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The Crystal Structure of Tris(Dimethylammonium) Monochloride Tetrachlorocuprate(II), $[(CH_3)_2NH_2]_3Cl\cdot CuCl_4$

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The crystal structure of tris-dimethylammonium monochloride tetrachlorocuprate(II), $[(CH_3)_2NH_2]_3Cl\cdot CuCl_4$, was determined using X-ray diffraction techniques. Crystals of the compound are orthorhombic, space group Pnma, with cell dimensions $a=11.304$, $b=15.638$, and $c=9.957$.

The crystal structure was refined to a conventional R of 0.106. The structure consists of a distorted tetrahedral $CuCl_4^{2-}$ ion, a lattice chloride ion, and three dimethylammonium ions. The D_{2d} distortion of the $CuCl_4^{2-}$ ion is more pronounced than in previously reported structures. The Cu–Cl bond distances are all 2.230±0.009 Å, but two Cl–Cu–Cl angles of 98±0.7° and two of 136±0.8° were found. The dimethylammonium groups are all involved in hydrogen bonding of the type N–H - - - Cl, and one bifurcated hydrogen bond was found. The lattice chloride ion and one dimethylammonium ion are disordered, as a result of hydrogen bonding.

Introduction

As part of a study of the structural and spectral properties of anhydrous copper(II) halide species, the crystal structure of the compound tris (dimethylammonium) monochloride tetrachlorocuprate(II) $[(CH_3)_2NH_2]_3Cl\cdot CuCl_4$ (henceforth DMA_3CuCl_5) has been determined. Interest in this compound was aroused by the observation that this compound, yellow at room temperature, turned green when cooled to liquid nitrogen temperature. This thermochromism is characteristic of a number of compounds such as $(NH_4)_2CuCl_4$,[1] $(C_2H_5NH_3)_2CuCl_4$,[2] $(NH_3CH_2CH_2NH_3)CuCl_4$,[3] and $[(NH_3CH_2CH_2)_2NH_2]Cl\,.\,CuCl_4$,[4] which contain a layer structure of square-planar $CuCl_4^{2-}$ ions. These compounds undergo a phase transition which disrupts this layer structure, generally in the temperature range –20° to –60°C. Subsequent spectral and thermal investigations of DMA_3CuCl_5 have revealed that no major structural change occurs during the thermochromic change but found rather that the color change is due to a change in band width with temperature. Details of the spectral investigation will be published later.

Preparation and Data Collection. Crystals of $[(CH_3)_2NH_2]_3CuCl_5$ are easily grown from absolute alcohol. A preparation was reported by Remy and Laves in 1933,[5] and by Shagisultanova, *et al.*[6] The crystals grow as yellow irregular prisms, needles, or flat platelets depending on the conditions of development.

Analysis: Calcd: Cu, 16.78%; Cl, 46.80%; N, 11.09%; C, 19.00%; H, 6.33%. Found: Cu, 16.69%; Cl, 46.85%; N, 11.06%; C, 19.21%; H, 6.26%.

Examination of X-ray diffraction photographs revealed that the crystals are orthorhombic. The lattice constants, measured with Zr filtered Mo K_α (λ = 0.7107) radiation with a Picker diffractometer and G. E. single crystal orienter, were found to be $a=11.304\pm0.010$ Å, $b=15.638\pm0.012$ Å, and $c=9.957\pm0.006$ Å. Systematic extinctions $[k+\ell=2n+1$ for $\{0k\ell\}$, $h=2n+1$ for $\{hk0\}]$ limited the choice of space group to Pnma or $Pn2_1a(Pna2_1)$. The calculated density ($Z=4$) of 1.43 g/cc is in good agreement with the observed value of 1.41 g/cc measured using flotation.

A set of initial intensity data (746 observed reflections) was collected on a Weissenberg camera. Because difficulty was encountered in obtaining a satisfactory trial structure with these data and since decomposition of the crystal was suspected during the final stages of the data collection, it was decided to collect a set of data utilizing counter techniques. A total of 1072 reflections to a sin θ/λ limit of 45° were recorded from a crystal (0.17 mm×0.20 mm×0.23 mm) on a Picker diffractometer equipped with a G. E. single crystal orienter. A θ–2θ scan technique with 40 second scan, and 4 second background counts on each side of the peak was used. Of the reflections examined, 770 had a net count greater than 4.5% of the background. Those with a net count of less than this were assigned a net count of 4.5% of the background and treated as unobserved reflections. The standard deviation for each reflection was calculated by

$$\sigma(F)=|F|(TC+BG+0.01NC^2+0.01BG^2)^{1/2}/2NC$$

where TC = total count, BG = background count, and NC = net count. Absorption corrections were not made ($\mu=19.3$ cm^{-1}).

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Structure Determination. An initial attempt was made to solve the structure through the interpretation of a three-dimensional Patterson function. Computations, based on the film data, were made with the Sly and Shoemaker ERFR2 Fourier program.[7]

In searching for models consistent with the Patterson function in the space group Pnma, it was not possible to find a reasonable model in which the copper atoms were located at centers of inversion. Hence a model was chosen in which the copper atoms were located on the mirror planes perpendicular to the b axis and were tetrahedrally coordinated with four chlorine atoms. Refinement of this model with the Busing, Martin, and Levy least squares program[8] gave a value of $R_1 = 0.37$ (see Table II for definition of R_1).

Attempts to further elucidate the structure with these data were not successful.

