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The Crystal Structure of Dimethylammonium Copper(II) Formate, $NH_2(CH_3)_2[Cu(OOCH)_3]$

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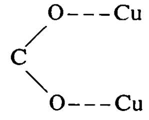
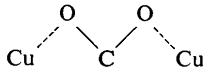
The crystal structure of dimethylammonium copper(II) formate has been determined by single-crystal X-ray structural analysis. The crystals are monoclinic, space group $I2/c$, with $a=11{\cdot}4204$ (5), $b=8{\cdot}7139$ (5), $c=8{\cdot}8502$ (5) Å, $\beta=96{\cdot}247$ (5)°. Data were collected on a Picker four-circle diffractometer with Nb-filtered Mo $K\alpha$ radiation. The structure was refined by full-matrix least squares to $R=0{\cdot}017$. The copper ion is situated at a center of symmetry surrounded by six formate ions. The equatorial Cu–O bonds are 1·969 and 1·971 Å and the axial Cu–O bonds 2·492 Å. The formate ions act as bridges between copper atoms forming an infinite *anti–anti* chain through the crystal. There are two crystallographically independent formate ions, one of which is located on a twofold axis. The C–O bonds in the formate ion in the general position are slightly different, 1·240 and 1·253 Å. The ∠O–C–O is 124·39°. In the formate ion with crystallographically required twofold symmetry the corresponding dimensions are 1·247 and 1242·4°. The dimethylammonium ion is also located on a twofold axis, with C–N bonds of 1·467 Å.

Introduction

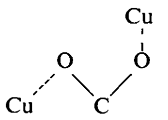
The neutral copper(II) formate complex appears in a variety of modifications, several of which have been investigated by X-ray crystallographic methods. Copper(II) formate tetrahydrate is found in an *anti–anti* configuration (II) (Kiriyama, Ibamoto & Matsuo, 1954), the anhydrous compound has an *anti–syn* arrangement (III) (Barclay & Kennard, 1961) and the dihydrate is found both as *anti–anti* and *anti–syn* in the same crystal (Bukowska-Strzyzewska, 1965).



(I)
syn–syn



(II)
anti–anti



(III)
anti–syn

In a copper formate monourea adduct (Yawney & Doedens, 1970) the configuration is *syn–syn* (I) as in most higher alkanates of copper(II). Several factors may be considered to explain the variety of configurations exhibited by copper formate in the solid state. Martin & Waterman (1959) have suggested that ligands which most effectively reduce the residual charge on the copper ion may favour a *syn–syn* structure. This may account for the *syn–syn* configuration in the mono-adduct where the basic ligand reduces the charge on copper. However, in copper formate dihydrate the copper ions surrounded by six formate groups are bridged *anti–anti* while the copper ions coordinated by two formate groups and four water molecules are connected *anti–syn*. To assess the importance of packing effects in this scheme more structural data are needed.

Experimental

The present compound was formed during the recrystallization of a copper-hypoxanthine chloro complex from *N,N*-dimethylformamide. Usually the amide does not undergo hydrolysis without drastic heating in concentrated acidic or basic solution. Apparently the copper ions in some way catalyze this reaction.

Turquoise crystals were obtained from the yellow copper hypoxanthine formamide solution after slow evaporation for several weeks. The space group was determined from Weissenberg films as Ic or $I2/c$. The density was measured by flotation in a mixture of chloroform and tetrabromoethane. Accurate cell dimensions were obtained from a least-squares treatment of the 2θ settings of 17 reflections measured on a four-circle diffractometer.

Crystal data

$(CH_3)_2NH_2[Cu(HCOO)_3]$ F.W. 244·7
$a=11{\cdot}4204$ (5) Å
$b=\ 8{\cdot}7139$ (5)
$c=\ 8{\cdot}8502$ (5)
$\beta=96{\cdot}247$ (5)°
$D_m=1{\cdot}90$ g cm^{-3} $D_x=1{\cdot}86$ g cm^{-3}
$Z=4$, $\lambda(\text{Mo }K\alpha)=0{\cdot}71069$ Å, $\mu=25{\cdot}9$ cm^{-1}

The crystal used for data collection had an irregular wedge shape with approximate dimensions $0{\cdot}11\times0{\cdot}16\times0{\cdot}22$ mm. 1009 unique reflections ($2\theta\le60°$) were measured on a manually operated four-circle diffractometer with niobium-filtered Mo $K\alpha$ radiation. Of these, 48 reflections were less than the threshold value

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of $2\sigma_c$, where $\sigma_c=(N_{B1}+B_{pk}+N_{B2})^{1/2}$. N_{pk} is the number of counts in the scan and N_{B1} and N_{B2} are the background counts.

During the data collection three standard reflections were measured every four hours to check the stability of the crystal and the electronics. A slight deterioration of the crystal was observed (Fig. 1). The fluctuation of the intensities of the standard reflections indicated that the X-ray source and detecting circuitry were stable to within 1 %. Thus the total error assigned to the net intensity of each reflection is

$$\sigma_i=[\sigma_c^2+(0{\cdot}01\sigma_c^2)^2]^{1/2}.$$

The data were corrected for Lorentz and polarization effects. In the final stage of refinement absorption and extinction corrections were also applied.

