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4-Chloro-5-methylamino-2,3,6-pyridinetrione Monohydrate

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Monoclinic, $P2_1/c$, $a=5·276$ $b=19·31$ (3), $c=7·968$ (8) Å, $\beta=93·06$ (6)°, 25°C, $C_6H_5N_2O_3Cl.H_2O$, $M=206·6$, $Z=4$, $D=1·695$ g cm^{-3}. The exocyclic carbon–nitrogen bond has considerable double-bond character resulting in a planar structure.

Introduction

An X-ray diffraction study of 4-chloro-5-methylamino-2,3,6-pyridinetrione (I) was undertaken to identify the substituent positions in this compound and a series of related compounds (Johnston, 1971). The results also are of interest with regard to the valence structure assumed by I in the monohydrate crystal state.

Experimental

Efforts to recrystallize I from a variety of organic solvents gave twinned specimens exclusively. However, prismatic single crystals could be obtained as the monohydrate by recrystallization from aqueous solution. A crystal of approximate dimensions 0·20 × 0·05 × 0·50 mm was sealed within a 0·2 mm diameter Lindemann glass capillary. Preliminary Weissenberg and precession photographs showed diffraction symmetry $2/m$ and the systematic absences characteristic of space group $P2_1/c$. The crystal was aligned with **a** collinear with the φ axis of a Picker four-circle diffractometer, and the cell constants were determined by least-squares refinement of the setting angles of 23 reflections. Intensity data were taken by the θ–2θ scan mode using Mo $K\bar{\alpha}$ radiation monochromated by reflection from the 002 planes of highly oriented graphite. Within the sphere $\sin\theta < 0·461$ a total of 1943 unique reflections could be measured, of which the 1286 satisfying the condition $I > 3\sigma(I)$ were retained for solution and refinement. The 112 reflection was remeasured after each 50 reflections and showed r.m.s. stability of 1·6%. No absorption correction was made ($\mu=4·61$ cm^{-1}); transmission factors range from 0·92 to 0·98.

The crystal structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations minimizing $\sum w(|F_o|-|F_c|)^2$. All

Table 1. *Atomic parameters with standard errors*

Errors in parentheses refer to last significant digit(s). Thermal parameters are of the form

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times 10^4\right].$$

	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
N(1)	0·7074 (5)	0·2098 (1)	0·3693 (4)	204 (10)	20 (1)	144 (2)	−2 (5)	−69 (6)	−5 (2)
C(1)	0·5544 (6)	0·2587 (2)	0·2882 (4)	232 (12)	18 (1)	142 (6)	−0 (3)	−34 (7)	−3 (2)
C(2)	0·3283 (6)	0·2317 (2)	0·1769 (4)	206 (12)	21 (1)	108 (6)	2 (3)	−22 (7)	−2 (2)
C(3)	0·2938 (6)	0·1597 (2)	0·1641 (4)	182 (12)	20 (1)	110 (6)	0 (2)	−51 (6)	−2 (2)
C(4)	0·4536 (5)	0·1127 (2)	0·2484 (4)	187 (12)	18 (1)	113 (6)	−2 (3)	−12 (6)	−1 (2)
C(5)	0·6759 (6)	0·1396 (2)	0·3574 (4)	188 (11)	20 (1)	135 (6)	−2 (3)	−35 (6)	−2 (2)
O(1)	0·5917 (4)	0·3194 (1)	0·3036 (3)	353 (12)	19 (1)	250 (6)	−5 (2)	−135 (6)	−6 (2)
O(2)	0,1982 (4)	0·2756 (1)	0·1022 (3)	324 (10)	20 (1)	195 (5)	12 (2)	−108 (6)	3 (2)
Cl	0·0422 (2)	0·1360 (1)	0·0291 (1)	271 (3)	23 (1)	158 (2)	−5 (1)	−111 (2)	−3 (1)
N(2)	0·4479 (5)	0·0448 (1)	0·2479 (4)	268 (12)	19 (1)	167 (6)	−2 (3)	−86 (7)	1 (2)
C(6)	0·2597 (9)	−0·0023 (2)	0·1685 (8)	359 (20)	21 (1)	282 (12)	−18 (4)	−144 (12)	−0 (3)
O(3)	0·8199 (4)	0·0998 (1)	0·4295 (3)	300 (10)	23 (1)	213 (6)	4 (2)	−139 (6)	8 (2)
O(H_2O)	0·2698 (6)	0·4299 (2)	0·1340 (4)	375 (13)	23 (1)	256 (7)	−15 (3)	−139 (7)	8 (2)