Because of the aforementioned possibility of decomposition due to the hygroscopic nature of the compound, the set of counter data was collected at this point. A distribution of intensities was calculated to determine the correct space group. With these data, as indicated in Table I,[9] the evidence is quite strong that the structure is centrosymmetric. The Patterson function was recalculated; its features were very similar to the initial Patterson, but peak resolution was much better. The same model of a tetrahedral ion was used and a value of $R_1 = 0.27$ was obtained for the 620 strongest reflections. A Fourier synthesis revealed the location of the two equivalent dimethylammonium groups and the fifth chlorine atom at a center of inversion (1/2,0,0). Refinement of these positions lowered the value of R_1 to 0.17. However, two features of the structure still were not satisfactory. The thermal parameter for the fifth chlorine atom was too large to be physically reasonable and this atom appeared as a peak of only 6 electrons on an electron density map. The approximate location of the third dimethylammonium group was found near the mirror plane. Attempts to refine structure models with the nitrogen atom and both carbon atoms on the mirror plane, or with only the nitrogen atom on the mirror plane and a carbon atom on each side were unsuccessful.

Table I. Statistical Distribution for the E's as Calculated from a Wilson Plot for DMA_3CuCl_5 [a]

Quantity	Film Data Calculated	Counter Data Calculated	Theoretical Centric	Theoretical Acentric
Average magnitude of $\|E\|$'s	0.82	0.731	0.798	0.886
Average of E^2	1.00 [b]	1.00 [b]	1.00	1.00
Average of $\|E^2-1\|$	0.906	1.087	0.968	0.736
% $\|E\|$'s>1	35.12	34.57	32.00	37.00
% $\|E\|$'s>2	3.33	4.81	5.00	1.80
% $\|E\|$'s>3	0.0	0.0	0.30	0.01

[a] The E's are normalized structure factors defined by:

$$E_{hkl} = \frac{|F_{hkl}|}{(\sum_{j=1}^{n} f_j^2)^{1/2}}$$

where the sum is over the j atom in the unit cell.
[b] Rescaled so the average $|E|^2 = 1.00$.

Examination of a difference Fourier synthesis revealed maxima on both sides of the mirror plane at the location of the nitrogen atom. Hence, a disordered model was postulated in which this nitrogen was present at half-occupance on each side of the mirror plane. Anisotropic thermal refinement of the heavy atoms dropped the R_1 value to 0.093 for the 620 strongest reflections and although the β_{11} and β_{33} components of the temperature factor for the lattice chloride ion were reasonable, the β_{22} was much too large. Examination of a difference Fourier[10] in the region of this chloride ion revealed maxima at either side of (1/2,0,0) along the y-direction. A disordered model with equal occupancy factors of 0.5 was postulated. Examination of the difference Fourier allowed the determination of the y-parameter of this chloride ion to be approximately 0.02. It was not possible to simultaneously refine both the y-parameter and the

Table II. Final Parameters for DMA_3CuCl_5 [a]

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu(1)	0.4702(2)	0.25	0.5144(2)	0.0070(2)	0.0028(1)	0.0074(2)	0.0	0.0010(2)	0.0
Cl(2)	0.6417(5)	0.25	0.4034(5)	0.0065(5)	0.0054(3)	0.0125(7)	0.0	0.0015(5)	0.0
Cl(3)	0.4145(6)	0.25	0.7272(5)	0.0162(8)	0.0054(3)	0.0097(6)	0.0	0.0043(6)	0.0
Cl(4)	0.4126(4)	0.1181(2)	0.4604(4)	0.0131(5)	0.0041(2)	0.0165(6)	–0.0019(2)	0.0024(4)	–0.0025(3)
Cl(5)	0.5	0.02	0.0	0.0241(13)	0.0069(7)	0.0208(10)	0.0001(9)	0.0010(10)	0.0022(8)
C(6)	0.1979(16)	0.0936(10)	0.8093(16)	0.0143(22)	0.0043(8)	0.0181(22)	0.0023(11)	0.0061(18)	0.0024(12)
N(7)	0.3002(17)	0.0567(7)	0.7438(17)	0.0292(33)	0.0032(7)	0.0302(27)	0.0007(11)	0.0227(25)	–0.0009(11)
C(8)	0.3013(17)	–0.0271(10)	0.7038(15)	0.0181(27)	0.0062(10)	0.0144(22)	0.0044(14)	0.0086(19)	–0.0028(12)
C(9)	0.4315(28)	0.25	0.1213(25)	0.0127(38)	0.0160(31)	0.0138(36)	0.0	0.0029(27)	0.0
C(10)	0.6329(21)	0.25	0.0269(27)	0.0131(23)	0.0131(23)	0.0206(42)	0.0	0.0029(28)	0.0
N(11)	0.5406(26)	0.2068(17)	0.1194(24)	0.0104(30)	0.0084(19)	0.0161(36)	0.0004(20)	0.0023(28)	–0.0009(19)

$$R_1 = \frac{\Sigma||F_{obs}|-|F_{calc}||}{\Sigma|F_{obs}|} = 0.106 \qquad R_3 = \frac{\Sigma(|F_{obs}|-|F_{calc}|)^2}{\Sigma|F_{obs}|^2} = 0.092$$

[a] Standard deviations on the least significant digit are given in parenthesis.

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β_{22} thermal parameter for this chloride ion. However, the R_1 values for a series of least squares calculations with fixed y-parameter indicated the initial choice of $y=0.02$ was the best value. Final anisotropic refinement of all data gave a value of $R=0.106$ for the 770 observed reflections. The final parameters are listed

Table III. Observed and Calculated Structure Factors for DMA$_3$CuCl$_5$ [a]

