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The Crystal Structure of $(C_2H_5NH_3)_2CuCl_4$*

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The structure of the complex salt $(C_2H_5NH_3)_2CuCl_4$ has been determined by conventional X-ray diffraction techniques. The space group is Pbca with lattice constants a = *21.18 Å* b = *7.47 Å, and* c = *7.35 Å. A square planar $CuCl_4^{2-}$ ion was found with Cu–Cl distances of 2.28 Å. The coordination sphere about each copper atom is completed by sharing additional chlorine atoms from adjacent $CuCl_4^{2-}$ ions yielding two Cu–Cl distance of 2.98 Å. This ties the $CuCl_4^{2-}$ groups into a two-dimensional framework lying in the yz plane. The nitrogen atom is located in a « hole » formed by the chlorine atoms in this framework. Several short N–Cl distances are found which are presumably associated with hydrogen bonds. The ethyl groups are disordered in this structure.*

Introduction

Recently there has been much interest in structural and electronic properties of copper(II) chloride complexes.[1,2,3,4,5] Because of the thermochromic properties of several complexes between substituted ammonium chlorides and copper(II) chloride[1] as well as an indication that several of the yellow chlorocuprates contained essentially a square planar coordination around the copper atom, we have undertaken the structural study of the high temperature form of $(C_2H_5NH_3)_2CuCl_4$.

Experimental Section

The general method of preparation has been described by Remy and Laves.[6] Single crystals were obtained most readily by slowly evaporating a stoichiometric mixture of $C_2H_5NH_3Cl$ and $CuCl_2$ (or $CuCl_2 . 2H_2O$) in methanol. The crystals grow as flat yellow sheets which are not hygroscopic and thus are one of the few stable anhydrous copper(II) chloride complexes. An infrared spectrum of a thin single crystal showed no evidence of an O–H bond, indicating that no solvent of crystallization was present. The crystals grew with the (100), (011)) and (01$\bar{1}$) faces normally developed. The crystals crush easily with cleavage taking place perpendicular to the a-axis. The compound is thermochromic, becoming a light green below –39°C.[7] This color change must be associated with a change in the coordination around the copper atom.

The lattice constants and space group have been reported previously[1] and were found to be $a = 21.18 \pm .02$ Å, $b = 7.47 \pm .01$ Å, and $c = 7{\cdot}35 \pm 01$ Å with space group Pbca· The two crystals used to collect intensity data were mounted in Lindemann glass capillaries. The density was found to be 1.701 g/ml by a flotation technique. The calculated density, assuming four molecules per unit cell, is 1.703 g/ml.

Weissenberg intensity photographs were taken using Mo Kα radiation. Time exposures of 1 2/3, 10, and 60 hours were taken using the multiple film technique. The zero through sixth layers were collected from a crystal mounted with the [001] direction parallel to the rotation axis. Similarly, the zero through tenth layers; with the exception of the ninth, were collected from a crystal mounted with the [01$\bar{1}$] direction parallel to the rotation axis. In this manner 1116 reflections were recorded. A total of 546 unique reflections were measured, 423 of which had an observable intensity. The intensities of all reflections were estimated visually. The weights for the reflections, for use in the least squares refinement procedure, were assigned using a modified version of the Hughes weighting scheme.[8]

Solutions of Structure

With four molecules per unit cell, the copper atoms are required to be located in a four fold set of spe-

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(*) Taken in part from the M. S. thesis of J. Paul Steadman, Washington State University.

(1) Roger D. Willet, *J. Chem. Phys.*, *41*, 2243 (1964).

(2) Roger D. Willett, D. Dwiggens, Jr., R. Kruh, and R. E. Rundle, *J. Chem. Phys.*, *38*, 2429 (1963).

(3) Mark Sharnoff, *J. Chem. Phys.*, *42*, 3383 (1965).

(4) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, *3*, 841 (1964).

(5) C. Furlani and G. M. Morpurgo, *Theor. Chim. Acta*, *1*, 102 (1963).

(6) H. Remy and G. Laves, *Ber.*, *66*, 401 (1933).

(7) The transition temperature was obtained from a differential thermal analysis study of the compound. The authors would like to thank Dr. Ruth Denison of the Perkin-Elmer Corporation for obtaining the necessary thermograms.

