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Crystallographic Studies of Metal–Nucleotide Base Complexes. IV.* Tetraaquo-(9-methyladenine)copper(II) Sulphate Monohydrate

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Tetraaquo-(9-methyladenine)copper(II) sulphate monohydrate is triclinic, space group $P\bar{1}$, with $Z=2$, $a=14{\cdot}079$, $b=7{\cdot}150$, $c=7{\cdot}853$ Å, $\alpha=100{\cdot}52$, $\beta=75{\cdot}87$, $\gamma=107{\cdot}98°$. The structure was determined from counter intensities measured with Nb-filtered Mo $K\alpha$ radiation. Final $R=0{\cdot}026$ for the 2911 reflexions above the threshold value. The copper ion is octahedrally surrounded, the equatorial positions being occupied by one adenine molecule coordinated through N(7), Cu–N(7) = 1·995 Å, the other three sites being occupied by water molecules. The axial positions are occupied by the sulphate group and a water molecule. Centrosymmetrically related adenine molecules are hydrogen-bonded through N(1) and the amino group. The adenine ligands are stacked the same way as in the crystal structure of the uncomplexed molecule. The amino group is hydrogen-bonded to the coordinated sulphate oxygen, thus completing an indirect chelate formation involving N(6)···SO_4^{2-}–Cu^{2+}–N(7).

Introduction

A systematic investigation of metal bonding to nucleic acid components is in progress at this laboratory. Recently the crystal structure of the copper complex of a nucleoside analogue of hypoxanthine has been published (Sletten, 1974: see this paper for references to related crystal investigations).

The present paper presents the crystal structure of a copper–adenosine analogue, 1:1 copper–9-methyladenine.

Experimental

The compound was synthesized by dissolving 9-methyladenine in 1N H_2SO_4 and adding saturated $CuSO_4$ solution (Weiss & Venner, 1963). The mixture was heated under dropwise addition of 1N NaOH until pH $\sim$4. The green solution was filtered and ethanol was added. After approximately 4 h, turquoise crystals appeared. The crystal used had dimensions $0{\cdot}3\times0{\cdot}5\times0{\cdot}1$ mm.

Crystal data

$[(C_6H_7N_5)Cu(H_2O)_4]SO_4.H_2O$, F.W. 398·8, space group $P\bar{1}$, $a=14{\cdot}079$ (3), $b=7{\cdot}150$ (3), $c=7{\cdot}853$ (2) Å, $\alpha=100{\cdot}52$ (2), $\beta=75{\cdot}87$ (2), $\gamma=107{\cdot}98$ (2)°. $D_m=1{\cdot}83$, $D_x=1{\cdot}83$ g cm^{-3}, $Z=2$, $\lambda(\text{Mo } K\alpha)=0{\cdot}71069$ Å, $\mu=17{\cdot}58$ cm^{-1}.

Integrated intensities were measured on an off-line Siemens four-circle diffractometer. The experimental procedure has been described elsewhere (Sletten, 1974). Within the sphere of reflexion limited at $\sin\theta/\lambda=0{\cdot}64$, 3156 unique reflexions were recorded. Of these, 245 were less than the threshold value of $2\sigma_c$, where σ_c is the error due to counting statistics. The two standard reflexions monitored during data collection showed individual fluctuations of ±2%. After collecting approximately 1000 reflexions the intensities suddenly dropped by about 4%. Since the crystal would not be expected to deteriorate abruptly the incident must be ascribed to electronic instability.

The expression $\sigma_I=[\sigma_c^2+(0{\cdot}02\sigma_c^2)^2]^{1/2}$ was used to calculate the random error in any one reflexion. The standard deviations in the structure factors were calculated according to $\sigma_F=\sigma_I/2(I\,\text{Lp})^{1/2}$. The data were corrected for Lorentz and polarization effects according to normal beam geometry. Absorption correction was carried out by a modified Busing & Levy (1957) procedure. The crystal was divided in a Gaussian grid of $8\times10\times10$ points, and six boundary planes were defined. The transmission coefficients lay in the range 0·83–0·94.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to an R of 0·026 ($R=\sum||F_o|-|F_c||/\sum|F_o|$). All non-hydrogen atoms were refined isotropically. H(11) on the water molecule with highest thermal motion did not refine satisfactorily and is probably disordered.

The final difference map showed the usual pattern of electron densities in the middle of each bond, ranging from 0·15 to 0·25 e Å^{-3}. Several negative regions of as much as 0·2 e Å^{-3} were found in the map. The positions of the four oxygen atoms in the sulphate group had positive peaks of roughly 0·2 e Å^{-3}, while the sulphur position was surrounded by three distinct, negative regions of 0·2 e Å^{-3}.

Scattering factors used for Cu, O, N, C, S are those given in *International Tables for X-ray Crystallography* (1962), and for H the curve published by Stewart, Davidson & Simpson (1965).

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Table 1. *Observed and calculated structure factors* (× 10)

Table 1 (*cont.*)