Structure determination

A sharpened Patterson synthesis showed the heavy atom to be located at a centre of symmetry $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. Structure-factor calculations based on this position gave an R of 0·45 ($R=\sum||F_o|-|F_c||/\sum|F_o|$). At the initial stage of the analysis the compound was assumed to be a copper complex of hypoxanthine. However, the first Fourier synthesis did not reveal any purine rings. Instead six separate three-atom groups were found coordinating to copper. Two of these groups were located on twofold axes giving one and a half ligand in the asymmetric unit. From the heights of the peaks in the Fourier map one carbon and two oxygen atoms were assigned as constituents of each three-atom group. Three cycles of least-squares refinement reduced R to 0·18 and the isotropic temperature factors were reasonable, corroborating the assumption that the ligands were formate ions. A difference map at this stage showed an additional three-atom group of atoms around the twofold axis, and not knowing the chemical composition of the compound we tentatively included another formate group in the refinement. Chemically, of course, this model cannot be correct. However, the refinement with isotropic temperature factors converged at $R=0{\cdot}10$ and a few additional cycles with anisotropic temperature factors decreased R to 0·042.

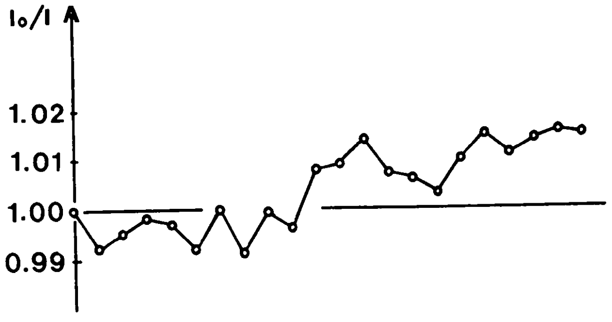


Fig. 1. The average fluctuations of standard reflections 080, 600, 415 measured every four hour.

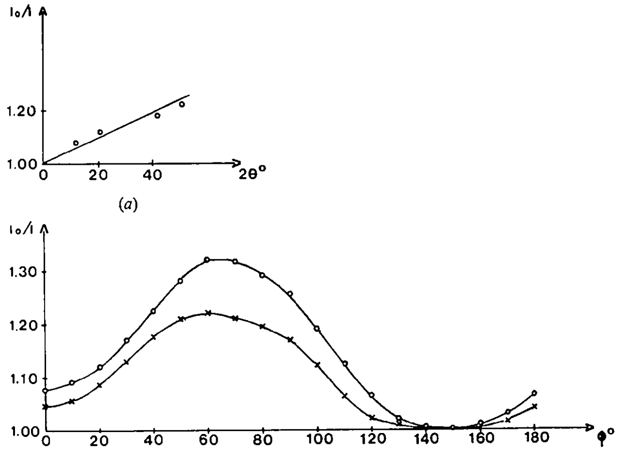
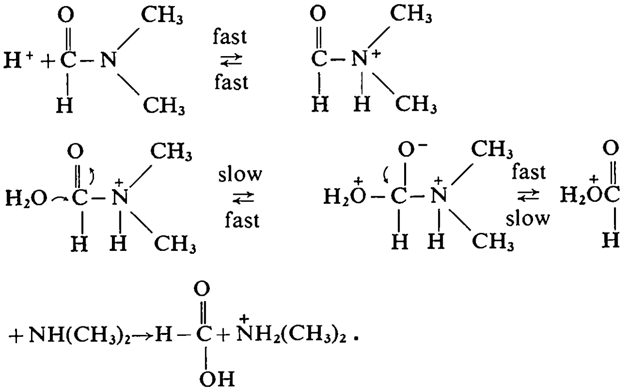


Fig. 2(*a*) The variation in intensity of *h*00 reflections *vs.* 2θ at $\chi=90°$. (*b*) The variation in intensity of reflection 600 and 14,0,0 *vs.* φ at $\chi=90°$.

At this low R value the thermal parameters of the 'formate group' last added were unreasonably low for carbon ($B=1{\cdot}8$ Å^2) and too high for oxygen ($B=6{\cdot}0$ Å^2). Moreover, the C–O distances were too long (1·46 Å), and the 'goodness of fit' $[w(F_o-F_o)^2/m-n]^{1/2}$ was unusually high, 8·5.

From purely crystallographic considerations a dimethylammonium ion was substituted for the erroneous 'formate group'. In retrospect this assignment could have been made by considering the chemistry of the decomposition of *N*,*N*-dimethylformamide.



The dimethylammonium ion was included with isotropic temperature factors and during two refinement cycles the R decreased to 0·031. The 'goodness of fit' was dramatically improved (3·8) suggesting that this quantity is more sensitive to errors in the model than R. Anisotropic thermal parameters for the non-hydrogen atoms in the DMA ion further improved R to 0·030 and the g.o.f. to 3·25.