K	L	FO	FC
	H = 0		
2	0	1231	-1290
4	0	1954	1903
6	0	2038	-2071
8	0	1813	1893
10	0	860	-800
12	0	401	415
14	0	770	-755
16	0	480	525
3	1	385	253
5	1	496	513
7	1	255	-205
9	1	-105	-147
11	1	423	-381
13	1	-119	53
15	1	112	-63
0	2	1295	1413
2	2	1109	-852
4	2	281	202
6	2	354	-384
8	2	1312	1296
10	2	143	-133
12	2	-113	130
14	2	411	-405
16	2	320	303
1	3	1682	-1632
3	3	-131	96
5	3	465	-481
7	3	705	725
9	3	362	-304
11	3	-130	50
13	3	-116	50
15	3	218	264
0	4	1699	1745
2	4	154	-39
4	4	664	673
6	4	676	-663
8	4	791	788
10	4	400	-386
12	4	279	253
14	4	420	-401
1	5	227	256
3	5	881	-860
5	5	762	781
7	5	-117	7
9	5	181	158
11	5	523	-511
13	5	-117	181
0	6	305	335
2	6	126	44
4	6	203	200
6	6	-128	-124
8	6	151	217
10	6	-112	25
12	6	197	155
1	7	166	183
3	7	567	-596
5	7	378	365
7	7	-119	-137
9	7	-113	77
11	7	380	-324
0	8	425	414
2	8	395	-414
4	8	545	583
6	8	252	-315
8	8	293	230
10	8	236	-236
1	9	225	247
3	9	411	-434
5	9	315	379
7	9	144	-126
9	9	278	267
0	10	-123	212
2	10	144	-154
4	10	285	321
6	10	-116	-157
	H = 1		
1	1	242	311
2	1	1329	-1440
3	1	274	342
4	1	286	-291
5	1	350	-362
6	1	1417	-1409
7	1	352	-279
8	1	1192	1175
9	1	-139	100
10	1	543	-545
11	1	197	160
12	1	282	288
13	1	-114	-80
14	1	508	-523
15	1	-119	-133
16	1	365	424
0	2	240	-229
1	2	213	74
2	2	360	397
3	2	575	-535
4	2	962	-894
5	2	289	314
6	2	182	182
7	2	172	125
8	2	105	-106
9	2	161	-137
10	2	311	304
11	2	116	-148
12	2	217	-177
13	2	118	69
14	2	-115	74
0	3	754	777
1	3	688	636
2	3	1165	-1110
3	3	255	285
4	3	135	-149
5	3	180	184
6	3	821	-845
7	3	313	-359
8	3	611	601
9	3	173	191
10	3	291	-303
11	3	-112	115
12	3	172	124
14	3	338	-334
15	3	155	-98
	H = 1		
16	3	307	286
0	4	303	282
1	4	358	-336
2	4	234	220
3	4	392	-395
4	4	122	-138
5	4	330	324
6	4	167	180
7	4	369	335
8	4	116	101
9	4	-107	-30
10	4	-111	1
11	4	208	-213
12	4	173	-214
13	4	-111	77
14	4	-109	11
15	4	128	82
0	5	702	692
1	5	457	466
2	5	834	-816
3	5	524	-548
4	5	246	284
5	5	327	312
6	5	711	-705
7	5	421	-416
8	5	416	425
9	5	219	229
10	5	253	-240
11	5	-137	-236
12	5	232	251
13	5	243	99
14	5	258	-274
0	6	155	120
1	6	198	216
2	6	-104	-45
3	6	677	-682
4	6	319	-331
5	6	573	569
6	6	-111	-81
7	6	-115	-198
8	6	-115	124
9	6	245	222
10	6	126	113
11	6	407	-448
12	6	-111	-87
13	6	223	243
0	7	-106	-43
1	7	-105	48
2	7	246	-277
3	7	-109	-27
4	7	-114	104
5	7	-117	112
6	7	247	-268
7	7	-112	-12
8	7	123	66
9	7	-109	32
10	7	-112	-141
11	7	216	11
12	7	-112	153
0	8	296	304
1	8	154	118
2	8	-115	-99
3	8	338	-345
4	8	176	81
5	8	334	303
6	8	-116	-135
7	8	-115	-26
8	8	185	166
9	8	191	156
10	8	-113	-45
11	8	194	-229
0	9	172	211
1	9	-111	21
2	9	404	-372
3	9	-116	-80
4	9	348	361
5	9	-110	86
6	9	-124	-326
7	9	-114	-22
8	9	223	184
9	9	-123	-19
0	10	-115	-63
1	10	240	292
2	10	-111	64
3	10	333	-363
4	10	-114	-95
5	10	254	290
	H = 2		
0	0	1383	1593
2	0	1623	-1377
4	0	1059	1029
6	0	525	-546
8	0	1178	1190
10	0	343	-319
12	0	314	330
14	0	415	-393
16	0	266	297
0	1	851	-882
1	1	141	-83
2	1	526	553
3	1	728	-706
4	1	1213	-1165
5	1	214	173
6	1	373	390
7	1	161	-68
8	1	198	-170
9	1	315	343
10	1	417	421
11	1	164	-93
12	1	246	-208
13	1	200	170
14	1	-116	117
15	1	-111	-12
16	1	-112	-102
0	2	2241	2181
1	2	197	131
2	2	425	380
3	2	1022	957
4	2	640	601
5	2	610	-615
6	2	572	-534
7	2	338	-344
	H = 2		
8	2	612	632
9	2	-106	80
10	2	275	-280
11	2	381	394
12	2	178	180
13	2	-108	53
14	2	386	-351
15	2	158	-111
16	2	129	201
0	3	567	543
1	3	170	-126
2	3	421	410
3	3	-101	-2
4	3	395	-441
5	3	231	256
6	3	100	82
7	3	-99	15
8	3	-108	147
9	3	-107	-19
10	3	139	33
11	3	274	-254