Table 1 (*cont.*)

	x	*y*	*z*	*B*
H(1)	0·831 (7)	0·224 (2)	0·430 (4)	4·1 (9)
H(2)	0·568 (7)	0·023 (2)	0·309 (4)	4·6 (9)
H(6*A*)	0·273 (7)	0·005 (2)	0·044 (5)	5·7 (11)
H(6*B*)	0·095 (9)	0·011 (2)	0·211 (6)	8·5 (15)
H(6*C*)	0·300 (9)	−0·046 (2)	0·208 (5)	8·4 (14)
H(H_2O-*A*)	0·313 (7)	0·390 (2)	0·178 (5)	4·8 (10)
H(H_2O-*B*)	0·148 (9)	0·424 (2)	0·079 (6)	7·3 (15)

hydrogen atoms were located. The final *R* values were $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0{\cdot}054$ and $R_2\{\sum w(F_o-F_c)^2/\sum wF_o^2\}^{1/2}=0{\cdot}046$, assuming anisotropic thermal parameters for C, N, O and Cl, and isotropic parameters for H. The final electron density difference map showed maximum amplitudes of $\pm 0{\cdot}4$ e Å^{-3}. Scattering factors for C, N, O and Cl were obtained from *International Tables for X-ray Crystallography* (1962); hydrogen scattering factors are from Stewart, Davidson & Simpson (1965). Computer programs used were those given by Boer & North (1972). Table 1 lists the final atomic parameters and Table 2 gives the observed and calculated structure factors.

Results and discussion

The molecular structure is shown in Fig. 1. The molecule was established as the 4-chloro-5-methylamino isomer and was shown to exist in this crystal as the pyridinetrione rather than as a hydroxypyridine tautomer.

The molecular skeleton is essentially planar. The six atoms of the ring are all within ±0·003 Å of the plane $3{\cdot}270x-0{\cdot}452y-6{\cdot}505z=-0{\cdot}181$. However, most of the substituent atoms deviate from this plane by significant amounts: O(1), −0·004; O(2), 0·040; Cl, 0·068; N(2), 0·013; O(3), 0·023; C(6), −0·065 Å. The plane of the methylamine group, defined by C(4), N(2),

Table 2. *Structure factors in electrons* ×10

The $10\bar{2}$ reflection, not included in the refinement, showed $F_o=2120$, $F_c=2540$.