At this stage an empirical absorption correction was carried out. Since the crystal was quite irregular in

Table 1. *Fractional atomic coordinates and thermal parameters and their estimated standard deviations (in parentheses)*

Anisotropic temperature factor: $T_i = \exp\left[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0·25000	0·25000	0·25000	0·82 (1)	2·06 (1)	1·45 (1)	0·164 (5)	−0·123 (7)	−0·354 (6)
O(1)	0·40315 (7)	0·14722 (10)	0·24419 (11)	1·07 (3)	2·07 (3)	2·76 (4)	0·01 (2)	0·09 (3)	−0·13 (3)
O(2)	0·32206 (9)	0·51685 (11)	0·62594 (12)	2·37 (4)	2·50 (4)	2·34 (4)	0·22 (3)	−0·38 (4)	−0·62 (3)
O(3)	0·31088 (8)	0·33920 (11)	0·44750 (11)	2·04 (4)	2·82 (4)	1·95 (4)	0·55 (3)	−0·38 (3)	−0·54 (3)
C(1)	0·50000	0·21403 (21)	0·25000	1·34 (6)	1·70 (6)	1·66 (6)	0·0	−0·08 (5)	0·0
C(2)	0·27831 (12)	0·46226 (16)	0·50318 (15)	1·66 (5)	2·11 (5)	2·11 (5)	−0·03 (4)	−0·24 (4)	0·06 (4)
C(3)	0·55813 (20)	0·77864 (24)	0·14183 (23)	3·67 (9)	3·69 (7)	2·97 (7)	−0·28 (7)	1·04 (7)	−0·30 (6)
N	0·50000	0·68522 (20)	0·25000	1·96 (7)	2·24 (7)	2·75 (7)	0·0	−0·54 (6)	0·0
H(1)	0·5000	0·3232 (33)	0·2500	2·9 (5)					
H(2)	0·2160 (17)	0·5188 (21)	0·4418 (23)	3·1 (4)					
H(3)	0·6106 (22)	0·8323 (28)	0·1969 (31)	5·5 (6)					
H(4)	0·4989 (18)	0·8353 (25)	0·0909 (24)	4·0 (5)					
H(5)	0·5839 (20)	0·7140 (29)	0·0813 (27)	4·8 (6)					
H(6)	0·4482 (18)	0·6339 (23)	0·1997 (25)	4·2 (5)					

Table 2. *Observed and calculated structure factors* (× 10)

The reflections with observed intensity less than the threshold value of $2\sigma_c$ are marked with < signs.