12	3	272	-255
13	3	-108	34
14	3	-108	3
15	3	129	-31
0	4	1049	999
1	4	980	954
2	4	558	-566
3	4	346	-364
4	4	721	716
5	4	554	534
6	4	554	-562
7	4	641	-653
8	4	816	823
9	4	426	386
10	4	306	-329
11	4	176	-224
12	4	362	381
13	4	216	193
14	4	345	-350
15	4	322	-295
0	5	124	-81
1	5	329	340
2	5	305	312
3	5	614	-673
4	5	758	-744
5	5	389	381
6	5	260	259
7	5	266	-253
8	5	-112	86
9	5	171	169
10	5	288	281
11	5	302	-270
12	5	284	-305
13	5	125	215
14	5	-113	17
0	6	564	559
1	6	182	190
2	6	228	-217
3	6	256	-255
4	6	461	487
5	6	187	164
6	6	239	-261
7	6	224	-213
8	6	282	320
9	6	126	118
10	6	255	-237
11	6	-110	-61
12	6	147	185
13	6	165	159
0	7	461	441
1	7	180	125
2	7	124	-67
3	7	298	-309
4	7	164	-131
5	7	238	265
6	7	189	-188
7	7	-112	23
8	7	232	216
9	7	-110	135
10	7	106	13
11	7	171	-172
12	7	196	-52
0	8	489	483
1	8	175	126
2	8	243	-255
3	8	-110	-154
4	8	354	406
5	8	279	248
6	8	282	-259
7	8	161	-86
8	8	252	244
9	8	-111	40
10	8	216	-146
0	9	-110	45
1	9	-112	184
2	9	146	56
3	9	252	-276
4	9	-111	-105
5	9	162	188
6	9	-110	23
7	9	203	-191
8	9	-109	51
0	10	134	74
1	10	155	-96
3	10	-111	-55
	H = 3		
0	1	324	-294
1	1	1139	1130
2	1	905	-855
3	1	334	346
4	1	232	176
5	1	-99	-32
6	1	617	-609
7	1	790	-800
8	1	118	218
9	1	370	394
10	1	326	-365
11	1	196	173
12	1	223	270
13	1	-113	131
14	1	182	-202
	H = 3		
15	1	286	-310
16	1	152	151
0	2	121	98
1	2	622	618
2	2	556	497
3	2	544	-560
4	2	595	-588
5	2	435	425
6	2	326	313
7	2	107	-175
8	2	-104	-81
9	2	358	351
10	2	212	167
11	2	167	-127
12	2	274	-314
13	2	-116	85
14	2	-113	64
15	2	125	-122
16	2	-111	31
0	3	885	847
1	3	718	709
2	3	1057	-1045
3	3	-104	-65
4	3	540	556
5	3	205	144
6	3	855	-875
7	3	612	-615
8	3	425	436
9	3	343	319
10	3	356	-368
11	3	-114	-46
12	3	327	386
13	3	137	85
14	3	206	-265
15	3	287	-271
0	4	413	380
1	4	530	525
2	4	-98	-69
3	4	327	-310
4	4	619	-582
5	4	219	267
6	4	131	-71
7	4	464	-464
8	4	278	315
9	4	145	172
10	4	201	205
11	4	226	-220
12	4	231	-180
13	4	119	143
14	4	170	-50
15	4	-112	-104
0	5	476	431
1	5	721	735
2	5	1018	-1031
3	5	437	-430
4	5	531	515
5	5	483	503
6	5	632	-637
7	5	567	-595
8	5	353	391
9	5	392	386
10	5	404	-447
11	5	-117	-148
12	5	290	254
13	5	246	319
14	5	217	-210
0	6	-126	215
1	6	132	51
2	6	294	298
3	6	-114	-51
4	6	440	-437
5	6	149	122
6	6	148	81
7	6	149	3
8	6	148	61
9	6	238	213
10	6	198	139
11	6	-114	-45
0	7	385	403
1	7	-109	57
2	7	452	-414
3	7	210	-83
4	7	274	276
5	7	-116	145
6	7	362	-385
7	7	112	-58
8	7	286	295
9	7	-110	-20
0	8	254	204
1	8	123	101
2	8	114	-85
3	8	-112	-94
4	8	113	-106
5	8	171	64
6	8	167	-96
7	8	-109	-126
0	9	-111	27
1	9	-111	119
2	9	173	-136
3	9	235	-266
4	9	-114	8
5	9	127	203
6	9	135	-115
7	9	147	-92
8	9	153	61
0	10	-109	-111
1	10	150	142
2	10	219	197
3	10	-112	-124
4	10	-115	-236
	H = 4		
0	0	-110	-29
2	0	501	508
4	0	569	609
6	0	192	146
8	0	172	-186
10	0	-111	-103
14	0	287	-75
0	1	-108	108
1	1	189	196
2	1	508	534
3	1	-101	62
	H = 4		
4	1	190	-44
5	1	-98	16
6	1	190	239
7	1	129	-188
8	1	-111	-104
9	1	129	84
10	1	-114	-49
11	1	-114	-20
12	1	-118	-203
13	1	129	10
0	2	385	345
1	2	636	637
2	2	322	-337
3	2	-100	41
4	2	1021	1017
5	2	123	155
6	2	197	-234
7	2	519	-527
8	2	309	292
9	2	269	291
10	2	325	-313
11	2	-108	-88
12	2	433	433
13	2	-109	34
14	2	141	-149
15	2	348	-321
0	3	396	403
1	3	825	798
2	3	458	-441
3	3	374	-432
4	3	216	-171
5	3	348	345
6	3	148	-293
7	3	592	-596
8	3	428	446
9	3	416	427
10	3	-108	34
11	3	-114	-174
12	3	134	16
0	4	484	507
1	4	683	689
2	4	248	-283
3	4	373	-396
4	4	704	719
5	4	248	286
6	4	256	-277
7	4	615	-574
