk4$ and $0kl$, $1kl$ reflexions were collected, their intensities being determined photometrically from integrated and non-integrated Weissenberg photographs (multiple film technique). 513 independent reflexions were observed out of a possible 588. The shape of the spots of non-equatorial layers was taken into account following Phillips (1956). To correct for absorption, the samples were taken as cylindrical with radius 0·01 cm.

Table 2. *Thermal parameters* (Å^2)

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Cl	2·81	4·60	3·48	0·08	0·04	0·16
O	2·80	4·05	2·61	0·22	0·22	0·37
N(1)	3·15	4·48	3·93	0·34	−0·38	−0·62
N(2)	2·62	3·31	2·72	0·19	0·59	0·09
N(3)	2·73	4·01	3·57	0·17	0·12	−0·09
C	2·63	3·38	2·35	−0·34	−0·32	0·66

Table 1. *Final atomic coordinates and their e.s.d.'s with ratios (e.s.d.)/(coordinate shift)*

	x/a	y/b	z/c	x(Å)	y(Å)	z(Å)	$\sigma(x)$	$\sigma(y)$ × 10^3 (Å)	$\sigma(z)$	$\|r(x)\|$	$\|r(y)\|$	$\|r(z)\|$
Present study												
Cl	0·2543	0·1399	0·9636	1·910	1·837	4·471	3	3	3	6	∞	2
O	0·7587	0·0874	0·8233	5·698	1·147	3·820	7	7	8	3	28	2
N(1)	0·9267	0·1605	0·4787	6·960	2·107	2·221	11	11	14	2	14	2
N(2)	0·6335	0·1320	0·3930	4·758	1·733	1·824	8	8	9	5	30	2
N(3)	0·4909	0·0655	0·4551	3·687	0·860	2·112	10	9	12	∞	36	3
C	0·7767	0·1236	0·5787	5·833	1·623	2·685	9	9	11	4	35	5
Johnson												
Cl	0·2540	0·1400	0·9654	1·916	1·851	4·506	2	2	4	—	—	—
O	0·7566	0·0869	0·8206	5·707	1·149	3·831	8	6	9	—	—	—
N(1)	0·9272	0·1614	0·4780	6·994	2·134	2·231	9	11	14	—	—	—
N(2)	0·6344	0·1329	0·3933	4·785	1·757	1·836	8	7	12	—	—	—
N(3)	0·4887	0·0647	0·4612	3·686	0·856	2·153	8	8	12	—	—	—
C	0·7781	0·1244	0·5771	5·869	1·645	2·694	9	7	15	—	—	—

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* Dr Johnson's results are quoted in the present paper with his knowledge and agreement. It is a pleasure to thank him for this.

Table 3. *Observed and calculated structure factors*

A minus sign after an F_o means 'less than'.