H,0,0		
2	1180	-1132
4	1121	1151
6	579	-585
8	365	374
10	129	-123
12	547	558
14	353	-357
H,0,2		
0	1273	-1295
2	287	-296
4	974	-1012
6	769	771
8	845	-847
10	312	308
12	544	-546
14	382	386
-14	256	257
-12	647	-651
-10	381	377
-8	975	-986
-6	1019	1028
-4	224	-235
-2	262	-266
H,0,4		
0	1200	1214
2	630	-657
4	1155	1170
6	917	-926
8	852	864
10	75	-71
12	277	279
-12	536	527
-10	210	-211
-8	853	864
-6	743	-755
-4	618	642
-2	442	-433
H,0,6		
0	376	-884
2	165	162
4	58	-53
6	262	262
8	566	-571
10	288	282
-12	323	-311
-10	46	32
-8	483	-475
-6	487	493
-4	532	-547
-2	551	554
H,0,8		
0	789	788
2	443	-429
4	435	440
6	415	-412
8	406	409
-10	253	-248
-8	373	373
-6	359	-355
-4	497	491
-2	231	-226
H,0,10		
0	495	-495
2	275	272
4	348	-354
-8	176	-174
-6	203	205
-4	169	-170
-2	110	110
H,1,0		
1	141	137
3	803	-760
5	925	889
7	86	-86
9	139	-115
11	<17	8
13	<19	-5
H,1,1		
14	404	409
12	553	-548
10	311	312
8	601	-607
6	673	689
4	97	-59
2	1189	1206
0	1236	-1253
-14	363	364
-12	402	-398
-10	275	284
-8	729	-733
-6	1009	995
-4	1191	-1190
-2	1375	1384
H,1,2		
1	623	617
3	395	-402
5	131	-123
7	82	-79
9	113	110
11	<19	-23
13	56	53
-1	16	14
-3	468	-453
-5	123	130
-7	446	-436
-9	177	176
-11	91	94
-13	36	-37
H,1,3		
12	410	407
10	391	-387
8	724	726
6	1177	-1196
4	644	663
2	796	-807
0	1056	1092
-14	332	-332
-12	425	431
-10	484	-486
-8	673	673
-6	858	-857
-4	590	611
-2	48	-46
H,1,4		
1	408	-387
3	345	332
5	152	156
7	180	-177
9	196	196
11	220	-220
13	61	65
-1	24	19
-3	219	206
-5	125	122
-7	35	37
-9	65	63
-11	204	-200
-13	72	71
H,1,5		
12	306	-305
10	255	253
8	331	-326
6	557	557
4	499	-511
2	661	667
0	1261	-1285
-12	392	-386
-10	299	290
-8	308	-308
-6	736	739
-4	524	-535
-2	679	692
H,1,6		
1	216	-208
3	46	-33
5	88	89
7	293	-294
9	241	240
11	<23	-35
-1	374	373
-3	110	-108
-5	177	-176
-7	70	68
-9	<19	12
-11	<20	-12
-13	92	91
H,1,7		
10	343	-344
8	497	477
6	445	-436
4	369	355
2	317	-313
0	550	546
-12	323	320
-10	203	-203
-8	401	397
-6	673	-667
-4	390	397
-2	483	-497
H,1,8		
1	<18	-13
3	54	-55
5	167	168
7	44	-41
9	<23	4
-1	<18	-6
-3	119	-118
-5	143	140
-7	<20	9
-9	<20	3
-11	58	-57
H,1,9		
6	338	339
4	358	-361
2	450	445
0	400	-405
-10	181	174
-8	325	-319
-6	283	279
-4	215	-220
-2	302	301
H,1,10		
-1	61	-62
-3	49	47
-5	<21	-11
-7	116	-111
1	111	115
3	45	-41
5	68	-64
H,1,11		
-4	298	301
-2	232	-234
2	255	-249
0	299	302
H,2,0		
14	259	265
12	435	-441
10	408	403
8	721	-717
6	832	839
4	554	-953
2	177	-141
0	1310	-1302
H,2,1		
1	84	-76
3	402	401
5	365	-345
7	112	-103
9	350	351
11	82	85
13	69	72
-1	993	961
-3	68	71
-5	315	-294
-7	165	164
-9	104	107
-11	205	209
-13	36	33
H,2,2		
14	237	-237
12	472	471
10	522	-525
8	831	834
6	478	-496
4	819	845
2	106	-118
0	1547	1569
-14	167	-174
-12	392	393
-10	223	-223
-8	688	697
-6	1047	-1065
-4	1365	1359
-2	1390	-1367
H,2,3		
1	942	-931
3	476	463
5	23	-24
7	<16	-26
9	28	-36
11	274	-272
13	28	27
-1	418	-401
-3	115	-121
-5	158	-154
-7	165	160
-9	151	-152
-11	211	-210
-13	37	34
H,2,4		
12	460	-452
10	253	247
8	536	-528
6	278	282
4	747	-747
2	759	782
0	1048	-1057
-14	331	340
-12	541	-538
-10	256	252
-8	493	-490
-6	191	188
-4	428	-442
-2	658	666
H,2,5		
1	148	148
3	218	213
5	257	-255
7	67	66
9	164	157
11	<21	39
-1	387	378
-3	239	231
-5	270	-271
-7	<16	3
-9	101	98
-11	91	90
-13	70	69
H,2,6		
10	133	-130
8	425	422
6	434	-436
4	664	664
2	730	-733
0	835	845
-12	317	316
-10	292	-291
-8	582	589
-6	368	-374
-4	678	689
-2	460	-458
H,2,7		
1	141	-133
3	64	61
5	102	-98
7	79	80
9	164	-160
-1	251	-248
-3	49	19
-5	119	118
-7	36	-31
-9	<20	-12
-11	163	-164
H,2,8		
8	441	-445
6	437	434
4	394	-406
2	194	191
0	318	-326
-10	293	284
-8	396	-396
-6	334	337
-4	424	-427
-2	59	52
H,2,9		
1	145	145
3	<20	-9
5	89	-81
7	121	115
-1	<19	10
-3	75	76
-5	<20	-2
-7	59	-60
-9	119	116
H,2,10		
4	291	290
2	212	-210
0	476	475
-8	192	191
-6	303	-298
-4	392	396
-2	327	-332
H,2,11		
1	<23	-30
-1	73	-75
-3	73	-72
H,3,0		
1	456	444
3	205	-199
5	357	-336
7	140	-134
9	56	63
11	37	37