8	4	309	325
9	4	291	342
10	4	339	-356
11	4	-116	-57
12	4	209	275
13	4	204	288
14	4	137	-169
0	5	234	168
1	5	320	340
2	5	434	426
3	5	-109	-22
4	5	511	-514
5	5	185	39
6	5	177	138
7	5	160	-213
8	5	-112	-79
9	5	211	215
10	5	188	210
0	6	677	663
1	6	123	171
2	6	359	-347
3	6	176	52
4	6	504	504
5	6	127	180
6	6	361	-329
7	6	152	-108
8	6	380	395
9	6	-111	22
10	6	241	-269
11	6	-111	-68
0	7	-115	21
1	7	215	220
2	7	-111	88
3	7	112	-23
4	7	282	-243
7	7	207	-230
0	8	220	231
1	8	195	185
2	8	-115	-124
3	8	346	-354
4	8	128	120
5	8	212	214
7	8	278	-205
8	8	135	167
9	8	136	147
0	9	111	-95
1	9	-110	136
2	9	238	220
3	9	-107	-66
4	9	329	-299
0	10	-114	103
1	10	166	76
2	10	177	15
	H = 5		
0	1	315	-313
1	1	970	999
2	1	602	-571
3	1	547	-565
4	1	658	656
5	1	653	633
6	1	329	-374
7	1	700	-726
8	1	-111	-130
9	1	474	465
10	1	340	-325
11	1	251	-282
12	1	381	381
13	1	329	322
14	1	-111	-46
15	1	315	-302
0	2	241	227
1	2	297	311
2	2	256	-249
3	2	138	196
4	2	-101	45
	H = 5		
5	2	141	-97
6	2	128	-93
7	2	312	-290
8	2	133	158
9	2	-107	39
10	2	-112	41
11	2	-111	38
0	3	151	-224
1	3	441	442
2	3	796	-861
3	3	275	-266
4	3	632	633
5	3	258	257
6	3	359	-355
7	3	454	-479
8	3	-109	85
9	3	291	302
10	3	450	-417
11	3	-114	-124
12	3	313	306
13	3	201	240
14	3	-107	-72
0	4	204	206
1	4	442	450
2	4	-104	84
3	4	144	-86
4	4	-107	-95
5	4	163	99
6	4	-111	-86
7	4	252	-273
8	4	-110	-17
9	4	346	397
10	4	158	5
11	4	-110	58
0	5	186	207
1	5	206	233
2	5	244	-225
3	5	-116	-38
4	5	142	186
5	5	198	219
6	5	196	-234
7	5	185	-204
8	5	-114	65
0	6	294	-287
1	6	163	195
2	6	224	266
3	6	130	214
4	6	304	-349
5	6	170	-129
6	6	214	230
7	6	254	-259
8	6	130	-62
9	6	-114	25
10	6	230	228
0	7	-116	186
1	7	-117	143
2	7	373	-414
3	7	195	-193
4	7	201	164
5	7	158	86
6	7	244	-244
7	7	-115	-156
8	7	194	228
9	7	140	99
10	7	194	-211
0	8	182	-163
1	8	295	279
2	8	251	269
3	8	-109	-91
4	8	296	-309
5	8	-112	138
6	8	153	139
7	8	188	-216
0	9	-113	47
1	9	202	245
2	9	-114	2
3	9	186	-189
4	9	-115	-90
	H = 6		
0	0	-103	7
2	0	-103	-9
4	0	765	781
6	0	-114	-14
8	0	-113	-95
10	0	219	-219
12	0	332	332
14	0	-121	19
0	1	111	-30
1	1	124	-144
2	1	188	-208
3	1	395	391
4	1	-101	-16
5	1	214	-236
6	1	205	-172
7	1	-110	75
8	1	-111	123
9	1	151	-158
10	1	167	45
11	1	201	116
12	1	-114	126
13	1	-115	-113
14	1	-110	-38
0	2	137	175
1	2	677	687
2	2	484	-513
3	2	624	-646
4	2	926	928
5	2	644	627
6	2	247	-227
7	2	481	-528
8	2	-114	161
9	2	345	371
10	2	411	-388
11	2	262	-280
12	2	322	340
13	2	346	376
14	2	-112	-89
0	3	-105	105
1	3	288	279
2	3	135	39
3	3	-105	18
4	3	205	209
	H = 6		
5	3	152	-52
6	3	-121	-84
7	3	263	-231
8	3	-110	-40
9	3	118	195
10	3	142	-93
0	4	-109	17
1	4	356	394
2	4	182	142
3	4	234	-279
4	4	263	258
5	4	335	352
6	4	-113	98
7	4	229	-220
8	4	115	-89
9	4	163	163
11	4	191	-199
0	5	279	-263
1	5	167	123
2	5	-110	86
3	5	331	281
4	5	-112	-77
5	5	154	-178
6	5	140	169
7	5	177	-168
8	5	185	-123
0	6	-119	122
1	6	230	179
2	6	192	-134
3	6	259	-249
4	6	-117	186
5	6	128	88
6	6	-120	-31
7	6	196	-193
8	6	-114	130
11	6	186	-97
0	7	190	-182
1	7	333	322
2	7	242	237
3	7	141	-91
4	7	203	-217
5	7	-111	108
6	7	161	138
7	7	351	-295
8	7	259	-225
9	7	164	196
0	8	-114	105
1	8	308	293
2	8	-107	41
3	8	151	-143
4	8	-105	-12
5	8	275	252
6	8	-110	12
7	8	143	-197
0	9	271	-214
1	9	168	147
2	9	290	211
3	9	120	-30
	H = 7		
0	1	180	-130
1	1	353	348
2	1	497	-502
3	1	683	-680
4	1	462	464
5	1	536	546
6	1	215	-200
7	1	199	-233
8	1	123	14
9	1	252	220
10	1	311	-293
11	1	352	-358
12	1	269	228
13	1	291	262
0	2	134	-64
1	2	215	-206
2	2	-106	5
3	2	314	277