K	L	FOBS	FCAL
**	H =	0	**
2	0	472	486
4	0	289	285
6	0	104	105
8	0	426	441
10	0	163	157
12	0	123	117
14	0	199	204
16	0	62	61
22	0	153	147
1	1	61	[illegible]
2	1	515	529
3	1	216	210
4	1	65	61
5	1	118	115
6	1	331	318
7	1	852	876
8	1	138	140
9	1	187	180
10	1	388	371
11	1	162	163
12	1	41	26
14	1	66	69
15	1	168	166
17	1	37	29
18	1	191	199
19	1	130	133
21	1	94	89
23	1	48	50
0	2	392	407
1	2	88	85
3	2	63	68
4	2	608	613
5	2	196	190
7	2	77	74
8	2	272	275
9	2	156	155
11	2	259	254
12	2	158	156
13	2	145	148
14	2	272	271
15	2	90	88
18	2	155	163
19	2	105	109
20	2	44	28
21	2	55	58
22	2	74	66
24	2	48	28
1	3	187	194
2	3	224	226
3	3	228	233
4	3	330	333
5	3	370	370
6	3	336	338
7	3	68	72
8	3	52	47
9	3	46	44
11	3	357	357
12	3	65	63
15	3	289	301
16	3	131	127
17	3	181	182
19	3	81	74
20	3	87	89
21	3	38	17
23	3	58	51
24	3	69	53
0	4	46	43
1	4	206	207
2	4	170	178
3	4	106	102
4	4	247	251
5	4	162	160
6	4	104	106
7	4	73	77
8	4	201	195
9	4	179	177
10	4	151	152
12	4	128	128
13	4	130	134
14	4	167	159
16	4	108	106
17	4	183	166
18	4	63	68
19	4	46	26
21	4	81	80
22	4	49	47
23	4	49	40
1	5	306	316
2	5	260	270
3	5	316	321
4	5	272	275
5	5	105	106
8	5	164	168
9	5	124	124
10	5	86	62
11	5	131	132
13	5	121	119
14	5	133	136
19	5	71	63
20	5	63	33
21	5	57	51
22	5	41	1
0	6	85	86
1	6	65	63
2	6	92	92
4	6	52	43
5	6	208	214
6	6	177	185
8	6	49	51
9	6	159	161
10	6	106	104
11	6	81	79
12	6	58	60
13	6	184	187
14	6	138	131
15	6	77	68
16	6	51	35
17	6	62	56
18	6	49	54
19	6	53	56
2	7	100	108
4	7	95	97
5	7	56	56
6	7	101	93
7	7	64	70
8	7	48	30
11	7	43	26
12	7	163	163
14	7	51	51
15	7	42	29
16	7	61	60
18	7	55	38
0	8	42	43
1	8	97	112
2	8	53	35
3	8	54	47
5	8	83	78
9	8	82	85
11	8	70	52
12	8	89	85
14	8	46	35
16	8	41	0
1	9	39	18
2	9	128	132
4	9	45	48
5	9	53	44
6	9	57	61
8	9	46	47
10	9	80	80
11	9	40	17
0	10	57	55
3	10	69	73
4	10	65	63
5	10	58	47
**	H =	1	**
0	0	411	413
1	0	177	169
2	0	215	116
3	0	66	71
4	0	526	552
5	0	281	290
6	0	95	100
7	0	37	37
8	0	346	351
9	0	181	182
11	0	275	278
12	0	120	131
13	0	137	152
14	0	306	308
15	0	50	58
18	0	124	136
19	0	111	119
21	0	50	54
22	0	72	77
1	1	217	216
1	−1	308	304
2	1	279	270
2	−1	465	461
3	1	437	443
3	−1	196	192
4	1	463	464
4	−1	86	84
5	−1	95	93
5	1	537	542
6	1	418	408
6	−1	268	263
7	1	63	71
7	−1	792	812
8	−1	57	56
8	1	45	45
9	−1	120	115
9	1	100	93
10	−1	347	333
10	1	56	52
11	−1	177	183
11	1	399	410
12	1	125	127
14	−1	58	61
15	−1	155	156
15	1	345	360
16	1	91	95
17	1	225	234
18	−1	196	201
19	−1	85	92
19	1	99	97
20	−1	39	35
20	1	88	98
21	−1	90	93
22	1	92	40
23	−1	55	56
23	1	59	55
0	2	276	271
1	2	366	361
1	−2	284	281
2	2	120	116
2	−2	446	430
3	2	291	281
3	−2	82	79
4	2	469	457
4	−2	272	272
5	2	268	268
6	2	162	164
6	−2	116	117
7	2	160	160
7	−2	41	39
8	2	236	228
8	−2	318	315
9	−2	63	59
9	2	212	210
10	2	290	287
10	−2	164	158
12	−2	110	114
12	2	223	219
13	2	170	170
13	−2	35	23
14	−2	159	162
14	2	227	222
16	2	137	142
16	−2	49	43
17	2	198	208
18	2	146	137
21	2	103	100
22	2	58	63
22	−2	113	118
23	2	58	54
24	−2	41	22
1	−3	144	145
1	3	613	604
2	3	412	407
2	−3	291	286
3	−3	167	175
3	3	604	593
4	3	557	541
5	3	64	62
6	3	251	246
6	−3	206	208
7	−3	465	481
7	3	154	150
8	3	36	40
8	−3	119	122
9	−3	157	154
9	3	171	167
10	3	51	49
10	−3	238	226
11	−3	108	112
11	3	204	201
12	3	64	60
12	−3	61	53
13	3	88	93
14	3	182	186
14	−3	47	53
15	−3	117	110
16	3	46	26
17	3	56	53
18	3	55	44
18	−3	125	127
19	−3	128	130
19	3	95	94
20	3	49	37
21	3	77	71
21	−3	69	58
0	−4	135	135
0	4	173	175
1	4	34	28
1	−4	29	23
2	4	142	141
3	4	172	170
4	4	104	102
4	−4	329	333
5	−4	45	38
5	4	319	324
6	4	371	366
7	4	72	71
7	−4	57	59
8	−4	124	132
8	4	88	89
9	4	260	261
9	−4	84	82
10	4	159	160
11	4	173	169
11	−4	143	142
12	−4	126	123
12	4	61	58
13	4	265	274
13	−4	86	88
14	−4	174	175
14	4	241	238
15	4	70	72
15	−4	75	72
16	4	77	79
17	4	58	61
18	4	91	97
18	−4	139	134
19	−4	79	69
19	4	96	94
21	−4	44	46
22	−4	55	48
1	−5	122	126
2	−5	117	116
3	−5	72	67
4	−5	148	145
4	5	177	176
5	5	103	100
5	−5	149	151
6	−5	168	168
6	5	151	156
7	5	187	189
7	−5	77	75
8	−5	45	44
9	5	84	86
10	5	183	184
11	5	39	31
11	−5	195	193
12	5	284	294
13	5	47	50
13	−5	41	36
14	5	65	60
15	−5	191	185
16	−5	111	115
16	5	112	113
17	5	44	26
17	−5	99	97
18	5	76	67
19	5	49	38
20	5	77	77
20	−5	69	63
21	5	47	32
0	6	117	112
0	−6	36	28
1	−6	87	82
1	6	194	198
2	6	56	59
2	−6	95	98
3	6	101	111
4	6	55	47
4	−6	109	112
5	−6	76	70
5	6	159	166
6	−6	37	28
7	6	64	61
8	−6	113	110
9	−6	109	106
9	6	124	130
10	6	55	47
10	−6	53	50
11	6	101	106
12	6	134	132
12	−6	60	51
13	−6	78	74
14	−6	85	84
14	6	99	92
15	−6	44	34
16	−6	54	56
17	−6	95	96
17	6	94	85
1	−7	109	111
2	−7	120	126
2	7	242	251
3	−7	147	149
4	−7	109	103
4	7	144	148
5	7	98	100
6	7	100	94
6	−7	99	93
7	7	38	29
8	7	115	110
9	−7	61	60
10	7	151	157
11	−7	79	79
12	7	87	85
13	7	83	79
13	−7	90	89
14	−7	74	77
14	7	85	93
16	7	60	45
17	7	40	9
17	−7	51	8
0	8	92	103
1	8	41	27
1	−8	59	54
2	−8	57	52
2	8	68	67
3	8	177	184
3	−8	38	29
4	8	96	96
5	8	102	107
5	−8	107	109
6	−8	64	68
7	8	41	28
9	8	57	49
9	−8	74	73
10	−8	55	57
12	8	46	49
13	8	73	62
13	−8	105	97
14	−8	65	52
15	−8	52	47
1	−9	40	3
2	−9	54	45
5	9	49	42
6	9	63	63
6	−9	51	37
10	9	43	23
12	−9	78	73
1	−10	62	52
1	10	82	78
5	10	49	33
**	H =	2	**
0	0	277	267
1	0	340	333
2	0	45	45
3	0	311	313
4	0	387	396
5	0	266	267