-4	387	-376
-3	41	-32
-2	100	95
-1	378	377
0	565	562
1	566	550
2	79	-75
3	43	-47
4	112	-110
5	127	125
6	173	180
7	316	317
8	216	221
9	73	-31
10	151	-164
11	181	-181
12	-22	-15
13	53	40
14	148	151
H, 3, 2		
-16	142	140
-15	146	149
-14	235	240
-13	31	-23
-12	369	-373
-11	97	-100
-10	312	-308
-9	52	49
-8	242	241
-7	82	87
-6	86	-90
-5	449	-450
-4	427	-436
-3	120	-128
-2	209	-195
-1	476	494
0	278	286
1	99	-100
2	363	-379
3	163	-186
4	274	-264
5	236	226
6	224	221
7	52	51
8	73	67
9	347	-343
10	43	-37
11	152	-151
12	89	85
13	141	139
14	55	54
H, 3, 3		
-15	28	-19
-14	91	-87
-13	74	-75
-12	96	85
-11	228	237
-10	184	185
-9	-20	-9
-8	145	-149
-7	352	-356
-6	230	-233
-5	233	233
-4	468	453
-3	361	361
-2	73	73
-1	255	-261
0	377	-383
1	314	-308
2	63	64
3	317	313
4	300	307
5	113	111
6	223	-224
7	391	-390
8	236	-242
9	113	-121
10	330	303
11	148	143
12	138	143
13	103	-101
14	132	-135
H, 3, 4		
-13	30	-25
-12	137	135
-11	125	128
-10	133	128
-9	139	-135
-8	65	-51
-7	155	-159
-6	28	25
-5	185	188
-4	375	373
-3	306	304
-2	57	-71
-1	169	-173
0	65	-71
1	76	77
2	158	165
3	347	355
4	40	-36
5	146	-147
6	143	-149
7	56	-53
8	-21	27
9	-22	-9
10	110	104
11	-22	7
12	57	-55
13	-24	-5
H, 3, 5		
-12	52	-55
-11	241	-243
-10	274	-282
-9	198	-196
-8	167	167
-7	335	330
-6	204	209
-5	164	-171
-4	218	-213
-3	440	-447
-2	277	-273
-1	429	428
0	153	155
1	368	372
2	205	-203
3	164	-161
4	329	-326
5	253	-267
6	158	173
7	210	201
8	157	157
9	45	33
10	63	-54
11	157	-183
12	132	-134
H, 3, 6		
-10	-22	-1
-9	29	34
-8	157	153
-7	92	93
-6	-26	-25
-5	-20	-16
-4	45	-45
-3	40	-38
-2	27	23
-1	130	136
0	65	-68
1	37	36
2	115	-111
3	31	34
4	24	-14
5	69	-73
6	109	110
7	-23	-21
8	-23	26
9	-23	5
10	28	13
11	-24	9
H, 3, 7		
-8	85	-88
-7	188	-197
-6	133	-131
-5	29	-25
-4	167	161
-3	190	197
-2	103	99
-1	-22	-18
0	204	-199
1	245	-243
2	124	-123
3	30	25
4	235	236
5	140	135
6	-23	-13
7	144	-146
8	243	-241
9	84	-82
H, 3, 8		
-4	-22	18
-3	46	41
-2	55	-51
-1	-23	-5
0	35	-30
1	99	103
2	41	45
3	58	58
4	52	-53
5	72	-78
6	-24	5
7	46	51
H, -4, 9		
11	60	61
10	70	77
9	63	-61
8	-23	-1
7	46	-52
6	35	-41
5	150	151
4	162	155
3	-22	26
2	26	-23
1	162	-163
0	-22	0
H, -4, 8		
13	137	138
12	145	145
11	36	-36
10	230	-227
9	308	-313
8	100	-103
7	88	87
6	182	182
5	191	191
4	-25	-16
3	177	-173
2	244	-240
1	108	-108
0	134	135
-1	150	149
-2	122	122
-3	51	55
H, -4, 7		
15	173	179
14	55	65
13	-22	-11
12	188	-188
11	132	-135
10	83	-86
9	137	139
8	251	252
7	120	133
6	128	-133
5	286	-293
4	71	-69
3	-19	19
2	147	151
1	251	253
0	-20	12
-1	89	-89
-2	128	-132
-3	-21	-6
-4	26	27
-5	32	17
-6	151	147
H, -4, 6		
16	176	176
15	90	91
14	96	-96
13	225	-225
12	138	-132
11	111	113
10	73	65
9	186	186
8	96	91
7	104	-103
6	52	-47
5	165	-161
4	-18	17
3	28	-18
2	138	132
1	153	158
0	-19	-12
-1	226	-229
-2	88	-93
-3	121	-122
-4	27	34
-5	75	74
-6	-21	4
-7	66	-59
H, -4, 5		
17	-22	8
16	188	-184
15	196	-195
14	70	-72
13	-20	-17
12	249	251
11	81	87
10	41	46
9	98	-98
8	319	-319
7	139	-146
6	168	172
5	246	253
4	351	358
3	48	50
2	102	-103
1	280	-282
0	91	-91
-1	50	56
-2	326	325
-3	148	143
-4	98	97
-5	141	-137
-6	331	-327
-7	24	-23
-8	59	-63
-9	232	231
H, -4, 4		
17	37	-31
16	62	-63
15	85	-76
14	27	27
13	123	120
12	-26	-10
11	-18	4
10	30	-27
9	75	-71
8	64	-51
7	57	55
6	168	158
5	127	119
4	-31	-16
3	71	-70
2	185	-182
1	-16	-7
0	246	256
-1	186	189
-2	89	89
-3	108	-103
-4	168	-163
-5	63	-61
-6	51	55
-7	219	214
-8	71	65
-9	137	133
-10	57	-65
H, -4, 3		
17	32	-33
16	66	65
15	214	219
14	112	108
13	60	62
12	341	-346
11	323	-330
10	199	-209
9	278	298
8	343	347
7	292	285
6	176	-166
5	470	-483
4	513	-525
3	240	-237
2	278	275
1	156	170
0	133	132
-1	185	-187
-2	328	-325
-3	573	-526
-4	231	-237
-5	115	111
-6	216	211
-7	198	196
-8	-21	13
-9	139	-132
-10	251	-252
-11	89	-75
H, 4, 2		
-17	68	71
-16	92	97
-15	75	-75
-14	133	-142
-13	77	72
-12	44	45
H, -4, 2		
11	180	183
10	329	332
9	231	196
8	142	-146
7	25	20
6	91	-88
5	147	147
4	207	209
3	326	346
2	751	759
1	570	-570
0	27	-24
-1	327	-321
-2	102	-102
-3	265	266
-4	329	339
-5	267	270
-6	146	-146
-7	164	-176
-8	69	-75
-9	20	15
-10	64	65
-11	173	176
-12	49	45
H, 4, -1		
-17	62	64
-16	110	-109
-15	344	-342
-14	225	-232
-13	20	-21
-12	169	164
-11	399	398
-10	226	223
-9	217	-213
-8	622	-622
-7	357	-354
-6	-15	-4
-5	189	191
-4	531	549
H, -4, 1		
3	195	191
2	113	-125
1	732	-724
0	203	-213
-1	143	-139
-2	207	209
-3	404	398
-4	204	208
-5	31	27
-6	264	-262
-7	103	-98
-8	38	-41
-9	112	107
-10	65	60
-11	138	113
-12	63	-70
H, 4, 0		
-17	165	-166
-16	-31	-26
-15	141	143
-14	154	152
-13	216	213
-12	110	-112
-11	123	-119
-10	363	-358
-9	138	-139
-8	57	67
-7	351	349
-6	260	254
-5	23	-19
-4	413	-422
-3	686	-695
-2	271	-262
-1	193	145
0	359	359
1	393	396
2	76	-73
3	264	-261
4	207	-214
5	27	-25
H, -4, 0		
-6	147	147
-7	215	218
-8	174	175
-9	67	67
-10	143	-140
-11	89	-86
-12	91	-87
H, 4, 1		
-16	102	96
-15	233	235
-14	310	304
-13	154	145
-12	218	-210
-11	125	-121
-10	327	-326
-9	363	369
-8	194	201
-7	256	262
-6	178	168
-5	222	-226
-4	123	-130