(8) The procedure outlined in reference 2 was used. The scheme may be summarized as follows:

$$(W)^{-1/2} = C(F_o/F_{med}) \text{ when } I_o > I_{med}$$
$$(W)^{-1/2} = C \qquad \text{when } 2I_{min} < I_o < I_{med}$$
$$(W)^{-1/2} = C(\sqrt{2F_{min}}/F_o) \text{ when } I_o < 2I_{med}$$

where I_o, I_{med}, I_{min} are the observed intensity, median intensity for a given layer, and minimum intensity for a given layer respectively and C is a constant. F_o, F_{med}, and F_{min} are defined similarly. Unobserved reflections were assigned an intensity equal to $\frac{1}{2}I_{min}$ and omitted from definement if $F_{calc} < F_o$.

Table I. Final parameters, temperature factors, and R factors for $(C_2H_5NH_3)_2CuCl_4$.

Final Parameters

Atom	x	y	z	σx	σy	σz
Cu	0	0	0	0	0	0
Cl(1)	0.1067	0.0368	—0.0062	0.0002	0.0005	0.0005
Cl(2)	-0.0110	0.2846	0.2814	0.0002	0.0005	0.0005
N	0.0961	0.4810	0.0152	0.0009	0.0019	0.0064
C(1)	0.164	0.527	0.046	0.003	0.006	0.007
C(1')	0.166	0.568	0.032	0.003	0.008	0.009
C(1, 2)	0.208	0.418	—0.015	0.005	0.014	0.019
C(1',2)	0.220	0.467	0.044	0.006	0.013	0.016
C(1,2')	0.209	0.423	0.127	0.005	0.015	0.015
C(1',2')[c]	0.214	0.551	0.104	0.005	0.014	0.017

Temperature Factors[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.00124	0.0121	0.0092	—0.0001	0.0021	0.0022
	(0.00007)[b]	(0.0004)	(0.0004)	(0.0002)	(0.0004)	(0.0004)
Cl(1)	0.00177	0.0175	0.0306	0.0000	—0.0004	—0.0004
	(0.00014)	(0.0010)	(0.0014)	(0.0002)	(0.0007)	(0.0022)
Cl(2)	0.00198	0.0138	0.0098	0.0003	0.0008	—0.0030
	(0.00013)	(0.0006)	(0.0005)	(0.0003)	(0.0003)	(0.0008)
N	0.0018	0.025	0.018	—0.0008	—0.0009	0.0022
	(0.0004)	(0.003)	(0.005)	(0.0011)	(0.0016)	(0.0039)
C(1)[c]	0.0028	0.022	0.023	0.0	0.0	0.0
	(0.0006)	(0.005)	(0.005)			
C(1')[c]	0.0030	0.024	0.025	0.0	0.0	0.0
	(0.0005)	(0.004)	(0.004)			

R Factors

$R_1=0.089$ for all reflections
$R_1=0.081$ for observed refections only
$R_3=0.097$

[a] The anisotropic temperature factors are defined by $T=\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$. [b] Standard deviations are given in parentheses. [c] Anisotropic temperature factors were not varied. The temperature factors from C(1') were assigned to the remainder of the carbon atoms.

cial positions in the space group Pbca and they were subsequently placed at the origin and the corresponding symmetry related positions. A two-dimensional Patterson synthesis[9] parallel to (001) allowed approximate positions for the two unique chlorine atoms and the unique nitrogen atoms to be deduced. A Fourier synthesis computed from structure factors obtained from the first crystal, based on signs obtained from structure factor calculations using the positions obtained above, failed to yield positions of the carbon atoms. Least squares refinement[10] of the positional parameters and isotropic temeprature factors of the copper, chlorine, and nitrogen atoms was begun immediately at this point in order to eliminate as many uncertainties as possible from the Fourier synthesis. Fourier and difference Fourier syntheses, again with data from the first crystal, indicated two possible positions for the carbon atom attached to the nitrogen atom. The maximum of the electron density for both positions was about one-half of the maximum of the electron density of the nitrogen atom. At this time the data from the second crystal was available, and a difference synthesis with these data again indicated two possible positions which gave equally satisfactory agreement but yielded isotropic temperature factors which unrealistically high. Refinement of a disordered model, with one-half contribution from each carbon atom, yielded substantially better agreement and isotropic temperature factors which were reasonable.

Further refinement was initiated with anisotropic thermal parameters on the copper, chlorine, and nitrogen atoms. A value of $R_1 = 0.105$ was obtained with no contribution from the carbon atoms while $R_1 = 0.095$ was obtained with one carbon atom present with two-fold disorder. No unusual shifts of the positional parameters of the two carbon atoms occurred during the refinement and reasonable values were obtained for the N–C bond distances considering the large standard deviations. No attempt was made to refine occupation factors. Difference Fourier syntheses at various stages of this process revealed four small peaks, of approximately equal intensity, in the general region where the second carbon atom was expected. These positions were reasonable in terms of the expected geometry of the ethylammonium ion and the crystal packing. Car-

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(9) W. G. Sly, D. P. Shoemaker, and J. H. Vanden Hende, « Two and Three Dimensional Crystallographic Fourier Summation Program for the IBM 7090 Computer », ESSO Research and Engineering Co. Report CBRL-22M-62 (1962). This program was used for all subsequent electron density summations also.