6	0	174	185
7	0	129	131
8	0	212	207
9	0	149	151
10	0	282	282
12	0	208	213
13	0	147	154
14	0	181	182
15	0	47	39
16	0	150	151
17	0	178	181
18	0	166	163
21	0	81	83
22	0	67	62
23	0	64	50
24	0	45	6
1	−1	210	211
1	1	662	640
2	−1	163	154
2	1	342	325
3	−1	326	338
4	−1	309	319
4	1	627	602
5	1	77	71
5	−1	339	344
6	−1	260	260
6	1	248	245
7	1	220	206
7	−1	104	105
8	−1	36	26
8	1	78	70
9	−1	114	119
9	1	144	145
10	−1	77	80
11	−1	254	271
11	1	233	237
12	−1	87	91
12	1	64	65
13	1	37	16
13	−1	49	49
14	−1	42	49
14	1	180	185
15	−1	308	319
16	1	45	48
17	1	61	60
17	−1	199	203
18	1	43	48
19	1	101	103
19	−1	86	83
20	−1	83	77
21	1	74	69
23	−1	54	54
24	1	61	42
0	2	239	233
0	−2	195	190
1	−2	150	147
2	−2	104	102
2	2	201	187
3	2	291	281
3	−2	36	31
4	−2	275	284
4	2	197	195
5	2	326	321
5	−2	199	197
6	−2	113	113
6	2	458	434
7	2	126	121
8	2	84	91
8	−2	217	227
9	−2	125	123
9	2	291	292
10	2	207	207
11	2	237	240
11	−2	178	178
12	−2	78	77
13	−2	84	84
13	2	275	283
14	2	283	294
14	−2	228	233
15	2	52	50
16	2	94	91
17	−2	43	46
18	−2	88	78
18	2	127	130
19	2	108	110
19	−2	88	91
22	−2	72	68
22	2	61	41
23	−2	43	19
1	−3	215	218
2	−3	222	219
2	3	232	223
3	−3	177	176
4	−3	46	45
4	3	266	253
5	3	113	113
6	3	171	165
6	−3	110	112
7	−3	410	411
7	3	336	329
9	−3	51	42
10	−3	182	178
10	3	256	257
11	−3	159	155
12	3	383	396
13	3	113	116
15	−3	85	88
16	3	150	147
18	3	90	87
18	−3	135	133
19	−3	46	44
19	3	46	41
20	3	96	93
21	3	63	56
21	−3	75	63
23	−3	48	37
0	−4	993	1024
0	4	241	239
1	4	284	281
1	−4	236	236
2	−4	240	239
2	4	115	115
3	4	179	179
3	−4	62	64
4	−4	154	154
5	4	268	263
6	4	38	24
6	−4	51	58
7	4	113	110
8	−4	176	178
9	−4	74	68
9	4	137	137
10	4	78	77
10	−4	128	122
11	4	153	163
12	4	137	140
12	−4	77	79
13	−4	38	31
13	4	46	42
14	4	154	163
14	−4	99	91
17	4	129	126
19	4	51	51
21	4	45	37
22	−4	64	64
1	−5	79	81
1	5	50	50
2	5	354	360
2	−5	145	141
3	−5	71	71
4	5	305	307
5	5	152	145
6	5	109	105
6	−5	100	96
7	−5	190	185
7	5	86	84
8	5	179	187
8	−5	74	69
9	−5	80	76
9	5	52	51
10	5	226	233
10	−5	104	102
11	−5	57	53
12	−5	47	45
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13	5	123	127
14	5	128	128
15	−5	54	50
16	5	72	64
17	5	38	14
18	−5	55	53
19	−5	94	87
20	5	80	79
0	−6	36	40
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1	6	99	103
2	6	126	127
3	6	343	355
4	6	87	101
4	−6	135	140
5	6	179	178
6	6	60	59
7	6	58	52
8	6	47	46
8	−6	39	40
9	−6	47	34
9	6	97	96
10	6	40	34
11	6	58	50
11	−6	64	58
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12	6	53	34
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19	6	45	40
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1	7	42	44
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2	−7	47	48
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3	7	37	13
4	−7	59	53
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5	7	60	64
6	−7	70	66
7	−7	47	47
7	7	61	61
8	7	84	86
8	−7	40	29
9	7	51	42
10	7	57	54
11	−7	76	72
12	7	59	49
13	−7	68	38
14	7	92	94
15	7	68	49
15	−7	90	87
16	−7	77	75
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17	−7	49	38
1	8	139	145
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2	−8	49	37
4	−8	47	42
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5	8	79	74
7	8	97	98
8	−8	51	44
9	−8	46	46
9	8	115	118
10	8	46	13
13	8	113	106
13	−8	50	29
14	−8	44	39
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2	−9	48	46
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8	0	75	74
9	0	199	203
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11	0	219	224
12	0	55	54
13	0	193	196
14	0	238	247
16	0	53	53
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21	0	42	11
22	0	44	36
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7	1	326	329
7	−1	113	109
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11	−1	185	186
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12	1	352	365
13	1	140	145
14	−1	134	137
15	−1	49	43
15	1	36	13
16	1	130	134
16	−1	44	51
17	−1	55	52
18	1	89	83
19	−1	83	80
20	1	90	86
21	1	68	52
21	−1	59	49
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15	2	40	15
16	−2	123	123
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21	2	49	43
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3	−3	173	174
3	3	51	48
4	3	411	411
4	−3	119	127
5	−3	130	132
5	3	127	121
6	3	96	96
6	−3	82	84
7	−3	97	97
7	3	145	146
8	3	199	207
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9	3	54	53
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11	−3	123	126
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13	3	130	136
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18	3	38	18
19	−3	52	50
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20	3	83	88
21	3	77	55
21	−3	40	12
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7	4	70	62
8	−4	91	93
9	−4	69	65
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10	−4	49	43
11	−4	72	73
11	4	51	61
12	4	43	40
13	4	167	168
14	4	105	103
14	−4	126	120
17	4	79	73
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18	4	47	27
19	4	57	50
19	−4	69	52
20	4	48	47
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1	−5	129	138
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3	−5	106	119
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5	5	67	66
6	5	218	213
6	−5	40	37