-3	178	-178
-2	23	-25
-1	38	-27
0	224	230
1	163	157
2	133	135
3	175	-176
4	130	-130
5	33	-35
6	22	16
7	172	155
8	106	103
9	165	-155
10	84	-81
11	115	-115
12	30	31
H, 4, 2		
-15	136	-135
-14	231	-235
-13	181	-184
-12	-19	1
-11	248	255
-10	119	115
-9	118	123
-8	208	-203
-7	259	-252
-6	241	-236
-5	230	-228
-4	393	382
-3	202	205
-2	248	238
-1	-16	-6
0	245	-263
1	411	-436
2	-18	0
3	154	157
4	435	437
5	165	155
6	72	-76
7	245	-245
8	391	-390
9	118	-117
10	127	126
11	146	144
12	125	122
H, 4, 3		
-14	127	-128
-13	76	-73
-12	27	11
-11	140	139
-10	28	33
-9	-18	-8
-8	91	97
-7	254	-250
-6	131	-136
-5	66	52
-4	106	104
-3	188	183
-2	-18	5
-1	125	112
0	95	-103
1	58	-55
2	330	329
3	189	193
4	63	57
5	67	-66
6	64	-69
7	-20	-2
8	45	44
9	185	186
10	24	21
11	-23	-2
12	64	-71
H, 4, 4		
-13	163	159
-12	84	33
-11	120	-115
-10	293	-295
-9	154	-151
-8	41	-47
-7	256	250
-6	254	253
-5	188	190
-4	300	-303
-3	518	-520
-2	288	-283
-1	135	133
0	299	334
1	334	336
2	48	45
3	281	-283
4	398	-430
5	235	-235
6	22	22
7	131	123
8	135	138
9	76	72
10	55	-56
11	171	-175
H, 4, 5		
-11	33	-35
-10	-21	10
-9	102	106
-8	93	87
-7	68	72
-6	161	-155
-5	-20	15
-4	22	15
-3	61	52
-2	248	247
-1	24	15
0	46	49
1	130	-128
2	106	-106
3	48	52
4	36	-38
5	42	38
6	117	120
7	117	-125
8	52	-51
9	58	-56
10	-24	-13
H, 4, 6		
-9	111	117
-8	-22	-1
-7	185	-181
-6	238	-238
-5	-21	-3
-4	126	127
-3	227	222
-2	233	231
-1	46	49
0	104	-107
1	230	-236
2	50	-41
3	-22	5
4	146	167
5	177	182
6	100	103
7	73	-77
8	166	-156
9	49	-45
H, 4, 7		
-6	30	25
-5	79	71
-4	25	-22
-3	43	-57
-2	76	-75
-1	134	-131
0	62	-53
1	69	70
2	34	38
3	68	53
4	87	-93
5	115	-113
6	96	-94
7	-24	-1
H, 4, 8		
-1	-23	-15
0	48	48
1	122	123
2	38	40
H, -5, 9		
9	170	-173
8	27	-23
7	36	-34
6	78	78
5	133	137
4	83	-83
3	33	-34
H, -5, 8		
12	131	-100
11	156	-158
10	30	-31
9	122	125
8	206	210
7	107	109
6	62	-64
5	120	-119
4	257	-259
3	82	-81
2	82	80
1	249	253
0	115	112
-1	-21	-5
H, -5, 7		
14	35	37
13	147	-149
12	32	-26
11	58	-51
10	120	122
9	155	158
8	61	55
7	26	-29
6	116	-113
5	44	-47
4	39	37
3	95	95
2	170	168
1	116	114
0	30	24
-1	53	-55
-2	42	-43
-3	23	20
-4	79	72
H, -5, 6		
15	233	-224
14	149	-147
13	116	-126
12	268	265
11	88	87
10	172	177
9	158	-154
8	355	-359
7	310	-310
6	219	-220
5	215	213
4	313	319
3	158	158
2	139	-113
1	224	-225
0	314	-316
-1	-20	-23
-2	181	180
-3	152	154
-4	76	78
-5	89	-89
-6	115	-112
H, -5, 5		
16	65	-56
15	45	-35
14	100	134
13	141	143
12	158	157
11	77	-77
10	102	-101
9	110	-109
8	-19	11
7	219	218
6	135	134
5	114	114
4	171	-173
3	62	-64
2	-18	1
1	78	80
0	60	62
-1	133	120
-2	46	-43
-3	95	-96
-4	75	-74
-5	47	-48
-6	24	26
-7	57	60
H, -5, 4		
17	115	-113
16	76	70
15	162	160
14	281	281
13	56	55
12	223	-223
11	247	-244
10	198	-199
9	80	76
8	170	168
7	382	381
6	204	200
5	218	-214
4	153	-149
3	134	-133
2	-18	7
1	130	125
0	228	228
-1	94	99
-2	172	-170
-3	184	-183
-4	174	-171
-5	87	-83
-6	72	68
-7	145	142
-8	85	86
H, -5, 3		
17	56	55
16	50	53
15	146	-149
14	112	-114
13	151	-156
12	59	-72
11	173	174
10	231	198
9	160	-157
8	76	-74
7	187	-186
6	82	-79
5	44	45
4	190	193
3	198	191
2	123	119
1	77	-84
0	46	-45
-1	314	-311
-2	120	-125
-3	174	179
-4	245	249
-5	248	255
-6	-21	-24
-7	154	-155
-8	179	-177
-9	68	-69
H, 5, -2		
-17	115	118
-16	39	40
-15	106	-135
-14	82	-78
-13	125	-123
-12	-18	5
-11	196	199
H, -5, 2		
10	308	335
9	62	55
8	63	-62
7	384	-396
6	154	-155
5	86	47
4	236	241
3	419	415
2	133	-135
1	337	-347
0	270	-272
-1	129	-123
-2	150	134
-3	217	213
-4	114	113
-5	43	49
-6	216	-213
-7	-21	-15
-8	28	25
-9	65	53
-10	102	74
H, 5, -1		
-17	135	-135
-16	86	-87
-15	43	41
-14	152	144
-13	265	255
-12	49	-45
-11	139	-137
-10	290	-287
-9	238	-236
-8	69	70
-7	448	450
-6	423	425
-5	18	-13
-4	309	-311
-3	495	-505
H, -5, 1		
2	476	-483
1	33	-33
0	362	355
-1	393	403
-2	131	-36
-3	212	-213
-4	353	-353
-5	293	-297
-6	22	13
-7	196	188
-8	183	193
-9	-22	-5
-10	79	-77
H, 5, 0		
-16	83	-93
-15	133	131
-14	190	137
-13	89	92
-12	88	-93
-11	128	-128
-10	171	-153
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-8	333	341
-7	304	305
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0	198	203
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3	-19	16
4	39	41
5	-23	1
6	113	130
7	117	113
H, -5, 0		
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-9	-22	1
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-11	-23	-19
H, 5, 1		
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-13	380	-381
-12	72	77
-11	71	73
-10	376	379
-9	214	219
-8	170	-176
-7	368	-358
-6	446	-446
-5	179	-175
-4	132	131
-3	127	122
-2	374	371
-1	-17	4
0	266	-271
1	368	-355
2	129	-136
3	43	-35
4	371	369
5	261	259
6	61	59
7	54	-57
8	315	-317
9	28	-29
10	56	-53
11	159	150
H, 5, 2		
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-14	49	-51
-13	33	29
-12	78	53
-11	53	53
-10	72	73
-9	56	57
-8	131	-127
-7	129	-133
-6	40	-35
-5	22	5
-4	-18	21
-3	-18	23
-2	32	-31
-1	105	-101
0	100	-100
1	21	15
2	73	70
3	47	45
4	33	31
5	80	-79
6	82	-90
7	-21	-13
8	38	-31
9	149	150
10	27	-37
11	31	28