(10) A modified version of the ORFLS program was used throughout. See W. R. Busing, K. O. Martin, and H. A. Levy, « A Fortran Crystallographic Least Squares Program », U. S. Atomic Energy Commission Report ORNL-TM-305 (1962).

(11) W. R. Busing, K. O. Martin, and H. A. Levy, « A Fortran Crystallographic Function and Error Program », U. S. Atomic Energy Commission Report ORNL-TM-306 (1964).

Table II. Calculated and Observed Structure Factors.[a]

K= 0 L= 0		
6	2338	2283
8	3673	4027
10	4504	4568
12	2360	2203
14	562	647
16	585	674
18	1718	1922
20	1334	1325
K= 1 L= 0		
6	1149	1056
8	1515	1436
10	608	613
12	396	513
14	781	807
16	763	835
18	615	723
20	-297	424
K= 2 L= 0		
0	3606	3662
2	-150	50
4	2185	-1954
6	1116	919
8	1206	1091
10	2238	1952
18	1227	1191
20	1096	985
K= 3 L= 0		
2	1112	-1176
4	943	986
6	329	169
8	563	545
10	916	-998
12	1284	-1220
14	457	-468
16	-281	-101
18	-294	-151
20	-312	-550
K= 4 L= 0		
0	3274	3425
2	2372	2419
4	1098	1178
6	1206	1301
8	2131	2086
10	2232	2122
12	1300	1342
14	452	566
16	632	609
18	958	973
20	761	774
K= 5 L= 0		
2	734	-762
4	346	-395
6	734	799
8	904	1032
10	-281	-101
12	-295	-394
14	-294	238
16	565	633
K= 6 L= 0		
0	821	809
2	623	773
4	407	418
6	577	431
8	685	689
10	675	688
12	556	584
14	-315	351
K= 8 L= 0		
0	-306	283
2	436	414
4	441	445
K= 1 L= 1		
3	2583	2359
5	-163	134
7	2405	2188
9	2986	2729
11	1498	1604
13	317	329
15	640	731
17	1378	1345
K= 2 L= 1		
0	835	951
1	493	-526
2	831	774
3	637	-702
4	772	700
5	527	480
6	641	601
7	478	447
8	487	496
9	321	55
10	355	429
11	-232	-149
12	334	272
13	-249	-287
14	-258	191
15	-268	299
16	-283	129
17	-293	331
18	-302	96
19	-312	-59
K= 3 L= 1		
1	1853	1793
3	1311	1357
4	303	186
5	649	582
6	321	274
7	1475	1439
8	341	246
9	1926	1833
10	364	356
11	1198	1151
12	388	359
13	406	363
15	615	612
17	1001	992
19	852	892
K= 4 L= 1		
0	873	-912
1	469	591
2	919	-954
3	665	762
4	887	-921
5	436	348
6	811	-811
7	488	491
8	655	-650
9	-256	4
10	499	-501
11	444	415
12	485	-434
13	498	445
14	-296	-337
15	-298	259
17	-318	332
K= 5 L= 1		
1	1191	1354
3	1042	1084
5	932	1038
7	1050	1106
8	407	-388
12	455	-438
13	595	568
14	481	-415
15	542	624
16	-310	-436
17	664	686
18	-327	-378
19	811	610
20	691	-326
K= 6 L= 1		
0	718	731
1	466	-406
2	701	720
3	498	-472
4	636	630
5	-291	255
6	642	564
7	469	504
8	579	531
9	-306	146
10	492	442
11	607	-273
K= 7 L= 1		
1	491	459
3	461	485
5	635	617
7	482	479
K= 8 L= 1		
0	-340	-458
1	555	-218
2	-341	-434
K= 9 L= 1		
1	-389	302
3	-392	437
5	690	574
K= 0 L= 2		
4	2147	-2174
5	405	-449
6	1182	-948
7	397	-415
8	1303	1130
9	344	-247
10	2166	1975
11	-240	-432
12	702	698
13	-261	-325
14	477	-374
15	-282	-566
16	-274	95
17	-302	-318
18	1231	1237
19	-323	-284
20	1040	1033
K= 1 L= 2		
1	619	766
3	775	-580
6	385	-353
7	579	543
8	296	-257
9	446	440
10	870	-893
11	400	323