13	54	57
H,3,1		
14	243	-254
12	417	417
10	512	-512
8	752	747
6	719	-712
4	889	886
2	1054	-1059
0	527	524
-14	233	-242
-12	286	289
-10	398	-405
-8	591	594
-6	418	-420
-4	1020	1017
-2	785	-798
H,3,2		
1	179	178
3	156	145
5	56	-57
7	351	353
9	125	-126
11	190	-193
13	198	202
-1	867	-810
-3	585	570
-5	567	547
-7	134	-133
-9	205	201
-11	260	-264
-13	29	25
H,3,3		
12	359	-352
10	402	399
8	366	-374
6	430	441
4	513	-527
2	737	735
0	931	-924
-14	297	300
-12	339	-344
-10	516	517
-8	525	-518
-6	489	494
-4	1053	-1054
-2	774	771
H,3,4		
1	225	212
3	20	-10
5	366	-366
7	30	16
9	152	151
11	30	-32
-1	315	-313
-3	171	163
-5	348	-352
-7	260	-258
-9	332	332
-11	41	-38
-13	54	49
H,3,5		
10	432	-426
8	427	424
6	518	-508
4	745	750
2	592	-594
0	690	712
-12	263	264
-10	388	-384
-8	352	349
-6	401	-410
-4	553	554
-2	510	-522
H,3,6		
1	20	-10
3	<23	-12
5	299	307
7	48	-47
9	65	-65
11	<22	-18
-1	51	-44
-3	102	-102
-5	191	200
-7	57	-53
-9	32	33
-11	144	-151
H,3,7		
10	239	243
8	301	-300
6	285	282
4	521	-521
2	378	380
0	393	-392
-12	303	-301
-10	327	329
-8	417	-416
-6	415	419
-4	413	-413
-2	453	464
H,3,8		
1	237	246
3	328	-331
5	87	89
7	82	-90
-1	119	115
-3	122	-126
-5	108	105
-7	154	-153
-9	<20	2
H,3,9		
6	260	-258
4	343	348
2	313	-317
0	268	275
-8	268	268
-6	202	-208
-4	331	340
-2	364	-378
H,3,10		
-1	70	-69
-3	85	-83
-5	190	194
-7	46	-50
1	25	28
3	62	-64
H,3,11		
-2	215	220
0	212	-214
H,4,0		
12	321	325
10	551	-557
8	454	445
6	414	-426
4	972	978
2	948	-936
0	938	942
H,4,1		
1	74	-79
3	22	-17
5	141	-145
7	79	79
9	247	-254
11	165	-164
13	25	-8
-1	468	-453
-3	164	-173
-5	124	121
-7	356	-362
-9	20	-23
-11	155	-162
-13	100	-96
H,4,2		
12	230	-230
10	362	363
8	360	-354
6	353	360
4	1258	-1248
2	951	946
0	534	-558
-12	426	-426
-10	561	561
-8	469	-463
-6	204	208
-4	353	-353
-2	555	564
H,4,3		
1	235	240
3	69	56
5	<15	2
7	35	35
9	112	108
11	145	153
-1	482	480
-3	164	153
-5	202	201
-7	22	-12
-9	136	126
-11	124	125
-13	35	-37
H,4,4		
12	268	260
10	450	-447
8	574	567
6	390	-393
4	738	741
2	476	-489
0	230	230
-12	202	200
-10	367	-369
-8	623	626
-6	576	-573
-4	925	909
-2	809	-799
H,4,5		
1	371	-357
3	154	-156
5	83	86
7	115	-108
9	107	-110
11	34	-32
-1	21	-14
-3	427	-427
-5	218	210
-7	50	-42
-9	83	-79
-11	67	-47
H,4,6		
10	384	382
8	429	-421
6	333	326
4	456	-448
2	385	384
0	237	-237
-12	208	-212
-10	337	332
-8	399	-398
-6	233	230
-4	577	-587
-2	461	465
H,4,7		
1	107	103
3	44	29
5	126	126
7	36	29
9	104	106
-1	252	248
-3	130	-131
-5	77	72
-7	<18	3
-9	<20	2
-11	191	193
H,4,8		
8	156	153
6	155	-153
4	367	366
2	440	-440
0	523	530
-10	250	-250
-8	197	201
-6	159	-153
-4	468	479
-2	480	-488
H,4,9		
1	165	-164
3	60	56
5	78	-69
-1	50	47
-3	135	-137
-5	44	42
-7	77	-76
H,4,10		
2	187	188
0	184	-188
-6	179	177
-4	201	-207
-2	160	161
H,5,0		
1	73	68
3	335	-342
5	244	243
7	26	-35
9	31	26
11	77	72
13	<22	-15
H,5,1		
12	190	-189
10	275	277
8	383	-382
6	321	326
4	952	-943
2	905	897
0	423	-445
-12	411	-415
-10	620	626
-8	528	-628
-6	195	194
-4	687	-692
-2	483	491
H,5,2		
1	208	208
3	37	-31
5	30	38
7	64	60
9	28	-25
11	63	-60
-1	175	-173
-3	109	-109
-5	75	71
-7	176	-181
-9	28	25
-11	50	53
-13	37	-36
H,5,3		
12	329	331
10	424	-424
8	401	397
6	385	-383
4	755	757
2	696	-704
0	577	587
-12	153	145
-10	333	-332
-8	333	322
-6	188	-188
-4	787	784
-2	628	-619
H,5,4		
1	70	-68
3	160	160
5	85	-79
7	105	-107
9	97	100
11	91	-91
-1	142	156
-3	106	111
-5	35	-22
-7	81	-75
-9	51	38
-11	99	-103
H,5,5		
10	358	388
8	387	-382
6	290	289
4	488	-489
2	167	166
0	222	-224
-12	237	-233
-10	449	450
-8	517	-508
-6	465	468
-4	717	-713
-2	435	434
H,5,6		
1	168	-166
3	53	-52
5	90	55
7	131	-134
9	97	102
-1	97	95
-3	<17	0
-5	<17	1
-7	171	165
-9	55	-53
-11	34	14
H,5,7		
8	277	272
6	226	-223
4	575	570
2	457	-454
0	448	444
-10	201	-203
-8	189	179
-6	80	-76
-4	317	319
-2	443	-455
H,5,8		
1	<20	-18
3	35	-31
5	46	47
7	<22	11
-1	35	33
-3	150	-152
-5	42	41
-7	38	-36
-9	32	23
H,5,9		
4	250	-251
2	207	257
0	216	-210