H, 5, 3		
-13	250	243
-12	141	142
-11	-20	15
-10	243	-237
-9	123	-115
-8	113	-111
-7	166	154
-6	286	-297
-5	272	277
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0	177	178
1	198	[illegible]
2	191	[illegible]
3	78	-73
4	184	-178
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7	67	67
8	108	104
9	137	137
10	48	-47
H, 5, 4		
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-11	137	-135
-10	90	-85
-9	77	75
-8	55	52
-7	41	-32
-6	151	-154
-5	39	-34
-4	167	-170
-3	-20	5
-2	296	293
-1	52	-53
0	129	127
1	184	-186
2	22	5
3	117	-113
4	-22	-23
5	173	175
6	55	51
7	-22	-3
8	66	-71
9	94	-92
H, 5, 5		
-10	83	83
-9	169	164
-8	33	37
-7	93	-85
-6	134	-105
-5	170	-121
-4	29	-30
-3	150	149
-2	265	249
-1	27	19
0	-28	11
1	215	-218
2	54	-55
3	-22	-17
4	93	95
5	235	216
6	-23	-7
7	39	-38
8	93	-93
H, 5, 6		
-9	136	-132
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-6	77	71
-5	165	162
-4	95	91
-3	76	-34
-2	121	-118
-1	165	-169
0	55	-63
1	76	74
2	106	108
3	85	89
4	72	-74
5	133	-137
6	138	-135
H, 5, 7		
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-1	-23	-24
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1	49	47
2	62	60
3	62	-35
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10	24	23
9	30	28
8	-22	-7
7	40	-45
6	62	-65
5	-21	5
4	25	-21
3	54	55
2	121	121
1	-22	5
H, -6, 7		
13	44	-42
12	124	127
11	117	115
10	187	195
9	-21	3
8	192	-192
7	190	-193
6	143	-164
5	96	100
4	158	157
3	209	203
2	32	33
1	196	-199
0	256	-258
-1	59	-57
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H, -6, 6		
14	-22	12
13	138	138
12	-23	5
11	-21	-15
10	126	-127
9	217	-222
8	-20	-10
7	183	190
6	201	208
5	143	145
4	124	-129
3	186	-188
2	160	-159
1	77	74
0	160	156
-1	201	205
-2	-21	-17
-3	32	-35
-4	118	-122
H, -6, 5		
15	194	196
14	266	263
13	63	71
12	109	-109
11	244	-233
10	210	-207
9	-19	-16
8	199	201
7	235	239
6	121	117
5	22	-26
4	129	-126
3	154	-153
2	-19	-14
1	145	149
0	162	163
-1	163	160
-2	-21	26
-3	55	-53
-4	86	-86
-5	36	-37
H, -6, 4		
16	118	120
15	63	-66
14	133	-128
13	294	-292
12	84	-95
11	57	55
10	249	249
9	91	91
8	39	-37
7	259	-253
6	271	-273
5	153	-152
4	56	55
3	278	276
2	51	53
1	-19	-7
0	163	-171
-1	193	-202
-2	194	-195
-3	-20	9
-4	127	129
-5	90	96
-6	-22	20
-7	97	-95
H, -6, 3		
16	-21	-1
15	87	-73
14	44	-37
13	126	-125
12	38	37
11	159	164
10	175	175
9	65	67
8	134	135
7	136	-137
6	80	-87
5	49	-45
4	165	165
3	371	375
2	144	-144
1	174	173
0	192	-192
-1	106	-105
-2	42	37
-3	92	91
-4	93	92
-5	74	-79
-6	42	-36
-7	35	-36
H, 6, -2		
-16	185	-184
-15	-21	-12
-14	84	84
-13	119	119
-12	164	154
-11	36	-37
-10	248	-261
H, -6, 2		
9	293	-295
8	-18	17
7	188	194
6	261	269
5	249	253
4	84	-85
3	229	-239
2	349	-359
1	96	97
0	91	94
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-2	175	173
-3	69	-69
-4	182	-175
-5	256	-254
-6	32	-25
-7	74	67
-8	170	168
H, 6, -1		
-16	33	-28
-15	-21	-19
-14	84	85
-13	42	-39
-12	45	42
-11	135	-140
-10	47	-50
-9	50	-49
-8	45	43
-7	38	42
-6	-18	17
-5	59	-52
-4	158	-150
-3	45	-47
-2	-18	-8
-1	69	55
H, -6, 1		
0	99	93
-1	57	-59
-2	103	-98
-3	90	-92
-4	-20	-9
-5	66	57
-6	116	121
-7	97	95
-8	-22	10
-9	67	-73
H, 6, 0		
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-14	59	-55
-13	225	-226
-12	35	-34
-11	46	-43
-10	432	438
-9	188	185
-8	133	136
-7	108	-107
-6	366	-360
-5	158	-155
-4	19	24
-3	264	266
-2	232	226
-1	133	133
0	169	-174
1	280	-284
2	264	-265
3	-20	15
4	196	195
5	188	185
6	142	139
7	52	-47
8	191	-189
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H, 6, 1		
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-12	125	117
-11	-20	8
-10	76	92
-9	128	-126
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-7	110	-108
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-5	276	271
-4	68	55
-3	62	59
-2	152	-145
-1	225	-225
0	182	-182
1	112	116
2	123	122
3	151	154
4	58	-58
5	109	-113
6	85	-85
7	101	-96
8	51	51
9	65	70
H, 6, 2		
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-12	237	206
-11	50	-51
-10	183	-190
-9	157	-155
-8	199	-197
-7	165	164
-6	285	289
-5	166	163
-4	20	-15
-3	186	-188
-2	92	-85
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0	87	85
1	287	287
2	138	134
3	88	87
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5	57	-50
6	50	-45
7	-22	5
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H, 6, 3		
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-10	37	35
-9	69	68
-8	133	140
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-6	65	-33
-5	245	-241
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-3	33	-27
-2	83	89
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0	86	83
1	28	-36
2	117	-119
3	126	-113
4	34	-33
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7	73	67
8	-23	5
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-8	89	92
-7	58	-67
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-5	113	-112
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-2	34	35
-1	167	169
0	22	-15
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4	77	77