h	k	l	$\lvert 10F_o \rvert$	$10F_c$	$\alpha°$
0	0	2	403	595	0
0	0	4	97	70	0
0	2	0	129	58	0
0	2	2	79	93	180
0	2	4	29	26	180
0	4	0	790	1090	180
0	4	2	304	363	180
0	4	4	48	29	180
0	6	0	103	75	0
0	6	2	210	213	0
0	6	4	71	63	0
0	8	0	215	200	0
0	8	2	142	121	0
0	8	4	32	12	180
0	10	0	191	184	180
0	10	2	184	174	180
0	10	4	62	52	180
0	12	0	43	40	180
0	12	2	53	54	180
0	12	4	15	18	0
0	14	0	138	112	0
0	14	2	71	68	0
0	16	0	32	24	0
2	0	0	458	649	180
2	0	2	75	94	180
2	0	4	33	17	180
2	2	0	85	70	0
2	2	2	153	165	35
2	2	4	40	31	32
2	4	0	511	557	0
2	4	2	179	193	355
2	4	4	43	34	12
2	6	0	39	46	180
2	6	2	179	195	205
2	6	4	50	55	203
2	8	0	315	282	180
2	8	2	194	206	176
2	8	4	41	40	190
2	10	0	41	29	0
2	10	2	92	92	36
2	10	4	33	37	30
2	12	0	91	65	0
2	12	2	85	86	353
2	14	0	63	51	180
2	14	2	39	43	221
2	16	0	24-	0	0
4	0	0	499	520	0
4	0	2	189	213	0
4	0	4	108	98	0
4	2	0	114	106	0
4	2	2	49	46	255
4	2	4	99	46	258
4	4	0	297	284	180
4	4	2	142	152	176
4	4	4	77	72	183
4	6	0	70	70	180
4	6	2	74	75	19
4	6	4	36	38	30
4	8	0	56	45	0
4	8	2	81	80	348
4	8	4	37	40	0
4	10	0	81	59	180
4	10	2	93	99	189
4	10	4	30	43	186
4	12	0	40-	6	180
4	12	2	49	49	169
4	14	0	77	61	0
4	14	2	40	48	15
6	0	0	299	283	180
6	0	2	120	112	180
6	0	4	58	51	180
6	2	0	68	61	0
6	2	2	93	95	326
6	2	4	29	27	358
6	4	0	263	234	0
6	4	2	127	123	359
6	4	4	47	45	11
6	6	0	101	85	180
6	6	2	125	133	172
6	6	4	38	48	188
6	8	0	132	113	180
6	8	2	98	89	185
6	10	0	56	44	0
6	10	2	58	60	0
6	12	0	28-	2	0
8	0	0	240	203	0
8	0	2	88	80	0
8	2	0	43	23	0
8	2	2	29-	5	112
8	4	0	182	140	180
8	4	2	67	60	185
8	6	0	33-	12	180
8	6	2	28	22	356
8	8	0	72	54	0
0	2	1	164	205	0
0	2	3	70	56	0
0	2	5	77	61	0
0	4	1	103	107	0
0	4	3	91	81	180
0	4	5	92	62	180
0	6	1	57	68	180
0	6	3	116	115	180
0	6	5	105	86	180
0	8	1	80	80	180
0	8	3	48	38	0
0	8	5	59	48	0
0	10	1	26-	16	180
0	10	3	79	76	0
0	12	1	27-	16	0
0	12	3	23-	5	180
0	14	1	24	22	0
0	14	3	15	14	180
0	16	1	11	9	0
2	0	1	34	25	90
2	0	3	67	95	90
2	2	1	267	370	185
2	2	3	212	226	184
2	4	1	114	134	166
2	4	3	47	59	289
2	6	1	81	96	26
2	6	3	114	112	12
2	8	1	77	76	305
2	8	3	63	61	174
2	10	1	47-	12	325
2	10	3	54	52	193
2	12	1	57	40	63
2	12	3	46	51	3
2	14	1	41-	13	244
2	14	3	18	28.	0
2	16	1	23-	18	213
4	0	1	135	141	90
4	0	3	36	46	90
4	2	1	206	241	354
4	2	3	153	160	352
4	4	1	69	66	293
4	4	3	91	88	195
4	6	1	125	137	157
4	6	3	154	160	165
4	8	1	33	29	240
4	8	3	64	63	355
4	10	1	47	49	308
4	10	3	82	91	344
4	12	1	47	32	105
4	12	3	22	26	162
4	14	1	32-	11	95
6	0	1	79	75	90
6	0	3	26-	0	0
6	2	1	115	118	172
6	2	3	103	110	174
6	4	1	76	70	230
6	4	3	25-	8	70
6	6	1	44	41	4
6	6	3	57	64	345
6	8	1	41	33	60
6	8	3	29	32	209
6	10	3	22	36	167
6	12	1	34	26	293
8	0	1	43-	5	270
8	0	3	15-	3	270
8	2	1	49	36	22
8	2	3	19	26	0
8	6	1	36-	19	232
8	8	1	25	22	243
0	1	1	57	31	270
0	1	3	36	30	90
0	1	5	94	72	90
0	3	1	52	56	270
0	3	3	47	49	270
0	3	5	100	77	90
0	5	1	120	136	270
0	5	3	181	182	270
0	5	5	71	49	270
0	7	1	75	70	270
0	7	3	22	22	270
0	7	5	59	49	270
0	9	1	137	81	90
0	9	3	163	153	90
0	9	5	38	33	90
0	11	1	27-	1	90
0	11	3	25	31	90
0	13	1	26-	25	270
0	13	3	57	63	270
0	15	1	61	50	90
2	1	1	371	474	258
2	1	3	125	140	250
2	3	1	299	357	284
2	3	3	69	63	330
2	5	1	169	187	72
2	5	3	156	160	75
2	7	1	65	61	217
2	7	3	66	67	222
2	9	1	87	96	252
2	9	3	116	128	257
2	11	1	114	117	77
2	11	3	42	48	47
2	13	1	56	62	83