7	−5	169	168
8	5	131	128
9	5	86	88
10	5	93	86
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11	−5	97	96
12	5	62	64
14	5	128	122
15	5	100	92
15	−5	35	29
16	5	185	181
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18	−5	68	62
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8	−6	90	94
9	−6	49	55
9	6	182	181
10	−6	74	69
11	6	52	44
13	6	163	164
14	6	56	44
14	−6	54	39
15	6	106	104
16	6	89	90
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2	−7	65	71
2	7	188	195
3	7	115	113
3	−7	41	12
4	−7	39	20
4	7	45	27
5	7	82	83
5	−7	39	10
6	−7	43	39
6	7	123	130
7	7	60	49
7	−7	65	55
8	−7	42	28
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8	−8	39	6
8	8	54	62
9	8	91	93
11	−8	48	23
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2	9	103	102
3	9	64	72
5	−9	50	30
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5	0	167	172
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8	0	69	73
9	0	76	82
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11	0	140	146
12	0	44	36
13	0	78	76
14	0	128	126
17	0	105	101
19	0	44	33
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3	−1	50	44
3	1	78	66
4	−1	139	136
5	1	69	65
6	−1	51	36
6	1	86	81
7	−1	205	207
7	1	150	157
8	−1	39	35
8	1	147	151
9	−1	56	54
9	1	45	28
10	−1	167	177
10	1	179	184
11	−1	48	39
11	1	54	57
12	1	133	136
13	−1	113	118
13	1	97	99
14	1	85	81
15	1	72	77
16	−1	87	85
16	1	63	57
17	−1	40	34
18	−1	70	58
20	−1	60	62
20	1	69	65
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0	2	51	59
1	2	170	170
2	2	85	82
2	−2	79	82
3	−2	166	173
3	2	451	450
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5	−2	80	77
5	2	221	220
6	2	58	54
7	2	51	46
7	−2	61	70
8	−2	63	51
9	−2	81	84
9	2	133	135
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12	−2	65	71
13	−2	97	98
13	2	169	177
14	−2	149	150
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19	−2	48	42
19	2	53	46
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6	3	236	230
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7	−3	42	32
8	−3	51	42
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9	3	107	105
9	−3	60	63
10	−3	39	19
10	3	98	89
11	−3	109	103
12	−3	59	45
13	−3	52	43
14	−3	76	80
14	3	128	118
15	3	120	114
16	3	164	160
17	3	77	69
18	3	43	24
19	−3	48	42
0	−4	37	11
1	−4	63	67
1	4	213	212
3	4	107	104
3	−4	69	70
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6	5	172	178
7	5	52	47
7	−5	61	61
8	5	94	93
9	5	43	34
9	−5	48	23
10	−5	41	24
10	5	47	38
11	−5	48	65
13	−5	40	23
15	−5	108	108
15	5	82	85
17	−5	74	68
0	6	50	35
1	6	198	197
1	−6	49	58
2	−6	45	28
4	−6	45	45
4	6	71	60
5	6	121	118
7	6	46	34
8	6	75	76
9	6	131	133
10	−6	67	59
12	6	104	100
13	6	93	86
15	−6	44	18
1	−7	59	70
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2	7	175	182
2	−7	43	32
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3	7	81	76
4	7	66	61
4	−7	40	5
5	7	85	82
6	7	128	126
7	−7	50	57
8	7	77	62
10	7	53	45
10	−7	45	22
11	−7	55	47
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0	8	173	177
1	8	79	70
1	−8	69	75
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2	8	61	60
3	8	57	47
4	8	75	81
4	−8	42	17
8	−8	45	38
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14	0	54	62
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3	−1	67	62
4	1	91	93
4	−1	179	186
5	−1	43	32
6	1	177	176
6	−1	50	50
7	1	55	61
7	−1	110	111
8	1	91	92
8	−1	68	73
9	1	72	74
10	1	64	59
10	−1	99	96
11	−1	47	50
12	−1	72	85
13	−1	52	55
14	1	79	89
15	1	102	99
15	−1	65	66
16	1	103	96
16	−1	46	36
17	1	69	59
0	−2	123	122
1	2	156	158
1	−2	82	82
2	2	55	42
3	2	117	106
4	2	57	50
4	−2	43	33
5	2	93	94
5	−2	76	66
6	2	58	64
7	2	95	104
8	2	77	73
8	−2	53	44
9	2	169	163
9	−2	60	55
11	−2	98	96
12	2	45	17
13	2	156	160
13	−2	61	49
14	−2	66	55
15	2	102	93
16	2	98	92
2	3	230	235
2	−3	75	84
3	−3	48	45
3	3	98	96
4	−3	65	62
5	3	56	48
6	3	170	174
7	−3	99	93
9	−3	38	4
10	−3	96	97
12	3	79	75
12	−3	107	108
13	3	42	25
13	−3	76	73
15	3	85	89
0	4	86	83
0	−4	90	94
1	4	184	184
2	4	42	22
2	−4	43	41
3	−4	71	88
4	−4	80	76
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5	4	109	117
6	−4	57	50
8	4	67	73
9	4	125	137
10	4	61	47
10	−4	58	50
11	−4	79	79
12	−4	58	51
12	4	99	89
13	4	75	87
13	−4	57	35
14	−4	68	70
1	−5	48	60
1	5	124	123
2	5	223	229
3	5	62	60
4	5	61	62
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6	5	142	140
6	−5	48	42
7	5	42	13
8	5	70	63
9	5	43	19
9	−5	40	36
10	5	62	69
11	5	122	128
11	−5	57	37
13	−5	46	31
0	6	232	237
1	6	68	66
2	6	88	77
3	6	70	65
3	−6	40	27
4	6	97	96
5	6	122	118
6	6	59	38
2	−7	43	3
3	−7	45	21
**	H =	6	**
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3	0	76	74
7	0	48	51
8	0	59	48
9	0	84	90
12	0	50	16
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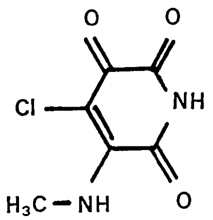
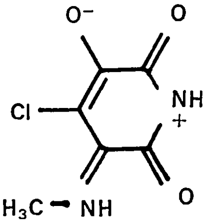
2	1	146	148
4	−1	66	66
5	−1	40	20
6	−1	91	101
6	1	118	121
8	−1	57	50
8	1	46	40
0	2	90	87
1	−2	60	63
1	2	132	124
2	−2	48	34
3	−2	136	146
4	2	45	36
5	−2	108	110
5	2	73	81
8	2	62	54
9	2	101	100
9	−2	49	54
10	2	46	18
1	−3	65	70
1	3	73	70
2	−3	57	63
2	3	202	206
3	−3	48	45
4	−3	81	81
4	3	55	50
5	3	78	74
6	3	117	110
7	−3	74	59
8	3	67	52
9	−3	40	8
9	3	41	14
0	−4	52	43
0	4	231	234
2	4	90	81
3	−4	40	20
3	4	55	68
4	4	90	88
5	4	118	119
2	−5	44	40
5	−5	44	7