4	2	-110	73
5	2	222	-239
6	2	-109	-7
7	2	-112	129
8	2	186	-173
9	2	109	-42
10	2	-114	33
11	2	199	168
12	2	-109	31
13	2	194	-74
0	3	157	-122
1	3	394	370
2	3	159	-46
3	3	445	-454
4	3	173	123
5	3	488	530
6	3	111	-62
7	3	305	-276
8	3	148	-116
9	3	308	266
10	3	-111	-128
11	3	351	-335
12	3	172	98
0	4	434	-436
1	4	-113	129
2	4	-118	188
3	4	205	192
4	4	108	-15
5	4	-111	-77
6	4	140	246
7	4	245	-168
8	4	191	-227
9	4	-110	-27
10	4	-110	129
11	4	-109	70
12	4	-116	-18
0	5	367	-442
1	5	129	184
2	5	-112	32
3	5	331	-322
4	5	-116	-134
5	5	201	177
6	5	-114	166
7	5	153	-213
8	5	-113	-133
	H = 7		
9	5	172	193
10	5	-115	24
11	5	154	-191
0	6	248	-246
1	6	237	216
2	6	173	143
3	6	-113	-50
4	6	139	-51
5	6	-116	55
6	6	-110	58
7	6	137	-165
8	6	-119	-208
0	7	-111	60
1	7	388	362
2	7	-113	-37
3	7	253	-213
4	7	-110	18
5	7	269	278
6	7	-113	-54
7	7	195	-223
8	7	-110	3
0	8	276	-271
1	8	296	280
2	8	193	202
3	8	-117	-123
	H = 8		
0	0	121	-29
2	0	138	-169
4	0	233	253
6	0	-115	16
8	0	158	88
10	0	133	-165
12	0	152	62
0	1	188	-127
1	1	-112	-121
2	1	-110	92
3	1	-112	46
4	1	-111	59
5	1	-111	-106
6	1	-109	44
7	1	-114	116
0	2	240	252
1	2	259	286
2	2	136	-32
3	2	617	-610
4	2	274	266
5	2	475	509
6	2	201	-56
7	2	213	-191
8	2	-109	62
9	2	131	230
10	2	122	-114
11	2	413	-385
12	2	-114	80
0	3	577	-572
1	3	121	19
2	3	389	345
3	3	-120	99
4	3	119	-183
5	3	-112	-24
6	3	296	311
7	3	-111	-32
8	3	325	-317
9	3	195	-83
10	3	178	181
11	3	-111	27
0	4	178	-145
1	4	326	314
2	4	-112	38
3	4	454	-477
4	4	-115	16
5	4	340	345
6	4	132	143
7	4	206	-208
8	4	-113	-65
9	4	148	212
10	4	-112	40
11	4	268	-251
0	5	262	-234
1	5	-114	-28
2	5	114	95
3	5	-111	54
4	5	-110	38
5	5	-110	-52
6	5	142	93
8	5	207	-225
0	6	177	30
1	6	403	398
2	6	-114	48
3	6	337	-324
4	6	-112	61
5	6	299	350
6	6	-111	29
7	6	271	-268
8	6	-110	-39
0	7	240	-211
1	7	121	135
2	7	-110	100
3	7	-116	-61
6	7	-113	143
0	8	-110	-37
1	8	150	141
	H = 9		
0	1	-113	-18
1	1	-116	148
2	1	-114	6
3	1	396	-398
4	1	-115	-132
5	1	347	328
6	1	-111	44
7	1	-114	-42
8	1	120	-22
0	2	271	-260
1	2	140	-16
2	2	-114	146
3	2	-113	-17
4	2	-113	-44
5	2	-114	50
6	2	207	204
7	2	-111	-30
	H = 9		
10	2	-108	87
0	3	192	-174
1	3	256	272
2	3	-112	27
3	3	555	-529
4	3	131	-127
5	3	345	383
6	3	-119	82
7	3	164	-208
8	3	152	-31
9	3	225	249
10	3	-113	28
0	4	350	-341
1	4	-113	-41
2	4	147	196
3	4	142	-48
4	4	-113	-124
5	4	-111	46
6	4	186	168
7	4	-109	24
8	4	293	-265
9	4	-109	-16
0	5	-112	-38
1	5	338	315
2	5	-108	29
3	5	262	-316
4	5	117	-26
5	5	317	335
6	5	160	-11
7	5	-119	-217
8	5	-114	-39
0	6	-118	-150
1	6	136	49
2	6	-112	37
3	6	-111	-57
4	6	-116	101
5	6	-114	85
6	6	113	76
0	7	123	-95
1	7	238	256
2	7	-111	9
	H = 10		
0	0	-110	-32
2	0	309	302
4	0	269	-299
6	0	162	162
8	0	182	-38
0	1	-114	-83
1	1	-111	128
2	1	-114	50
3	1	-117	-119
4	1	-112	-16
5	1	-113	121
6	1	-114	57
7	1	-115	-97
0	2	154	-128
1	2	243	200
2	2	-113	174
3	2	332	-350
4	2	248	-233
5	2	243	271
6	2	209	173
7	2	164	-134
9	2	-119	188
0	3	180	-271
1	3	-114	56
2	3	-114	195
3	3	204	-177
4	3	161	-148
5	3	-116	137
6	3	186	167
7	3	-110	-9
0	4	157	118
1	4	184	207
2	4	-108	1
3	4	258	-265
4	4	-112	13
5	4	257	231
0	5	121	-104
1	5	-113	-26
2	5	199	52
3	5	165	-76
0	6	-114	14
1	6	-117	193
	H = 11		
0	1	191	-67
1	1	172	249
2	1	165	153
3	1	312	-298
4	1	238	-275
5	1	212	226
6	1	-114	125
7	1	-116	-168
1	2	-110	48
2	2	-110	-23
4	2	-111	-8
5	2	-114	121
1	3	199	164
2	3	-114	67
3	3	169	-171
4	3	169	-144
5	3	-115	168
0	4	-111	-42
1	4	-109	-52
2	4	172	35
	H = 12		
0	0	-113	-87
2	0	248	158
0	1	-112	49
2	1	-118	-37