-4	352	-357
-6	197	202
-2	335	348
H,5,10		
-1	59	-58
-3	55	62
1	[illegible]	86
H,6,0		
12	207	-205
10	515	523
8	494	-496
6	594	594
4	578	-578
2	374	381
0	26	19
H,6,1		
1	117	-118
3	212	210
5	25	11
7	243	245
9	34	29
11	21	-15
-1	87	-94
-3	136	139
-5	337	341
-7	95	93
-9	93	86
-11	34	38
H,6,2		
10	347	-339
8	286	288
6	313	-311
4	582	582
2	648	-652
0	510	512
-12	212	213
-10	321	-323
-8	224	226
-6	337	-340
-4	567	572
-2	842	-829
H,6,3		
1	211	-210
3	50	55
5	192	-194
7	80	-78
9	31	32
11	44	-46
-1	120	116
-3	278	-280
-5	188	-194
-7	159	-159
-9	38	39
-11	25	14
H,6,4		
10	408	405
8	255	-256
6	172	167
4	329	-328
2	452	457
0	340	-349
-10	306	300
-8	305	-300
-6	333	329
-4	540	-542
-2	714	716
H,6,5		
1	24	-18
3	151	150
5	207	201
7	<20	22
9	<21	-4
-1	222	223
-3	35	-29
-5	135	140
-7	109	109
-9	105	-106
-11	48	52
H,6,6		
8	245	241
6	394	-389
4	530	526
2	551	-549
0	226	227
-10	380	-378
-8	318	322
-6	183	-178
-4	229	230
-2	299	-296
H,6,7		
1	111	-108
3	93	-88
5	173	-169
7	41	-40
-1	136	136
-3	164	-163
-5	57	57
-7	119	-115
-9	<20	-17
H,6,8		
6	224	223
4	267	-260
2	282	282
0	226	-223
-8	202	-201
-6	225	222
-4	318	-327
-2	320	324
H,6,9		
1	29	-24
3	105	96
-1	38	-25
-3	35	36
-5	72	71
H,7,0		
1	60	58
3	65	-66
5	280	285
7	<29	41
9	169	-170
11	33	35
H,7,1		
10	334	-342
8	536	537
6	490	-490
4	578	588
2	418	-411
0	361	375
-10	208	-209
-8	318	320
-6	240	-238
-4	431	431
-2	316	-310
H,7,2		
1	83	85
3	184	-189
5	197	-198
7	72	-68
9	29	29
11	73	71
-1	103	100
-3	93	-94
-5	<16	-7
-7	114	-105
-9	41	43
-11	58	57
H,7,3		
10	187	188
8	188	-187
6	104	103
4	254	-258
2	340	345
0	574	-584
-10	241	246
-8	315	-313
-6	329	326
-4	600	-603
-2	574	571
H,7,4		
1	190	-196
3	162	161
5	149	151
7	26	24
9	63	63
-1	111	-110
-3	78	73
-5	20	12
-7	207	207
-9	36	-34
H,7,5		
8	343	340
6	340	-340
4	469	470
2	345	-347
0	366	374
-10	236	-236
-8	273	265
-6	199	-195
-4	267	263
-2	225	-223
H,7,6		
1	79	-74
3	60	55
5	69	-66
7	102	-100
-1	199	202
-3	105	-104
-5	190	-189
-7	60	-51
-9	26	-23
H,7,7		
6	191	185
4	339	-335
2	255	250
0	292	-291
-8	279	-275
-6	234	237
-4	272	-270
-2	239	242
H,7,8		
1	23	28
3	23	17
-1	<20	-28
-3	84	90
-5	60	54
H,7,9		
-2	214	-224
H,8,0		
10	247	-254
8	204	202
6	359	-357
4	208	209
2	413	-416
0	408	410
H,8,1		
1	55	-58
3	156	155
5	224	-225
7	84	-82
9	82	79
-1	175	170
-3	98	-94
-5	172	-173
-7	130	-132
-9	28	12
H,8,2		
8	199	-202
6	420	426
4	339	-343
2	498	501
0	412	-418
-10	242	241
-8	230	-227
-6	368	362
-4	194	-193
-2	385	380
H,8,3		
1	240	-243
3	243	247
5	31	-10
7	<19	-5
9	62	60
-1	77	75
-3	161	159
-5	38	33
-7	172	175
-9	60	-58
H,8,4		
8	235	241
6	360	-363
4	199	204
2	275	-280
0	205	207
-8	269	270
-6	403	-397
-4	227	220
-2	287	-281
H,8,5		
1	162	-164
3	28	16
5	160	-162
7	<20	-7
-1	121	118
-3	110	-110
-5	68	-69
-7	31	-32
H,8,6		
6	293	291
4	171	-166
2	288	288
0	261	-261
-6	303	296
-4	227	-232
-2	321	325
H,8,7		
1	49	48
3	81	78
-1	85	-83
-3	<19	3
-5	60	62
H,8,8		
0	228	223
-2	250	-247
H,9,0		
1	72	-72
3	54	-53
5	132	-131
7	29	9
H,9,1		
8	159	-159
6	216	216
4	203	-200
2	289	285
0	466	-470
-8	264	-264
-6	312	310
-4	229	-231
-2	285	285
H,9,2		
1	111	112
3	152	152
5	30	5
7	185	188
-1	124	-119
-3	149	152
-5	<19	-14
-7	53	49
H,9,3		
6	386	-392
4	308	313
2	262	-264
0	294	300
-8	245	244
-6	297	-292
-4	165	156
-2	140	-130
H,9,4		
1	<18	-2
3	36	2
5	184	-191
-1	32	-31
-3	44	48
-5	98	-98
-7	109	-103
H,9,5		
4	112	-119
2	152	157
0	284	-291
-6	309	304
-4	258	-250
-2	228	222
H,9,6		
1	47	43
3	<22	-16
-1	30	-31
-3	77	81
-5	66	56
H,10,0		
6	314	313
4	162	-161
2	313	311
0	328	-332
H,10,1		
1	<17	5
3	<17	9
5	99	-96
-1	66	-58
-3	34	38
-5	41	37
H,10,2		
6	274	-275
4	33	28
2	146	-141
0	183	185
-6	327	-328
-4	167	167
-2	214	-213
H,10,3		
1	81	-87
3	71	71
5	<20	21
-1	28	21
-3	68	-64
-5	<19	13
H,10,4		
4	159	-163
2	294	305
0	313	-319
-4	125	-118
-2	239	241
H,10,5		
1	<19	21
-1	103	99
-3	62	-55
H,11,0		
1	107	106
3	38	46
H,11,1		
2	122	-122
0	210	205
-2	228	-226
H,11,2		
1	93	-91
-1	86	-91