2	13	3	47	57	79
2	15	1	62	55	256
4	1	1	216	267	76
4	1	3	71	75	42
4	3	1	105	111	113
4	3	3	70	72	221
4	5	1	266	306	263
4	5	3	147	139	260
4	7	1	44	40	290
4	7	3	47	44	35
4	9	1	152	153	88
4	9	3	91	97	90
4	11	1	47-	17	253
4	11	3	19	21	186
4	13	1	42	42	271
4	15	1	20-	40	87
6	1	1	128	135	270
6	1	3	42	43	277
6	3	1	146	145	268
6	3	3	27	23	274
6	5	1	61	58	81
6	5	3	47	53	90
6	7	1	42	36	71
6	7	3	21-	5	169
6	9	1	64	65	264
6	9	3	50	61	261
6	11	1	46	31	114
8	1	1	90	86	75
8	1	3	46	53	70
8	3	1	42	27	106
8	3	3	14	10	157
8	5	1	108	107	260
8	7	1	32-	3	161
0	1	2	282	358	270
0	1	4	78	56	270
0	3	2	155	196	90
0	3	4	110	98	90
0	5	2	146	157	90
0	5	4	27-	20	270
0	7	2	47	50	270
0	7	4	99	103	270
0	9	2	27	32	90
0	9	4	55	51	90
0	11	2	33	39	90
0	11	4	79	70	90
0	13	2	48	50	270
0	15	2	33	28	270
2	1	0	91	74	0
2	1	2	102	115	44
2	1	4	67	68	324
2	3	0	24-	9	180
2	3	2	96	88	278
2	3	4	89	72	289
2	5	0	21	10	180
2	5	2	103	85	227
2	5	4	63	66	141
2	7	0	74	73	0
2	7	2	60	53	44
2	7	4	112	112	88
2	9	0	54	36	180
2	9	2	36-	16	37
2	9	4	87	27	354
2	11	0	41	43	180
2	11	2	25	25	185
2	11	4	43	51	263
2	13	0	44	32	0
2	13	2	45	31	82
2	15	0	32-	9	0
2	15	2	20-	3	0
4	1	0	66	36	0
4	1	2	82	95	295
4	1	4	38	31	302
4	3	0	33-	28	180
4	3	2	31-	12	335
4	3	4	41	40	80
4	5	0	36-	20	180
4	5	2	49	39	103
4	5	4	21	18	245
4	7	0	75	71	0
4	7	2	69	59	61
4	7	4	43	46	277
4	9	0	42-	5	180
4	9	2	33	44	110
4	9	4	24	33	95
4	11	0	38	40	180
4	11	2	35	30	215
4	13	0	36-	11	0
4	13	2	38	43	290
4	15	0	22-	6	0
6	1	0	152	139	0
6	1	2	68	65	39
6	1	4	19	13	210
6	3	0	127	120	0
6	3	2	67	62	302
6	3	4	60	57	254
6	5	0	110	92	180
6	5	2	45	50	205
6	5	4	18	26	66
6	7	0	29	41	180
6	7	2	45	30	90
6	9	0	75	55	0
6	9	2	33	32	353
6	11	0	34-	0	0
6	11	2	22-	9	180
6	13	0	32	33	180
8	1	0	76	69	180
8	1	2	79	76	244
8	3	0	54	40	180
8	3	2	41	44	96
8	5	0	86	69	0
8	5	2	62	63	42
8	7	0	30-	21	0
8	7	2	21	22	267
8	9	0	41	32	180
1	1	1	137	142	0
1	1	3	131	133	96
1	1	5	99	72	102
1	3	1	209	223	318
1	3	3	121	120	36
1	3	5	79	56	59
1	5	1	188	211	232
1	5	3	116	122	263
1	5	5	56	54	270
1	7	1	118	134	149
1	7	3	66	73	179
1	7	5	25	23	194
1	9	1	124	127	86
1	9	3	71	72	90
1	11	1	48-	24	190
1	11	3	32	33	277
1	13	1	47	47	264
1	13	3	28	33	270
1	15	1	43	35	357
3	1	1	118	132	50
3	1	3	71	76	334
3	3	1	154	173	65
3	3	3	24	27	243
3	5	1	36	41	130
3	5	3	38	44	155
3	7	1	106	106	223
3	7	3	23	17	231
3	9	1	65	68	235
3	9	3	16	22	259
3	11	1	48-	10	96
3	11	3	22	31	108
3	13	1	43-	21	66
3	13	3	15-	13	67
3	15	1	30-	12	4
5	1	1	39	52	307
5	1	3	56	41	60
5	3	1	103	106	298
5	3	3	24	7	129
5	5	1	43	45	294
5	5	3	42	53	277
5	7	1	101	99	149
5	7	3	25-	19	111
5	9	1	68	74	143
5	9	3	29	31	135
5	11	1	52	38	344
5	11	3	17	27	266
5	13	1	32	24	336
7	1	1	101	109	355
7	1	3	41	67	309
7	3	1	91	94	170
7	3	3	42	46	239
7	5	1	55	54	128
7	5	3	41	42	104
7	7	1	57	56	345
7	7	3	15-	2	90
7	9	1	49	47	243
7	11	1	22-	40	180
9	1	1	31-	12	65
9	3	1	33	24	344
9	5	1	21-	35	270
1	1	0	237	162	270
1	1	2	199	233	110
1	1	4	115	107	101
1	3	0	102	108	270
1	3	2	174	191	235
1	3	4	124	112	245
1	5	0	184	179	90
1	5	2	124	121	270
1	5	4	75	74	250
1	7	0	220	217	90
1	7	2	98	89	75
1	7	4	85	83	85
1	9	0	76	71	270
1	9	2	25	23	192
1	9	4	24	24	83
1	11	0	138	122	270
1	11	2	57	53	270
1	11	4	48	47	276
1	13	0	53	39	90
1	13	2	56	55	52
1	15	0	35	34	90
1	15	2	19	27	74
3	1	0	125	144	270