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[a] The columns contain k,ℓ 10|F_{obs}|, and 10 F_{calc}. The unobserved reflections are denoted by a negative |F_{obs}|.

Table IV. Interatomic Bond Distances and Bond Angles in DMA_3CuCl_5

Bond Distances				Bond Angles			
Bond [a]	Distance (Å)	Bond	Distance (Å)	Angle [a]	Value(°)	Angle	Value(°)
Cu(1)-Cl(2)	2.232(6)	N(7)-C(6)	1.45(3)	Cl(2)-Cu(1)-Cl(3)	136.1(2)	C(6)-N(7)-C(8)	121.3(6)
Cu(1)-Cl(3)	2.229(9)	N(7)-C(8)	1.37(4)	Cl(2)-Cu(1)-Cl(4)	97.7(1)	C(9)-N(11)-C(10)	112.9(2.8)
Cu(1)-Cl(4)	2.229(6)	N(11)-C(9)	1.41(3)	Cl(3)-Cu(1)-Cl(4)	98.6(1)		
Cu(1)-Cl(4')		N(11)-C(10)	1.54(4)	Cl(4)-Cu(1)-Cl(4')	135.5(2)		

[a] A prime denotes an atom related by the mirror plane at y = ¼.

Table V. Hydrogen Bond Ditacne and Angle in DMA_3CuCl_5

Hydrogen Bond Distance				Hydrogen Bond Angles			
Bond	Distances (Å)	Bond	Distance (Å)	Angle	Value(°)	Angle	Value(°)
Cl(3)-N(7)	3.29(2)	Cl(2)-N(11)	3.13(3)	Cl(3)-N(7)-C(6)	88.1(1.4)	Cl(2)-N(11)-C(9)	101.8(2.0)
Cl(4)-N(7)	3.24(3)	Cl(5)-N(11)	3.19(4)	Cl(3)-N(7)-C(8)	149.6(1.6)	Cl(2)-N(11)-C(10)	101.4(1.5)
Cl(5)-N(7)	3.45(3)			Cl(4)-N(7)-C(6)	126.0(1.8)	Cl(5)-N(11)-C(9)	108.6(1.7)
				Cl(4)-N(7)-C(8)	91.5(1.9)	Cl(5)-N(11)-C(10)	106.0(1.5)
				Cl(5)-N(7)-C(6)	100.7(1.3)		
				Cl(5)-N(7)-C(8)	101.7(1.6)		

in Table II, observed and calculated structure factors are tabulated in Table III, and principal interatomic distances and angles[11] are given in Tables IV and V. The geometry of the $CuCl_4^{2-}$ ion is shown in Figure 1 and Figure 2 shows the relation of the $CuCl_4^{2-}$ to its nearest neighbors. These illustrations were made on the Washington State University CalComp plotter using the Oak Ridge FORTRAN Thermal-Ellipsoid Plot program (ORTEP).[12] A view of the contents of the unit cell is shown in Figure 3.

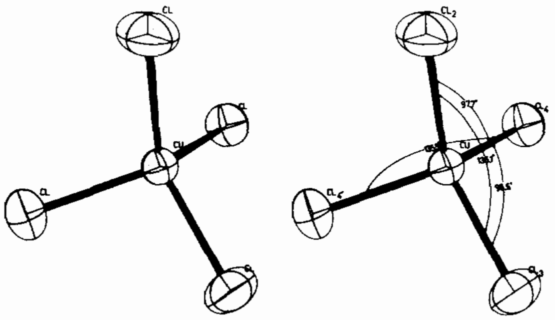

Figure 1. Stereoscopic Drawing of the $CuCl_4^{2-}$-Ion.

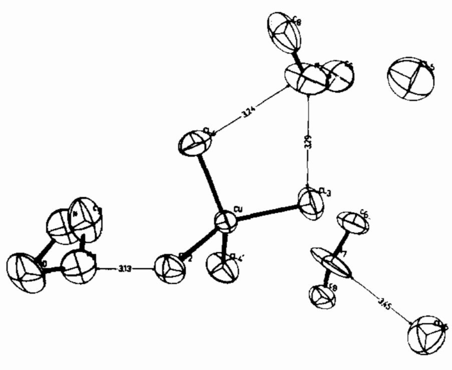

Figure 2. Illustration of the Environment of the $CuCl_4^{2-}$-Ion.

Discussion

This crystal structure analysis has established the chemical formula of DMA_3CuCl_5 to be best represented by $[(CH_3)_2NH_2]_3Cl \cdot CuCl_4$. It consists of discrete $CuCl_4^{2-}$ and Cl^- ions hydrogen-bonded to $(CH_3)_2NH_2^+$ ions to form an infinite three-dimensional network. The $CuCl_4^{2-}$ ion has essentially D_{2d} symmetry, corresponding to the familiar «flattened» tetrahedral coordination reported in Cs_2CuCl_4[13] and $[(CH_3)_4N]_2CuCl_4$.[14] One of the DMA ions and the lattice chloride ion were found to be distributed in a disorder manner between equivalent sites, thus providing for more efficient hydrogen-bonding than would be present in the corresponding ordered centrosymmetric structure.

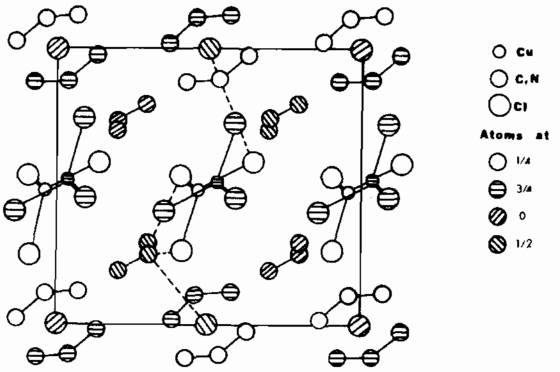

Figure 3. Unit Cell Packing Diagram for $[(CH_3)_2NH_2]_3Cl \cdot CuCl_4$. Projection along 0(10) direction . The c-axis is vertical, the a-axis is horizontal.