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H, 6, 5		
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-6	31	37
-5	97	96
-4	170	169
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-1	128	-125
0	121	-123
1	85	93
2	117	118
3	155	150
4	63	68
5	57	-55
H, 6, 6		
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-3	70	-67
-2	82	-84
-1	-23	5
0	88	83
1	35	30
2	35	23
H, -7, 7		
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10	154	-153
9	122	-125
8	22	-21
7	-25	15
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4	76	-71
3	154	-152
2	130	-127
H, -7, 6		
13	137	136
12	28	-27
11	53	-51
10	113	-117
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8	89	93
7	75	79
6	94	94
5	75	-76
4	58	-53
3	88	-86
2	30	-31
1	36	30
0	141	136
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H, -7, 5		
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13	187	-184
12	70	-66
11	44	37
10	182	179
9	159	157
8	149	146
7	105	-103
6	280	-276
5	152	-145
4	-20	-3
3	177	179
2	226	221
1	143	147
0	83	-87
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-2	179	-182
-3	-22	-21
H, -7, 4		
14	156	-155
13	114	-114
12	60	58
11	108	109
10	31	20
9	46	48
8	128	-125
7	152	-150
6	54	-53
5	88	88
4	131	132
3	96	95
2	-20	-11
1	-23	5
0	120	-121
-1	-21	13
-2	83	83
-3	42	42
-4	42	43
H, -7, 3		
15	50	-45
14	60	61
13	223	216
12	273	278
11	44	-47
10	220	-225
9	226	-219
8	233	-233
7	126	125
6	250	250
5	196	199
4	113	111
3	213	-217
2	187	-185
1	52	-50
0	32	37
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-2	120	117
-3	46	55
-4	28	-26
-5	144	-144
H, 7, -2		
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-13	56	-55
-12	55	-53
-11	133	-133
-10	66	-56
-9	61	54
H, -7, 2		
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7	31	31
6	97	-96
5	43	-49
4	56	-50
3	93	-95
2	-20	7
1	47	36
0	-20	14
-1	83	-85
-2	36	-40
-3	126	-120
-4	128	-124
-5	-22	-6
-6	70	58
H, 7, -1		
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-13	132	-134
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-10	92	90
-9	191	195
-8	183	189
-7	69	65
-6	86	-89
-5	61	-58
-4	104	-103
-3	102	99
-2	222	226
-1	187	185
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H, 7, 0		
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-12	94	-96
-11	174	172
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-8	110	-108
-7	145	-142
-6	-19	-9
-5	99	92
-4	108	103
-3	160	151
-2	119	-117
-1	210	-207
0	173	-170
1	26	32
2	78	79
3	222	229
4	32	28
5	75	-74
6	93	-99
H, 7, 1		
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-12	87	98
-11	94	102
-10	36	-34
-9	194	-197
-8	109	-111
-7	35	39
-6	133	134
-5	97	100
-4	74	-72
-3	150	-150
-2	184	-184
-1	77	-73
0	57	58
1	86	87
2	38	33
3	-21	9
4	75	-78
5	64	-43
6	-23	-9
H, 7, 2		
-12	104	-106
-11	196	-196
-10	23	31
-9	94	92
-8	252	252
-7	165	150
-6	-20	17
-5	165	-165
-4	199	-197
-3	29	-26
-2	70	74
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0	138	135
1	60	51
2	119	-124
3	106	-102
4	58	-58
5	32	32
6	82	91
H, 7, 3		
-10	93	92
-9	24	23
-8	-22	-22
-7	77	-74
-6	29	-18
-5	129	-131
-4	-21	15
-3	128	133
-2	71	-70
-1	98	103
0	96	-97
1	30	19
2	93	-95
3	-22	3
4	102	104
5	-23	19
H, 7, 4		
-7	116	-116
-6	87	-81
-5	22	21
-4	153	150
-3	191	192
-2	30	-40
-1	28	-29
0	169	-170
1	-27	10
2	32	33
3	132	130
H, -8, 6		
9	126	125
8	66	63
7	-22	9
6	64	-62
5	113	-116
4	68	-64
H, -8, 5		
11	32	39
10	-21	-3
9	-21	4
8	108	-111
7	179	-129
6	81	-78
5	29	30
4	116	118
3	-21	13
2	39	-29
1	123	-124
H, -8, 4		
12	197	197
11	76	78
10	88	-93
9	136	-97
8	159	-160
7	25	32
6	139	141
5	197	197
4	118	125
3	181	-186
2	23	-7
1	152	-152
0	-26	19
-1	111	109
H, -8, 3		
13	52	50
12	120	-119
11	199	-196
10	93	-93
9	114	116
8	151	150
7	137	137
6	36	35
5	129	-121
4	125	-120
3	88	-95
2	151	155
1	50	47
0	112	111
-1	39	31
-2	68	-68
H, 8, -2		
-13	77	-72
-12	173	-175
-11	34	-31
-10	-21	13
-9	78	79
-8	67	62
-7	-20	8
H, -8, 2		
6	57	-58
5	121	-117
4	58	-54
3	-20	-5
2	89	91
1	135	132
0	25	17
-1	46	-41
-2	78	-80
-3	43	-41
H, 8, -1		
-12	30	21
-11	254	261
-10	44	38
-9	43	42
-8	108	-103
-7	190	-185
-6	26	-20
-5	63	60
-4	167	169
-3	106	103
-2	28	26
-1	127	-128
0	137	-135
1	79	-75
H, -8, 1		
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-3	102	105
H, 8, 0		
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-10	66	-65
-9	-21	-16
-8	70	-67
-7	35	-34
-6	112	119
-5	-20	-5
-4	61	48
-3	53	-53
-2	80	-81
-1	78	-78
0	42	40
1	-22	6
2	37	38
3	43	-46
H, 8, 1		
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-9	63	-63
-8	170	170
-7	176	171
-6	80	78
-5	62	-60
-4	108	-107
-3	61	-59
-2	55	-56
-1	114	110
0	182	178
1	55	48
2	-22	8
H, 8, 2		
-8	-22	-14
-7	38	-37
-6	120	-118
-5	56	-57
-4	29	24
-3	62	59
-2	28	25
-1	28	28
0	92	-86
1	106	-109
H, 8, 3		
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-4	140	142
-3	47	47
-2	69	69
H, -9, 3		
7	60	-59
6	41	-38
5	83	-80
4	77	-79
H, 9, -2		
-8	98	-99
-7	140	-141
-6	51	-50
H, -9, 2		
5	24	27
4	179	177
3	162	158
H, 9, -1		
-7	66	69
-6	71	77
-5	26	28
-4	29	23
-3	82	-83