shape, it was difficult to determine an adequate description of the boundary planes required in the usual absorption-correction procedure. The crystal was mounted along **a*** and the variation in I_o/I *vs.* φ at $\chi=90°$ was recorded and is shown in Fig. 2(*b*). Inclusion of the φ-dependent absorption correction decreased R to 0·018.

The data were corrected for secondary extinction according to the method described by Zachariasen (1963). The g value in the expression $I=I_o(1+2gI_c)$ was found to be $1{\cdot}1\times10^{-7}$. The correction gave only a slight improvement in R.

A plot of I_o/I *vs.* 2θ, Fig. 2(*a*), shows an approximate linear variation of the absorption correction in addition to the usual φ vatiation. This trend was confirmed by a plot of $w\,.\,\Delta F$ *vs.* 2θ. Accordingly, an additional correction was made based on the linear relation I_o/I *vs.* 2θ obtained for the reflections 400–14,0,0 and modified by a sin χ factor which accounts approximately for the variation in absorption in the region $\chi=0$–$90°$.

After three more refinement cycles the shifts in parameters for nonhydrogen atoms were less than $0{\cdot}01\sigma$ and for hydrogen atoms less than $0{\cdot}03\sigma$. The final $R=0{\cdot}017$ and the g.o.f. 1·61. A difference map showed residual electron densities of approximately 0·26 e Å^{-3} in the middle of each of the Cu–O bonds and a correspondingly negative density at the copper site.

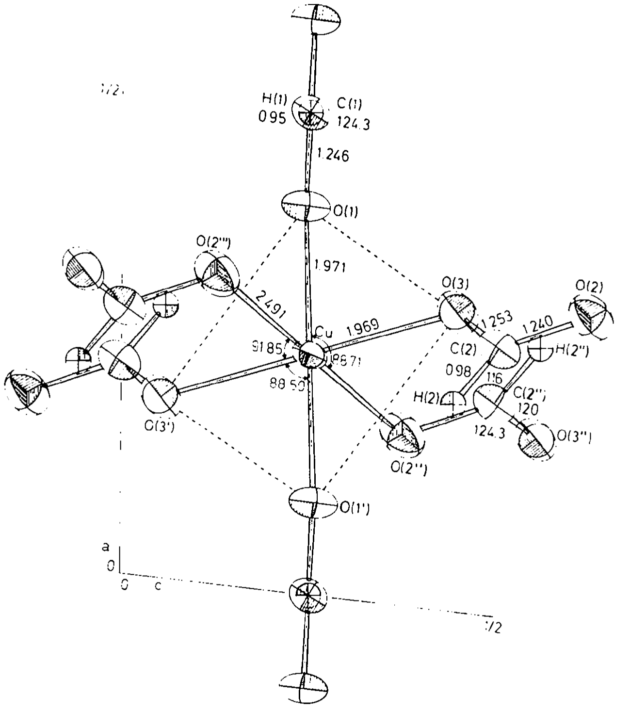


Fig. 3. Bond lengths and angles in the copper(II) formate complex. The nonhydrogen atoms are represented by thermal ellipsoids defined by the principal axes of thermal vibration and scaled to include 50% probability. The isotropic thermal spheres of the hydrogen atoms are scaled down by a factor of four.