and C(6), forms a dihedral angle of 4·6° with the ring plane given above.


(II)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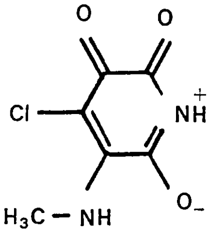
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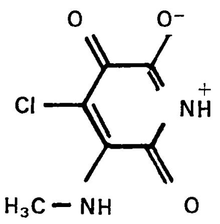
(V)

The bond distances (Table 3) largely reflect the contributions of four principal valence structures (II–V), which are given in their apparent order of importance. All four forms require single bonds at C(1)–C(2) and C(4)–C(5), as verified by the respective bond lengths of 1·539 and 1·514 Å. The most important ionic form is clearly (III), since C(4)–N(2) (1·311 Å) is the shortest C–N distance, and C(2)–O(2) (1·225 Å) is the longest carbonyl bond. The C–N bonds in the ring, C(1)–N(1) (1·380 ± 0·004 Å) and C(5)–N(1) (1·368 ± 0·004 Å) are, as expected, longer than the C–N bonds of 1·340 in pyridine itself (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958). The differences between the distances C(1)–N(1) and C(5)–N(1) and between C(1)–O(1) and C(5)–O(3) are significant at the 3σ level and suggest that structure (IV) contributes slightly more than V. Not surprisingly, the shortest C–C bond is C(3)–C(4) (1·388 Å) followed by C(3)–C(2) (1·404 Å).