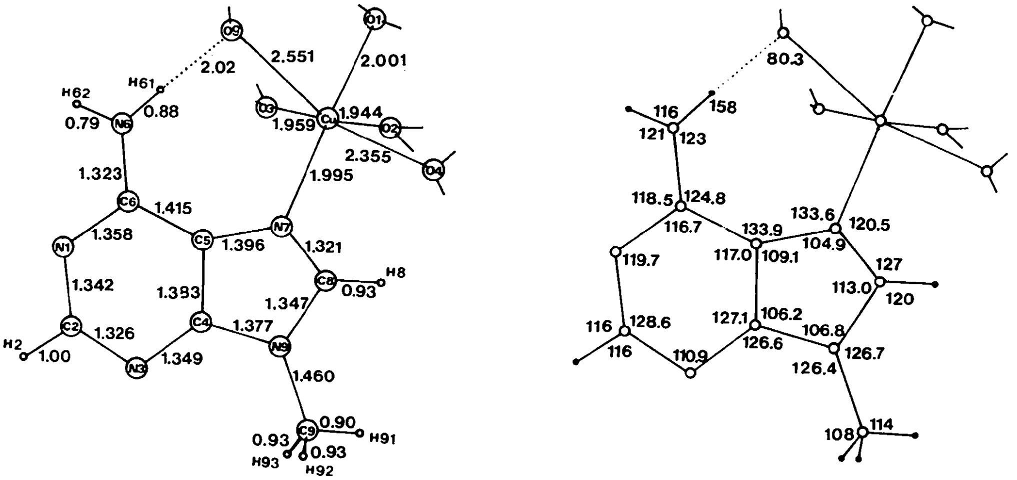

Fig. 1. Bond lengths and angles in the Cu(ade).$(H_2O)_4^{2+}$ ion. The σ's in bond lengths are: Cu–O(N) 0·001–0·002 Å, C–C(N) 0·002–0·003 Å, H–C(N) (O) 0·02–0·04 Å. The σ's in angles are in the range 0·05–0·14°.

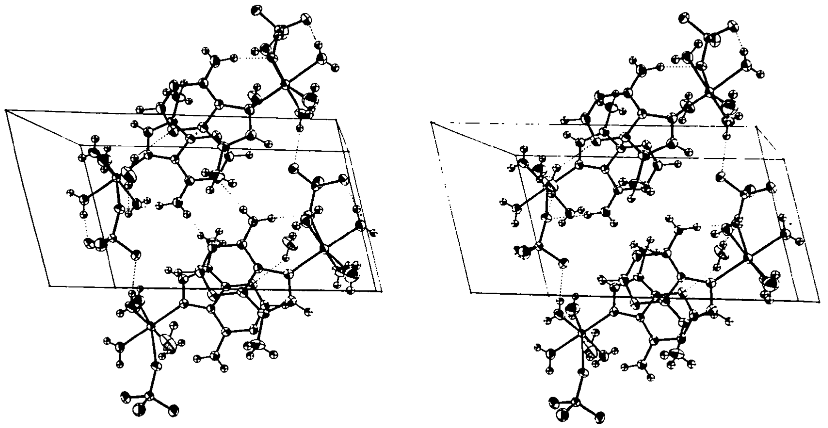

Fig. 2. Stereoscopic drawing of the crystal packing of tetraaquo-(9-methyladenine)copper(II) sulphate monohydrate viewed perpendicular to the *ac* projection.

Table 2. *The final atomic parameters*

(*a*) Non-hydrogen atoms. Temperature parameters × 10^4. Standard deviations are given in parentheses. Anisotropic temperature factor $= \exp\,[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{23}klb^*c^*+2U_{13}hla^*c^*)]$.