3	1	2	239	254	285
3	1	4	91	77	292
3	3	0	471	457	90
3	3	2	247	279	88
3	3	4	106	94	88
3	5	0	141	95	270
3	5	2	132	137	150
3	5	4	66	62	160
3	7	0	402	375	270
3	7	2	153	158	258
3	7	4	67	59	249
3	9	0	82	83	90
3	9	2	90	80	32
3	9	4	33	31	20
3	11	0	190	155	90
3	11	2	58	65	67
3	11	4	17	22	45
3	13	0	58	44	270
3	13	2	57	59	248
3	15	0	46	37	270
5	1	0	99	83	90
5	1	2	129	142	96
5	1	4	61	53	142
5	3	0	185	169	270
5	3	2	108	110	261
5	3	4	57	54	210
5	5	0	40	16	270
5	5	2	87	86	267
5	5	4	26	23	286
5	7	0	215	194	90
5	7	2	69	69	101
5	7	4	23	18	67
5	9	0	42-	8	270
5	9	2	35-	5	150
5	11	0	174	134	270
5	11	2	49	51	282
5	13	0	30-	12	90
5	13	2	23	26	68
7	1	0	43-	13	270
7	1	2	79	86	257
7	1	4	36	39	275
7	3	0	117	107	90
7	3	2	90	98	106
7	5	0	42-	15	270
7	5	2	41	42	101
7	7	0	160	130	270
7	7	2	75	72	269
7	9	0	33-	12	90
7	9	2	22-	7	344
7	11	0	79	71	90
9	1	0	47	40	90
9	3	0	88	69	270
9	5	0	22-	9	90
1	0	2	14-	0	0
1	0	4	223	220	0
1	2	0	136	110	270
1	2	2	65	70	181
1	2	4	41	39	73
1	4	0	334	277	270
1	4	2	145	163	255
1	4	4	164	155	196
1	6	0	26	34	270
1	6	2	117	119	337
1	6	4	36	32	265
1	8	0	69	52	90
1	8	2	114	91	32
1	8	4	70	65	22
1	10	0	41-	14	270
1	10	2	68	54	174
1	10	4	20	21	147
1	12	0	45	39	90
1	12	2	60	53	162
1	12	4	20-	14	191
1	14	0	40	42	90
1	14	2	25	22	63
1	16	0	15	17	270
3	0	2	153	162	180
3	0	4	237	212	180
3	2	0	35	14	270
3	2	2	95	86	351
3	2	4	24	22	288
3	4	0	220	187	270
3	4	2	170	182	334
3	4	4	178	170	356
3	6	0	148	115	270
3	6	2	139	144	200
3	6	4	27	22	169
3	8	0	91	67	90
3	8	2	131	133	170
3	8	4	70	68	180
3	10	0	61	58	90
3	10	2	80	77	15
3	10	4	31	29	353
3	12	0	42-	2	270
3	12	2	70	67	7
3	14	0	35-	4	90
3	14	2	31	26	153
5	0	2	93	109	0
5	0	4	159	149	0
5	2	0	38-	21	270
5	2	2	81	81	246
5	2	4	56	58	279
5	4	0	40-	5	270
5	4	2	104	108	187
5	4	4	108	111	180
5	6	0	91	82	270
5	6	2	72	68	342
5	6	4	28-	22	100
5	8	0	47	41	270
5	8	2	88	96	349
5	8	4	40	48	347
5	10	0	80	68	90
5	10	2	68	62	143
5	12	0	41	33	90
5	12	2	59	60	160
5	14	0	22-	18	270
7	0	2	40	19	180
7	0	4	76	80	180
7	2	0	145	134	270
7	2	2	44	50	311
7	2	4	17-	19	83
7	4	0	42-	28	270
7	4	2	30	29	350
7	6	0	43	35	90
7	6	2	38	45	180
7	8	0	37-	2	270
7	8	2	48	37	198
7	10	0	29-	3	270
7	10	2	15-	22	16
9	0	2	16-	7	0
9	2	0	33	20	270
9	4	0	25-	7	90
1	0	1	118	150	270
1	0	3	88	92	270
1	2	1	557	731	184
1	2	3	272	282	189
1	2	5	36	32	320
1	4	1	265	304	14
1	4	3	34	38	76
1	4	5	55	40	345
1	6	1	303	405	4
1	6	3	125	123	18
1	6	5	29	27	119
1	8	1	219	235	184
1	8	3	39	35	183
1	8	5	41	39	155
1	10	1	170	169	177
1	10	3	26-	15	127
1	12	1	119	113	8
1	12	3	42	47	23
1	14	1	56	53	351
1	14	3	15	22	220
1	16	1	42	42	195
3	0	1	78	83	90
3	0	3	20-	30	90
3	2	1	187	202	354
3	2	3	190	208	351
3	4	1	91	97	242
3	4	3	59	74	305
3	6	1	166	184	175
3	6	3	111	120	163
3	8	1	99	102	33
3	8	3	62	66	89
3	10	1	124	122	2
3	10	3	32	39	0
3	12	1	78	78	192
3	12	3	38	45	215
3	14	1	47	49	180
5	0	1	32	36	270
5	0	3	23	38	270
5	2	1	181	205	186
5	2	3	181	188	186
5	4	1	125	141	3
5	4	3	27	28	13
5	6	1	146	151	11
5	6	3	99	104	11
5	8	1	113	121	172
5	8	3	36	41	162
5	10	1	74	66	187
5	10	3	15	18	176
5	12	1	60	55	354
5	14	1	21-	7	17
7	0	1	48-	13	270
7	0	3	47	40	270
7	2	1	162	167	1
7	2	3	96	96	356
7	4	1	51	55	176
7	4	3	19	15	90
7	6	1	103	103	189
7	6	3	41	39	190
7	8	1	75	68	[illegible]
7	10	1	57	52	20
9	0	1	37	31	270
9	2	1	69	69	187
9	1	1	36	38	30