Table 3. *Bond distances and angles with standard errors*

Errors in parentheses refer to the last significant digit given, and were calculated from the variance-covariance matrix obtained in the final least-squares cycle.

Distances (Å)		Angles (°)	
N(1)–C(1)	1·380 (4)	N(1)—C(1)–C(2)	117·0 (3)
C(1)–C(2)	1·539 (4)	C(1)—C(2)—C(3)	118·1 (3)
C(2)–C(3)	1·404 (4)	C(2)—C(3)–C(4)	122·6 (3)
C(3)–C(4)	1·388 (4)	C(3)—C(4)–C(5)	119·0 (3)
C(4)–C(5)	1·514 (4)	C(4)—C(5)–N(1)	117·8 (3)
C(5)–N(1)	1·368 (4)	C(5)—N(1)–C(1)	125·4 (3)
C(1)–O(1)	1·194 (4)	N(1)—C(1)–O(1)	122·3 (3)
C(2)–O(2)	1·225 (3)	O(1)—C(1)–C(2)	120·7 (3)
C(3)–Cl	1·725 (3)	C(1)—C(2)–O(2)	116·2 (3)
C(4)–N(2)	1·311 (4)	O(2)—C(2)–C(3)	125·6 (3)
N(2)–C(6)	1·466 (5)	C(2)—C(3)–Cl	113·6 (2)
C(5)–O(3)	1·205 (4)	Cl—C(3)—C(4)	123·7 (2)
		C(3)—C(4)–N(2)	129·7 (3)
N(1)–H(1)	0·84 (3)	C(4)—N(2)–C(6)	129·6 (3)
N(2)–H(2)	0·88 (3)	N(2)—C(4)–C(5)	111·2 (3)
C(6)–H(6A)	1·01 (4)	C(4)—C(5)–O(3)	120·2 (3)
C(6)–H(6B)	0·98 (5)	O(3)—C(5)–N(1)	122·0 (3)
C(6)–H(6C)	0·92 (4)		
Water O–H	0·87 (4)	C(5)—N(1)–H(1)	117 (2)
	0·77 (4)	C(1)—N(1)–H(1)	117 (2)
		C(4)—N(2)–H(2)	117 (2)
		C(6)—N(2)–H(2)	113 (2)
		N(2)—C(6)–H(6A)	105 (2)
		N(2)—C(6)–H(6B)	107 (3)
		N(2)—C(6)–H(6C)	107 (3)
		H(6A)–C(6)–H(6B)	114 (4)
		H(6A)–C(6)–H(6C)	115 (3)
		H(6B)–C(6)–H(6C)	108 (4)
		H–O–H (water)	107 (4)

Resonance structure (III) is undoubtedly responsible for the methylamine ligand adopting a conformation coplanar with the ring. The bond angles C(6)–N(2)–C(4) (129·6°), N(2)–C(4)–C(3) (129·7°), and C(4)–C(3)–Cl (123·7°) are all significantly greater than the trigonal angle, indicating that this conformation is not achieved without some cost in strain energy. The locations of the methyl hydrogens are also consistent with a very close chlorine–methyl contact. The C(1)–N(1)–C(5) angle of 125·4° is typical for nitrogen atoms bearing an extra-annular hydrogen atom in 6-membered rings (Chatar Singh, 1965).