	X/*a*	*Y*/*b*	*Z*/*c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu	0·14291 (2)	0·22381 (4)	0·25332 (3)	171 (1)	309 (1)	227 (1)	87 (1)	66 (1)	−11 (1)
S	0·13615 (4)	0·53693 (8)	0·68570 (6)	194 (2)	386 (3)	182 (2)	132 (2)	36 (2)	−15 (2)
O(1)	0·00316 (11)	0·19007 (22)	0·40407 (19)	211 (7)	345 (8)	295 (7)	90 (6)	75 (6)	−30 (6)
O(2)	0·11991 (13)	0·40779 (28)	0·12398 (21)	450 (10)	636 (11)	274 (8)	374 (9)	209 (8)	115 (7)
O(3)	0·17066 (11)	0·07569 (22)	0·41348 (20)	252 (7)	340 (8)	353 (8)	122 (6)	118 (6)	−9 (6)
O(4)	0·06232 (15)	−0·06837 (29)	0·09097 (25)	478 (11)	550 (11)	431 (10)	−13 (9)	30 (8)	−133 (8)
O(5)	0·29627 (13)	0·84942 (25)	0·32513 (24)	478 (13)	418 (9)	577 (11)	236 (8)	196 (8)	196 (8)
O(6)	0·13313 (12)	0·74488 (24)	0·74018 (22)	355 (9)	396 (9)	404 (9)	148 (7)	−100 (7)	−128 (7)
O(7)	0·19460 (12)	0·48026 (30)	0·78822 (21)	331 (8)	827 (13)	278 (8)	291 (9)	173 (8)	−33 (7)
O(8)	0·02845 (11)	0·40754 (23)	0·71399 (20)	216 (7)	419 (8)	305 (8)	98 (6)	69 (6)	28 (6)
O(9)	0·18039 (11)	0·51176 (22)	0·49477 (18)	263 (7)	349 (7)	187 (7)	104 (6)	51 (5)	9 (5)
N(1)	0·52218 (13)	0·38112 (27)	0·26363 (24)	201 (8)	383 (10)	287 (9)	95 (7)	−7 (7)	−65 (7)
N(3)	0·54184 (13)	0·24083 (26)	−0·04107 (23)	201 (8)	339 (9)	277 (9)	100 (7)	34 (7)	15 (7)
N(6)	0·37148 (13)	0·42541 (30)	0·43741 (24)	229 (8)	522 (11)	236 (9)	146 (8)	−90 (8)	−68 (7)
N(7)	0·27956 (12)	0·23399 (26)	0·09914 (22)	198 (8)	341 (9)	221 (8)	83 (7)	17 (7)	−38 (6)
N(9)	0·38254 (13)	0·14758 (27)	−0·14601 (22)	273 (9)	381 (9)	174 (8)	121 (7)	−29 (7)	−29 (6)
C(2)	0·57482 (15)	0·32067 (32)	0·10744 (30)	205 (9)	359 (11)	333 (11)	93 (8)	36 (8)	−25 (8)
C(4)	0·44145 (15)	0·22225 (28)	−0·01944 (26)	228 (9)	233 (9)	218 (9)	69 (7)	39 (7)	−9 (7)
C(5)	0·37730 (14)	0·27584 (28)	0·13291 (25)	165 (8)	239 (9)	211 (9)	62 (7)	36 (7)	−25 (7)
C(6)	0·42131 (15)	0·36238 (29)	0·28268 (26)	210 (9)	254 (9)	226 (9)	70 (7)	18 (7)	−35 (7)
C(8)	0·28760 (16)	0·15867 (34)	−0·06863 (28)	258 (10)	417 (12)	243 (10)	106 (9)	−19 (8)	−75 (8)
C(9)	0·41716 (20)	0·07455 (40)	−0·32986 (30)	485 (14)	568 (15)	208 (11)	227 (12)	−62 (10)	−20 (10)

Table 2 (*cont.*)

(*b*) Hydrogen atoms (parameters ×10^3). Isotropic temperature factor = exp $[-8\pi^2U\sin^2\theta/\lambda^2]$.

	X/a	Y/b	Z/c	U
H(2)	649 (2)	341 (3)	101 (3)	30 (6)
H(8)	235 (2)	109 (3)	−131 (3)	36 (6)
H(11)	−33 (2)	218 (3)	361 (3)	41 (6)
H(12)	5 (2)	269 (4)	512 (3)	56 (8)
H(21)	84 (2)	450 (3)	165 (3)	36 (6)
H(22)	139 (2)	427 (3)	36 (3)	47 (7)
H(31)	202 (2)	12 (3)	381 (3)	41 (7)
H(32)	121 (2)	18 (4)	475 (3)	49 (7)
H(41)	75 (3)	−112 (5)	0 (5)	214 (26)
H(42)	36 (3)	−133 (6)	146 (6)	126 (14)
H(51)	321 (3)	816 (6)	222 (6)	125 (14)
H(52)	272 (3)	762 (5)	374 (5)	83 (10)
H(61)	306 (2)	419 (4)	459 (3)	46 (7)
H(62)	400 (2)	476 (3)	516 (3)	40 (6)
H(91)	366 (3)	−5 (5)	−382 (5)	114 (13)
H(92)	460 (3)	168 (5)	−403 (5)	98 (12)
H(93)	437 (3)	−39 (5)	−332 (5)	99 (12)

A list of observed and calculated structure factors is given in Table 1. Atomic parameters are listed in Table 2. All the above calculations were carried out on a UNIVAC 1110 computer. The main programs used originate from the Weizmann Institute of Science, Rehovoth, Israel, and were modified by Dr D. Rabinovich, cand. real. L. Milje and cand. real. K. Åse. The *ORTEP* program was used for making the stereo drawings (Johnson, 1970).

Results and discussion

Environment of copper

The copper ion has octahedral (4+2) coordination (Fig. 1). The equatorial positions are occupied by N(7) of the adenine ligand and by three water molecules. The Cu–N(7) distance, 1·995 Å, is significantly shorter than the corresponding distance, 2·054 Å, in the copper–hypoxanthine complex (Sletten, 1974). The copper ion is displaced 0·045 Å from the equatorial plane towards a fourth water molecule, O(4), in the axial position. The coordination sphere is completed by one of the sulphate oxygens, the distance Cu–O(9) = 2·551 Å indicating a very weak interaction.

In Table 3 the angles around copper are listed. The sulphate ligand is shown to be 'pushed' away from the adenine ligand to accommodate an intramolecular hydrogen bond to the amino group. This indirect chelate formation involving N(6)· · ·O(9)–Cu–N(7) seems to be a characteristic feature in complex formation between copper and purine bases.

The coordination pattern described above is the normal arrangement for copper(II) complexes which have no crystallographic symmetry restraints. The preference for water molecules rather than the sulphate ion in equatorial positions has also been found in the tri- and pentahydrate of $CuSO_4$ (Zahrobsky & Baur, 1968; Bacon & Curry, 1962).

Table 3. *Bond angles* (°) *in the coordination sphere of copper* (σ = 0·05–0·07°)

O(1)–Cu–O(2)	90·63
O(1)–Cu–O(3)	87·74
O(4)–Cu–O(1)	83·25
O(4)–Cu–O(2)	96·69
O(4)–Cu–O(3)	92·36
O(4)–Cu–N(7)	92·85
O(4)–Cu–O(9)	162·94
N(7)–Cu–O(2)	92·19
N(7)–Cu–O(3)	90·06
N(7)–Cu–O(9)	103·65
O(9)–Cu–O(1)	80·08
O(9)–Cu–O(2)	87·12
O(9)–Cu–O(3)	83·44

Table 4. *Bond lengths* (Å) *and angles* (°) *in the sulphate ion*

$\sigma(l)$ = 0·001–0·002 Å, σ(angle) = 0·1°

O(6)–S–O(7)	111·3	S–O(6)	1·481
O(6)–S–O(8)	107·9	S–O(7)	1·462
O(7)–S–O(8)	110·0	S–O(8)	1·500
O(9)–S–O(6)	109·3	S–O(9)	1·477
O(9)–S–O(7)	110·6		
O(8)–S–O(9)	107·7		
S–O(9)–Cu	132·2		