The absolute scale was established by Wilson's method using the *hk*0 reflexions, and reflexions from the remaining layers were put on the same scale by cross-correlation.

Structure analysis and refinement

The two-dimensional Patterson $P(U, V)$ and $P(V, W)$ projections were used to derive the Cl coordinates and to give a rough idea of the orientation of the semicarbazide molecule. A complete solution of the structure was obtained by means of a three-dimensional Patterson synthesis, followed by three-dimensional Fourier syntheses.

The refinement was carried out, first by two F_o-F_c syntheses, then by six anisotropic cycles of Booth's 'differential synthesis'. At the end, the ratios $r(x)=\sigma(x)/\varepsilon(x)$ between the e.s.d.'s and the shifts of the coordinates were as shown in Table 1, in which the final coordinates with e.s.d.'s calculated following Cruickshank (1949, 1950), are also quoted. For comparison, the coordinates found by Johnson are reported in the same table after transformation to the orientation assumed in the present paper; their e.s.d.'s calculated with Cruickshank's formulae (quoted values), are much larger than the 'least-squares' ones. The agreement between these two sets of coordinates is very good and accounts for the agreement between bond distances and angles reported in the next section.

The anisotropic thermal parameters, determined following the method of Nardelli & Fava (1960) using the second derivatives of the electron density from differential synthesis, are listed in Table 2. The structure factors F_c reported in Table 3 are calculated with the final parameters of Tables 1 and 2 and do not include the contributions of hydrogen atoms, which could not be located directly. The H coordinates of Table 4 were calculated with the application of the criteria discussed in the next section.

Table 4. *Calculated hydrogen coordinates*

	x/a	y/b	z/c
H(1)	0·041	0·158	0·603
H(2)	0·934	0·190	0·272
H(3)	0·655	0·163	0·190
H(4)	0·445	0·079	0·659
H(5)	0·389	0·077	0·309
H(6)	0·532	−0·009	0·440

The final agreement indices, R (for observed reflexions only) and R' (including $F_o=\frac{1}{2}F_{\min}$ when $F_c \geq F_{\min}$ for unobserved reflexions; multiplicities not considered for both R values), are: $R=12·9\%$, $R'=15·3\%$. Inclusion of the contributions from the hydrogen atoms hardly alters these factors: $R=12·8\%$, $R'=15·2\%$.