The crystal structure (Fig. 2) consists of two-dimensional sheets corresponding to the $\{10\bar{2}\}$ planes and held together by hydrogen bonds. One of the two water protons is approximately equidistant from oxygen atoms O(1) and O(2) of the basic molecule, as can be seen in Fig. 1, while the second water proton is directed toward O(3) of a molecule related by $x-1, \frac{1}{2}-y, z-\frac{1}{2}$.

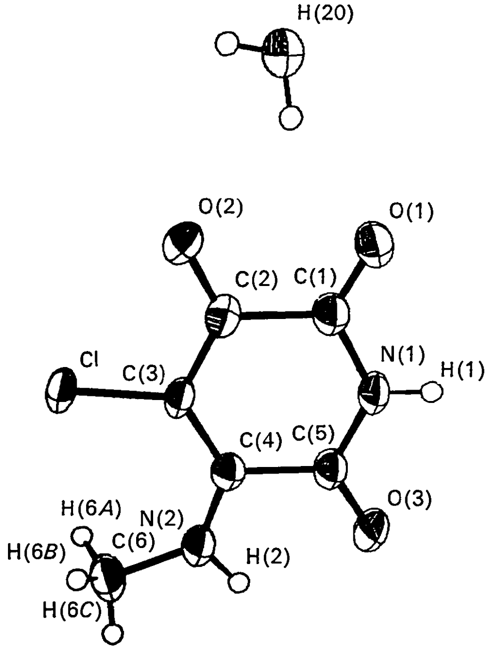

Fig. 1. Molecular structure with thermal ellipsoids drawn at 50% probability of occupancy.

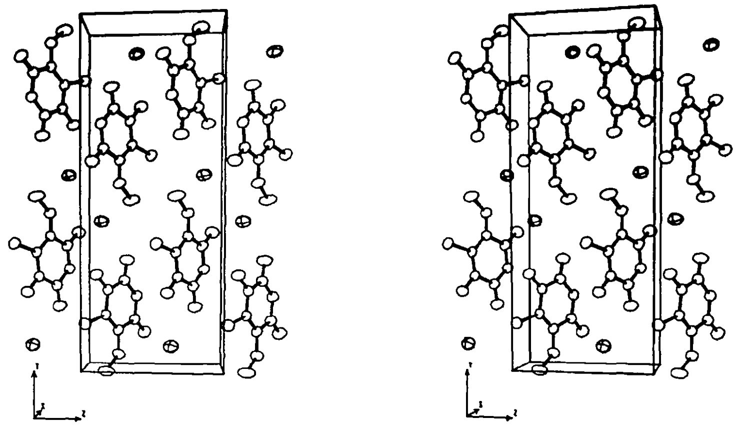

Fig. 2. Three-dimensional view of the crystal structure of 4-chloro-5-methylamino-2,3,6-pyridinetrione monohydrate.

The O–H···O distances are 3·001, 3·011, and 2·864 Å to O(1), O(2) and O(3) respectively. In addition, the amine [N(2)] hydrogen of a molecule related by $1-x,\frac{1}{2}+y,\frac{1}{2}-z$ forms an N–H···O bond of 2·808 Å to the H_2O oxygen. The basic molecule and that related by $x-1,\frac{1}{2}-y,z-\frac{1}{2}$ may also interact weakly through an N(1)–H···O(2) contact of 3·117 Å. We note that these hydrogen-bonded interactions are not only critical in determining the crystal structure of the monohydrate, but also may play an important role in stabilizing the valence structures inferred from the molecular bond lengths.

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The Crystal and Molecular Structure of the Tetraphenylarsonium Salt of the Monoanion of Adenine, $[C_{24}H_{20}As]^+[C_5N_5H_4]^-. 3H_2O$*

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The tetraphenylarsonium salt of the monoanion of adenine crystallizes from aqueous solution as the trihydrate. The crystals are monoclinic, space group $P2_1/n$, with $a=9·878$ (4), $b=21·347$ (7), $c=13·407$ (4) Å, $\beta=103·19$ (3)° and $Z=4$. 2982 independent intensities (2418 above zero) were collected by counter methods. A structural solution was obtained by the heavy-atom method. The adenine anion is disordered in the crystal and accurate values for its bond lengths and angles have not been obtained. Full-matrix least-squares refinement based on the 2418 non-zero *F*'s led to an *R* value of 0·103 with all atoms treated isotropically.

Introduction

Our recent interest in the coordination chemistry of purines and pyrimidines (Kistenmacher, Marzilli & Chang, 1973) has led to the synthesis and structural investigation of several cobalt(III) complexes containing the monoanion of adenine (I) as a coordinated ligand. In an effort to compare the bond lengths and angles in the free anion *versus* those in the complexed anion, we have undertaken a structural study of the tetraphenylarsonium salt of the monoanion of adenine. Our efforts to obtain accurate dimensions have been thwarted by a disordering of the adenine anions.

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