Geometry of the adenine ligand

The bond lengths and angles of the adenine ligand are given in Fig. 1. To assess the influence of metal bonding, a comparison with the molecular dimensions of un-

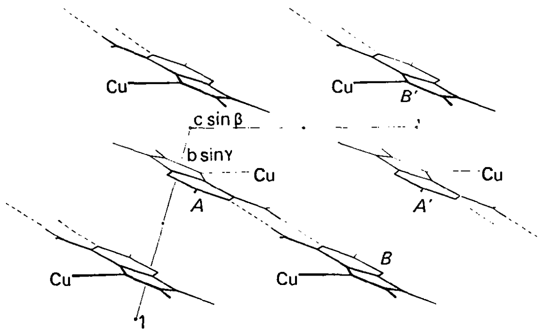

Fig. 3. Base stacking of the adenine ligands projected along the *a* axis.

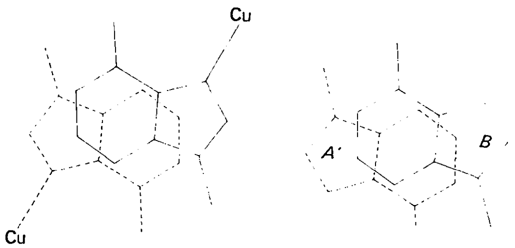

Fig. 4. Base stacking of: (*a*) 9-methyladenine ligands D = 3·39 Å, (*b*) uncomplexed 9-methyladenine D = 3·33 Å.

Table 5. *Hydrogen-bond distances and angles*

Bond	Position of acceptor atom	Distances (Å)		Angle (°)
		D···A	H···A	D–H···A
O(1)–H(11)···O(6)	$\bar{x}$, $1-y$, $1-z$	2·643 (3)	1·89 (3)	173 (2)
O(1)–H(12)···O(8)	x, y, z	2·677 (2)	1·76 (3)	170 (2)
O(2)–H(21)···O(8)	$\bar{x}$, $1-y$, $1-z$	2·742 (2)	2·09 (3)	177 (2)
O(2)–H(22)···O(7)	x, y, $z-1$	2·671 (2)	1·97 (3)	178 (3)
O(3)–H(31)···O(5)	x, $y-1$, z	2·639 (3)	1·95 (3)	171 (2)
O(3)–H(32)···O(1)	$\bar{x}$, $\bar{y}$, $1-z$	2·840 (2)	2·06 (2)	167 (2)
O(4)–H(41)···O(6)	x, $1-y$, $z-1$	2·916 (2)	2·19 (3)	171 (4)
O(4)–H(42)···O(8)	$\bar{x}$, $\bar{y}$, $1-z$	2·889 (3)	2·26 (4)	165 (4)
O(5)–H(51)···N(3)	$1-x$, $1-y$, $\bar{z}$	2·914 (2)	2·20 (4)	145 (4)
O(5)–H(52)···O(9)	x, y, z	2·819 (2)	2·09 (3)	170 (3)
N(6)–H(61)···O(9)	x, y, z	2·856 (3)	2·02 (3)	158 (2)
N(6)–H(62)···N(1)	$\bar{x}$, $\bar{y}$, $\bar{z}$	2·986 (3)	2·20 (3)	179 (2)

complexed 9-methyladenine may be made. The structure determination of 9-methyladenine is not of comparable accuracy, being based on film data and without hydrogen refinement (Stewart & Jensen, 1964). However, differences between corresponding bond lengths and angles are less than 0·02 Å and 2·1°, respectively. The bonds adjacent to the coordination site show a small *trans* effect consistent with that found in the corresponding copper–hypoxanthine complex (Sletten, 1974). The indirect chelate ring involving the hydrogen bond between the amino group and the sulphate ion is formed without imposing noticeable strain in the adenine geometry. The angles N(6)–C(6)–C(5) and C(6)–C(5)–N(7) are only slightly adjusted relative to the uncomplexed adenine geometry.

The adenine ligand shows the characteristic bend around the C(4)–C(5) bond found in most purine structures. The angle between the planes through the pyrimidine ring and the imidazole ring is 0·96°. The amino group is slightly bent out of the pyrimidine plane, but shows no twist around the C(6)–N(6) bond. The copper ion is located 0·312 Å from the plane through the purine ring.

The sulphate ion

Bond lengths and angles in the sulphate ion are listed in Table 4. The shape of the sulphate group is seen to be irregular. In the crystal structure of $CuSO_4.3H_2O$ the longest S–O bond is the one coordinated to copper (Zahrobsky & Baur, 1967). However, in the present compound the variation in bond lengths is not related to coordination effects. The oxygen atoms of the sulphate group are involved in relatively strong hydrogen bonds and there seems to be a correlation between the number of hydrogen bonds established and the S–O bond lengths. Thus, the longest bond, S–O(8) = 1·500 Å, participates in three hydrogen bonds, while the shortest, S–O(7) = 1·462 Å, participates only in one. The two intermediate S–O bonds are each involved in two hydrogen bonds.

Molecular packing and hydrogen bonding

A stereographic drawing of the molecular packing is shown in Fig. 2. Centrosymmetrically related adenine ligands are hydrogen-bonded in a DNA-like pattern, the distance N(6)–H(62)···N(1) being 2·986 Å and the angle at H(62) being 179°. The uncomplexed 9-methyladenine molecule is found to be hydrogen-bonded through N(6)–H(61)···N(7). This change in hydrogen bonding corroborates the assumption that N(7) rather than N(1) is the preferring binding site for metal ions in adenine.

The adenine ligands stack pairwise on top of each other in the usual pattern found in the uncomplexed purines (Fig. 3). The interplanar distance between molecules *A'* and *B* is 3·396 Å. The degree of overlap is shown in Fig. 4 together with the corresponding projection of the uncomplexed 9-methyladenine molecule. The similarity of the two projections is remarkable considering the differences in crystallographic and ionic environment.

The hydrogen-bonding network in the crystal is extensive, with all the available hydrogen donors occupied. A complete list of hydrogen bonds is given in Table 5; in addition some of the bonds are indicated as dashed lines in the stereo drawing (Fig. 2). There are two intramolecular hydrogen bonds in the complex; one between the amino group and the coordinated sulphate oxygen O(9), and one between water molecule O(1) and sulphate oxygen O(8).

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