In Table 5 are compared the observed and calculated values of electron density and the second derivatives at the atomic peaks. The scattering factors used throughout the calculations were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for Cl, O, N, C and of McWeeny (1951) for H. The calculations were performed on an Olivetti ELEA 9002 computer for Fourier syntheses and on an IBM 650 and an ELEA 6001 computer for structure factors and differential syntheses.

Table 5. *Atomic peak heights* (e.Å^{-3}), *curvatures* (e.Å^{-5}) *and e.s.d.'s*

		ϱ	$-A_{hh}$	$-A_{kk}$	$-A_{ll}$	A_{kl}	A_{hl}	A_{hk}
Cl	obs.	30·0	316	269	268	6	1	7
	calc.	31·3	318	271	269	6	1	5
O	obs.	12·7	110	104	115	4	1	4
	calc.	13·2	112	105	116	4	1	4
N(1)	obs.	8·6	77	69	65	5	−2	−5
	calc.	8·9	77	69	65	5	−2	−5
N(2)	obs.	10·6	99	98	96	−2	9	2
	calc.	11·3	101	99	97	−2	10	1
N(3)	obs.	9·6	81	81	75	−2	1	3
	calc.	9·7	82	81	76	−2	1	2
C	obs.	9·0	89	84	82	1	3	3
	calc.	9·4	86	84	82	2	2	3
	e.s.d.	0·4	3	3	4	2	2	2

Discussion

The arangement of Cl^- and $OC(NH_2)NHNH_3^+$ ions in the crystal is shown in Fig. 1. Distances and angles in the organic ion are given in Table 6 (the e.s.d.'s are calculated from the formula of Ahmed & Cruickshank (1953) for distances and from that of Darlow (1960) for angles). The nitrogen atoms are numbered as follows:

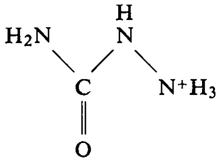
$$H_2N(1)\text{–}CO\text{–}N(2)H\text{–}N^+(3)H_3\,.$$

N(3) is the proton acceptor atom, as can be deduced from its environment and from the value of the distance N(2)–N(3).

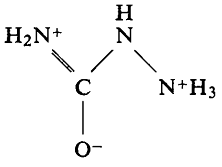
Table 6. *Interatomic distances and bond angles in* $OC(NH_2)NHNH_3^+$

	Present study	Johnson	Calculated
C–O	1·238 ± 0·016 Å	1·251 ± 0·022 Å	1·252 Å
C–N(1)	1·311 ± 0·018	1·311 ± 0·021	1·329
C–N(2)	1·382 ± 0·016	1·387 ± 0·020	1·402
N(2)–N(3)	1·411 ± 0·014	1·457 ± 0·015	
N(3) · · · O	2·655 ± 0·016	2·643 ± 0·019	
O–C–N(1)	124·1 ± 1·2°	125·5 ± 1·5°	
N(1)–C–N(2)	114·7 ± 1·1	115·0 ± 1·4	
O–C–N(2)	121·1 ± 1·1	119·5 ± 1·3	
C–N(2)–N(3)	114·4 ± 0·9	113·9 ± 1·0	

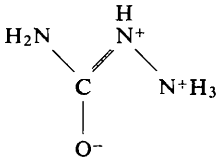
Bond distances in the organic ion, calculated in terms of valence-bond theory, agree satisfactorily with those given in Table 6, assuming the following resonance structures:



(I) 42 %



(II) 43 %



(III) 15 %

Bond-order/distance curves were derived with the use of the well-known Pauling relation: $r_x = r_1 - (r_1 - r_2)3x/(2x+1)$, with $r_1 = 1{\cdot}474$, $r_2 = 1{\cdot}265$ Å for C–N (Donohue, Lavine & Rollett, 1956) and $r_1 = 1{\cdot}43$, $r_2 = 1{\cdot}17$ Å for C–O (Abrahams, 1956). The double bond character of the N–N bond is almost negligible, in agreement with the tetrahedral configuration assumed by N(3). The double-bond character of the C–N(2) bond, corresponding to the contribution of the resonance-structure (III), seems to indicate a trigonal configuration for N(2) with a complete coplanarity of the heavy atoms. However, this coplanarity is not observed: N(3) is as much as 0·44 Å from the plane of the other atoms. The same value is found from Johnson's data. Table 7 gives the results from the analysis of planarity (Schomaker, Waser, Marsh & Bergman, 1959; Blow, 1960). The angle between the N(2)–N(3) bond and its projection on the ON(1)N(2)C plane is 18·3°. It is probable that the observed departure from planarity, which can arise from by steric packing requirements, causes the N(2) atom to lose its strictly trigonal symmetry, even with the possibility of π-overlapping. This accounts for the observed amount of double-bond character for C–N(2).