Final coordinates and thermal parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2. Atomic scattering curves for the heavier atoms were obtained from *International Tables for X-ray Crystallography* (1962), and those for the hydrogen atoms were from Stewart, Davidson & Simpson (1965).

Results and discussion

The copper ion located at a center of symmetry has octahedral coordination with four short equatorial and two long axial Cu–O bonds (Fig. 3). This arrangement is often found in copper complexes where the metal occupies a special position in the unit cell. In complexes with no crystallographic restrictions the regular, elongated octahedra is rarely found.

Since the structure is determined with high precision some molecular details not usually discernible in heavy-atom structures, can be pointed out. The formate ion in the general position is asymmetric with the oxygen in the long C–O bond (1·253 Å) coordinated equatorially, Cu–O = 1·969 Å and the oxygen in the short C–O bond (1·240 Å) coordinated axially, Cu–O = 2·491 Å.

The formate ion located on the twofold axis has C–O bond lengths of 1·246 Å and is coordinated equatorially with Cu–O = 1·971 Å. Thus at the three crystallographically nonequivalent coordination sites a long Cu–O bond corresponds to a short C–O bond and *vice versa*. This so-called *trans* effect is much less pronounced in complexes of transition metals than in complexes with central atoms such as Se and Te.

The dimethylammonium ion is located on a twofold axis and hydrogen bonded to the axial formate oxygen, O(2). The unusually long axial Cu–O(2) bond may be a result of the hydrogen bonding. The methyl group of the ion is well defined but deviates somewhat from regular sp^3 symmetry. The three C–H bond lengths are 0·88 (3), 0·89 (3), and 0·91 (3) Å, and the three N–C–H angles are 106 (2), 106 (2), and 107 (2)°. The consistent deviations in bond lengths and angles from the values usually found by X-ray methods appear to be significant.

The arrangement of atoms in the crystal is shown in Fig. 4. The copper ions related by twofold axes and screw axes are bridged by formate groups forming a three-dimensional network. The two types of bridges are both in the *anti–anti* configuration. Theoretically a *syn–syn* configuration would give a denser crystal packing and enhance the proposed super-exchange between the metal centers. Thus, the reason for the adopted *anti–anti* arrangement remains uncertain.

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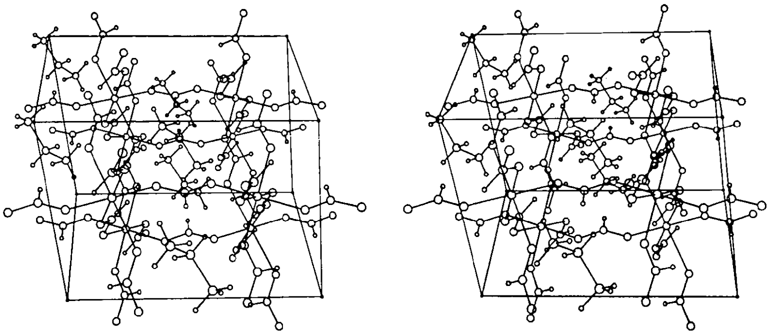

Fig. 4. A stereoscopic view of the molecular packing in the unit cell of dimethylammonium copper(II) formate.

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The Crystal and Molecular Structures of Reaction Products from γ-Irradiation of Thymine and Cytosine: *cis*-Thymine Glycol, $C_5H_8N_2O_4$, and *trans*-1-Carbamoyl-imidazolidone-4,5-diol, $C_4H_7N_3O_4$

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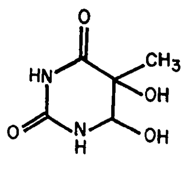
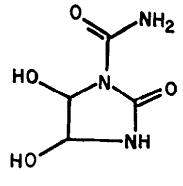
As part of a study on the mutagenetic effects of ionizing radiation on nucleic acids, solutions of thymine and cytosine were subjected to γ-radiation. In both cases the reaction conditions were the same; however, the products differed significantly. The product of the thymine reaction was *cis*-thymine glycol (I), $C_5H_8N_2O_4$ [space group $P2_12_12_1$ with $a=9{\cdot}745$ (6), $b=10{\cdot}806$ (6), $c=6{\cdot}282$ (4) Å]. The reaction on the cytosine molecule involved a rearrangement of the six-membered ring to give an imidazolidone derivative (II), $C_4H_7N_3O_4$ [space group $Pbca$ with $a=13{\cdot}228$ (8), $b=13{\cdot}260$ (8), $c=7{\cdot}139$ (4) Å]. The calculated crystal densities are 1·61 g cm^{-3}for (I) and 1·71 g cm^{-3} for (II). Both structures were solved by the symbolic addition procedure. Intensities were collected on an automatic diffractometer (Cu $K\alpha$ radiation) and refined to final R values of 0·052 for (I) and 0·064 for (II). Hydrogen bonding plays a significant role in the packing systems of both molecules.





Introduction

The radiation chemistry of the nucleic acid bases, thymine, cytosine and uracil, has been the subject of extensive research in attempts to determine the molecular origin of biological radiation damage (Fahr, 1969). When solutions of thymine and cytosine were subjected to γ-radiation, under the same reaction con-