The geometry of the $CuCl_4^{2-}$ ion is summarized in Table IV and Figure 1. The Cu–Cl bond distances average 2.230 Å ± .007 Å, all three independent distances being the same length to within one-half a

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[11] W.R. Busing, K.O. Martin, and H.A Levy, *A FORTRAN Crystallographic Function and Error Program,* U.S. Atomic Energy Commission eRport ORNL-TM-306 (1964).

[12] C.K. Johnson, *A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations,* Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).

[13] L. Helmholz and R.F. Kruh, *J. Am. Chem. Soc., 74,* 1176 (1952).

[14] B. Morosin and E.C. Lingafelter, *J. Phys. Chem., 65,* 50 (1961).

Table VI. Bond Lengths and Angles in the $CuCl_4^{2-}$ Ion

	Cs_2CuCl_4	$[N(CH_3)_4]_2CuCl_4$ [010] data	$[N(CH_3)_4]_2CuCl_4$ [001] data	DMA_3CuCl_5
Cu-Cl(1)	2.229	2.18Å	2.22Å	2.28Å
Cu-Cl(2)	2.229	2.25	2.20	2.24
Cu-Cl(3)	2.232	2.18	2.23	2.23
Cl(1)-Cu-Cl(2)	136.1	124.9°	129.8°	131.5°
Cl(1)-Cu-Cl(3)	97.7	102.5	99.6	99.4
Cl(2)-Cu-Cl(3)	98.6	102.9	102.2	101.5
Cl(3)-Cu-Cl(3′)	135.5	123.3	127.1	127.4

standard deviation. The bond angles fall into two groups, one in which the two angles are compressed from idealized tetrahedral angles to approximately 98°, while in the other group the two angles have opened up to 136°. The two larger angles are equal within three standard deviations at $136.1 \pm 0.2°$ and $135.5 \pm 0.2°$. The two shorter angles lie outside of the three standard deviation criteria, the observed values being $97.7 \pm 0.1°$ and $98.6 \pm 0.1°$. The center of mass of the $CuCl_4^{2-}$ ion is displaced 0.011 Å from the copper atom in the direction of the bisector of the Cl(4)–Cu–Cl(4′) bond angle.

Comparison of the configuration of the $CuCl_4^{2-}$ ion in Cs_2CuCl_4 and $[(CH_3)_4N]_2CuCl_4$ with that in DMA_3CuCl_5, given in Table VI, shows that the $CuCl_4^{2-}$ ion in DMA_3CuCl_5 is closest to D_{2d} symmetry. This is the symmetry expected if the ion is considered to be distorted from T_d symmetry by a Jahn-Teller mechanism or from D_{4h} symmetry by coulombic and Van der Waal's repulsion forces between the chloride ions. Thus one is tempted to infer that the interionic steric forces are smaller in DMA_3CuCl_5 than in the other two compounds.

In the two independent DMA ions, all four C–N distances are within three standard deviations of the accepted C–N single bond distance of 1.47 Å. Although standard deviations are quite high (.03 or .04 Å) and the individual C–N distances range from 1.37 to 1.54 Å, the average C–N distances is 1.44 Å. Both C–N–C bond angles are larger than the tetrahedral value of 109.4 Å. The angle for the DMA ion located in general position, C(6)–N(7)–C(8), is considerably larger at $121.3 \pm 0.6°$. In the disordered DMA ion, this angle is $112.9 \pm 2.8°$. The large standard deviation probably arises from the fact that in the least squares refinement the two carbon atoms were restricted to lie on the mirror plane although this is not required for a disordered molecule. The final difference Fourier gave no indication of significant displacement of either of these carbon atoms from the mirror plane, nor did it give definitive evidence about the location of the hydrogen atoms.

Another important aspect of the structure is the disorder found for one of the DMA ions and the lattice chloride ion. The cause of the disordering is easily understood when the hydrogen bonding in the structure is examined. If N(11) were located on the mirror plane and Cl(5) on the center of inversion, the N–Cl distance would be over 4.0 Å, much too long for hydrogen bonding. In addition, the C–N–Cl angles would not be favorable for hydrogen bonding. By tipping the DMA ion away from the mirror plane and displacing the chloride ion toward the DMA ion as shown in Figure 4, a N–Cl distance of 3.19 Å is obtained, a distance that is quite representative of N---Cl hydrogen bond distances. At the same time, the C(9)–N(11)–Cl(5) and C(10)–N(11)–Cl(5) bond angles now reach values (109 and 106° respectively) that will yield a nearly linear N–H---Cl hydrogen bond. This tipping of the DMA ion also produces favorable bond angles for the hydrogen bond from N(11) to Cl(2). The disorder thus allows this DMA ion to form stronger hydrogen bonds than the DMA ion in general positions, as evidenced by shorter N–Cl distances and C–N–Cl angles closer to 109°. This disorder is almost certainly of the dynamic type. Preliminary differential thermal analysis indicated two minor phase pransitions below room temperature, one of which may be due to the onset of some type of hindered rotation of the methyl groups while the other is presumably associated with an order-disorder phenomena in the DMA---Cl hydrogen bond system. Preliminary broadline NMR spectra support this conclusion. The DMA ion in general position forms a bifurcated hydrogen bond to Cl(3) and Cl(4) with N–Cl distances of 3.29 and 3.24 Å. The hydrogen bond from this DMA ion to the lattice chloride ion is much weaker, the N(7)–Cl(5) distance being 3.45 Å.

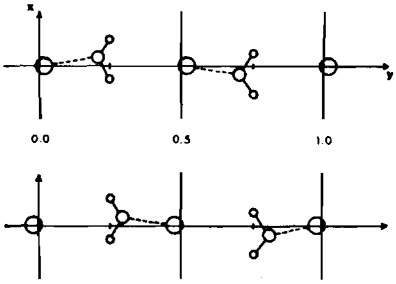

Figure 4. Schematic Illustration of Two Possible Hydrogen Bonding Arrangements for the Disordered Chloride and Dimethylammonium Ions.

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