The interactions between the organic cations and chloride ions occur mainly through the hydrogen atoms bonded to N(3), as shown by the following distances which correspond to hydrogen bonds:

	present study	Johnson
N(3) · · · Cl =	3·111 ± 0·015 Å	3·109 ± 0·018 Å
N(3) · · · Cl ($x, y, z-1$) =	3·052 ± 0·015	3·079 ± 0·018

(When the coordinates are not indicated the atom is at x, y, z). The angle Cl–N(3)–Cl($x, y, z-1$), 97·7 ± 0·5° (Johnson: 97·9 ± 0·3°), is appreciably smaller than the tetrahedral angle of 109·5°. The chloride ions are rather loosely packed around a 2_1 axis parallel to [001], with Cl–Cl($\frac{1}{2}-x$, $\bar{y}$, $z+\frac{1}{2}$) = 4·35 Å (Johnson: 4·38 Å) and Cl–Cl($x, y, z+1$) (which is along c) = 4·64 Å (Johnson: 4·67 Å); thus the chloride ions form nearly equilateral triangles containing the 2_1 axis. N(3)H_3 groups face these triangles. Because the N(2)–N(3) bond is inclined to these triangles, only two hydrogen bonds to chloride ions are possible.

The coordinates of H(4), H(5), H(6) were deduced assuming a tetrahedral environment of N(3) with a N–H = 1·03 Å distance and using the best orientation for hydrogen bonding to chloride ions.

The N(3)–O intramolecular distance (2·655 Å) is of the same magnitude as that observed for hydrogen

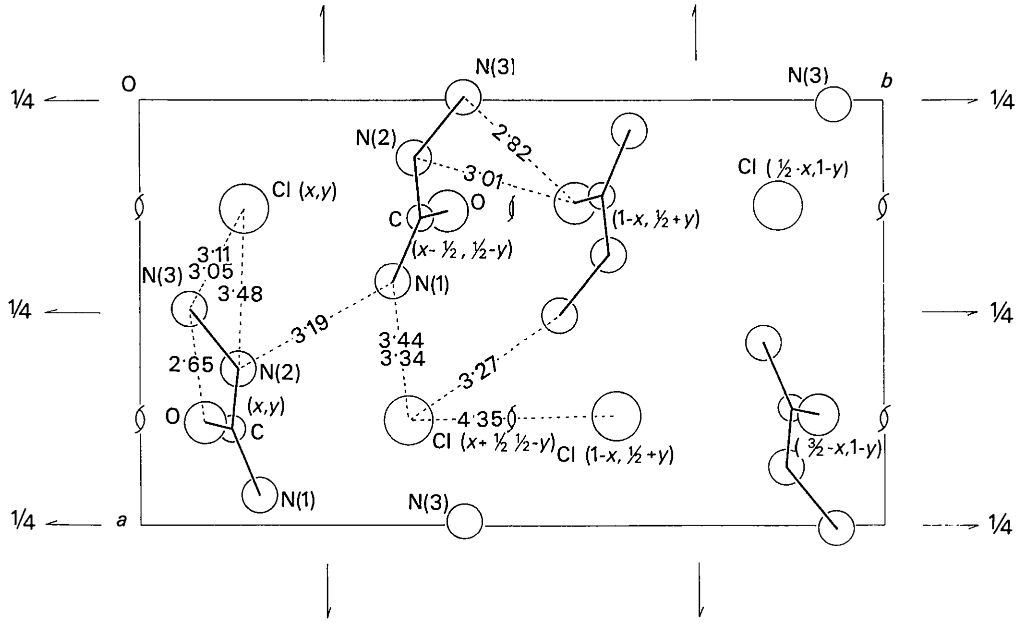


Fig. 1. Diagrammatic projection of the structure on (001).

Table 7. *Analysis of the planarity in* $OC(NH_2)NHNH_3^+$†

Equation of the plane: $m_1x+m_2y+m_3z=d$

Best plane through		ON(1)N(2)N(3)C		ON(2)N(3)C		ON(1)N(2)C	
m_1		−0·3352 (*−0·3361*)		−0·4226 (*−0·4199*)		−0·2199 (*−0·2208*)	
m_2		0·8751 (*0·8714*)		0·8043 (*0·8034*)		0·9031 (*0·8996*)	
m_3		0·3491 (*0·3573*)		0·4176 (*0·4222*)		0·3689 (*0·3768*)	
d		0·3859 (*0·4071*)		0·0581 (*0·0912*)		1·1874 (*1·2122*)	
	$\sigma\perp$*(Å × 10³)	Δ(Å × 10³)	$\Delta/\sigma\perp$	Δ(Å × 10³)	$\Delta/\sigma\perp$	Δ(Å × 10³)	$\Delta/\sigma\perp$
O	7 (7)	42 (*45*)	6·0 (*6·4*)	52 (53)	7·4 (*7·6*)	5 (5)	0·7 (0·7)
N(1)	11 (*11*)	−99 (*−101*)	−9·0 (*−9·2*)	(−377) (*−371*)	(−34·3) (*−33·7*)	5 (*4*)	0·5 (*0·4*)
N(2)	8 (*8*)	173 (*172*)	21·6 (*21·5*)	87 (*86*)	10·9 (*10·7*)	5 (*4*)	0·5 (*0·5*)
N(3)	10 (*8*)	−132 (*−132*)	−13·2 (*−16·5*)	−43 (*−43*)	−4·3 (*−3·4*)	(−443) (*−445*)	(−44·3) (*−55·6*)
C	9 (*9*)	16 (*16*)	1·8 (*1·8*)	−96 (*−97*)	−10·7 (*−10·8*)	−14 (*−13*)	−1·6 (*−1·4*)
$\Sigma(\Delta/\sigma\perp)^2$			761·0 (*863·3*)		305·9 (*318·0*)		3·5 (*2·9*)
$\chi^2_{95\%}$			6·0		3·8		3·8

* $\sigma\perp=\{m_1^2\sigma^2(x)+m_2^2\sigma^2(y)+m_3^2\sigma^2(z)\}^{\frac{1}{2}}$

† The figures in italics are calculated from Johnson's data.

bonds, but the angle criterion (Donohue, 1957) is not fulfilled, even if the $-NH_3^+$ tetrahedron is supposed to be orientated with an H as closed as possible to O. The observed displacement of N(3) from the plane of the other heavy atoms in the organic cation can be accounted for by the interactions of chloride ions with NH_3^+. These views on the distortion of semicarbazide ion are supported by the fact that semicarbazide is planar in bis-semicarbazide-copper(II) and bis-semicarbazide-zinc chlorides. There are no significant differences in bond lengths and angles between semicarbazide ion and metal-coordinated semicarbazide, indicating a tetrahedral configuration of N(3) in all these compounds (Nardelli, Fava, Boldrini & Giraldi, 1963). The coordinates of H(1) and H(2) were calculated assuming a trigonal configuration for N(1). This atom appears to form a weak hydrogen-bond N(1) · · · Cl(1 + x, y, z) = 3·345 ± 0·016 Å (Johnson: 3·356 ± 0·020 Å). The distance N(2)–O(x, y, $z-1$) = 2·866 ± 0·016 Å (Johnson: 2·892 ± 0·021 Å) suggests hydrogen bonding. The angle H(3)–N(2)–O(x, y, $z-1$) = 35·8° appears to be too large for hydrogen bonding, but, owing to the distortion of the molecule, the actual value of that angle may be more favourable. The coordinates of H(3) are derived assuming this atom to be in the plane OCN(1)N(2); this is only a rough approximation in view of the probable distortion of bonds formed by N(2), as discussed previously.

The other contacts less 3·5 Å than are:

	Present study	Johnson
N(3)–O($\frac{3}{2}-x$, $\bar{y}$, $z-\frac{1}{2}$)	2·818 ± 0·014 Å	2·853 ± 0·015 Å
N(2)–O($\frac{3}{2}-x$, $\bar{y}$, $z-\frac{1}{2}$)	3·010 ± 0·011	3·040 ± 0·013
N(2)–N(1)$x-\frac{1}{2}$, $\frac{1}{2}-y$, $1-z$)	3·192 ± 0·015	3·194 ± 0·017
Cl–N(3)($\frac{1}{2}-x$, $\bar{y}$, $z+\frac{1}{2}$)	3·266 ± 0·011	3·268 ± 0·011
Cl–N(2)(x, y, $z+1$)	3·477 ± 0·013	3·497 ± 0·017
Cl–N(1)($x-1$, y, $z+1$)	3·441 ± 0·017	3·447 ± 0·021
N(1)–O(x, y, $z-1$)	3·429 ± 0·019	3·470 ± 0·023

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