12	934	-956
13	-246	230
14	592	638
15	-264	170
18	-315	422
20	-335	-513
K= 2 L= 2		
0	5774	5799
2	3422	3365
3	308	195
4	1465	1289
5	-202	23
6	1711	1698
7	-218	69
8	3093	2931
9	-236	218
10	3203	3134
12	1701	1757
14	432	561
16	438	675
18	1298	1368
20	986	1048
K= 3 L= 2		
1	502	-487
2	673	645
3	524	-491
4	-216	256
5	563	-523
6	906	990
7	423	-354
8	1271	1279
9	335	-280
10	-253	124
11	-256	-265
12	-270	-90
13	-274	-238
14	618	479
15	-279	-173
16	724	759
18	-332	595
20	-351	152
K= 4 L= 2		
0	1539	1558
2	762	768
4	-221	-144
6	-232	79
8	978	913
10	1151	1151
12	567	632
14	-276	144
16	-304	312
18	747	736
20	620	658
K= 5 L= 2		
8	521	516
10	525	-472
12	742	-736
14	-311	-191
K= 6 L= 2		
0	1040	1130
2	972	1021
4	705	742
6	722	693
8	828	863
10	845	845
12	657	661
14	546	449
16	-397	401
18	-417	426
20	-438	385
K= 7 L= 2		
2	611	-451
K= 8 L= 2		
0	459	446
2	506	528
4	525	569
6	589	501
8	526	418
10	545	375
K= 1 L= 3		
1	1799	1903
3	1310	1328
5	588	562
7	1506	1378
9	2158	2030
11	1193	1164
13	-278	353
15	591	615
17	966	1026
19	842	976
K= 2 L= 3		
0	523	-459
1	476	-357
2	588	-567
3	470	-452
4	666	-611
5	-222	159
6	539	-494
7	-236	184
8	390	-362
9	-236	-70
10	-248	-263
11	-250	-298
12	-265	-244
13	-264	-319
K= 3 L= 3		
1	2150	1995
3	1691	1549
5	1203	1126
6	389	-382
7	1593	1548
13	530	635
15	730	723
17	826	954
19	769	854
21	638	474
K= 4 L= 3		
0	716	747
1	-275	-363
2	637	643
3	401	-425
4	484	486
5	441	360
6	462	451
7	555	550
8	478	481
9	-260	230
10	481	417
11	-272	-101
K= 5 L= 3		
1	581	602
3	434	448
5	435	393
7	594	557
9	682	610
11	438	467
13	404	290
15	429	360
17	678	476
19	-414	431
K= 6 L= 3		
0	519	-560
1	-338	292
2	549	-573
3	558	-433
4	627	-623
5	-345	60
6	618	-579
7	-353	223
8	-311	-401
10	-320	-314
12	-330	-316
K= 7 L= 3		
1	734	797
3	728	831
5	794	855
7	698	771
9	622	619
11	593	568
13	661	531
15	-400	484
17	-420	406
K= 0 L= 4		
0	3820	3901
2	2571	2681
4	1017	1049
6	1358	1363
8	2458	2314
10	2533	2412
16	518	637
18	967	1109
20	723	892
K= 1 L= 4		
1	937	-937
2	-221	-81
3	931	-917
4	-227	119
5	907	-848
6	489	502
7	727	-736
8	656	635
9	549	-570
10	-266	356
11	459	-504
12	-281	296
18	-352	415
K= 2 L= 4		
0	1604	1688
2	761	789
4	482	-373
5	408	-380
6	-228	-6
7	420	-468
8	1033	975
9	387	-434
10	1302	1270
12	582	669
14	-280	45
16	-298	335
18	746	844
20	749	764
K= 3 L= 4		
1	694	623
2	702	-570
3	594	525
4	414	-442
5	462	460
6	-262	117
7	474	444
8	-263	213
9	451	447
10	484	-476
11	-278	291
12	671	-640
K= 4 L= 4		
0	2000	1903
2	1556	1456
4	933	837
6	917	863
8	1388	1287
10	1377	1333
12	914	867
14	-280	447
16	436	472
18	750	654
20	732	558
K= 5 L= 4		
6	444	426
7	-293	-280
8	454	549
K= 6 L= 4		
0	637	716
2	595	610
4	358	468
6	376	437
8	492	567
10	541	599
12	607	467
14	611	369
16	-395	336
18	-417	368
K= 1 L= 5		
1	1586	1578
3	1171	1138
5	953	894
7	1228	1189
9	1541	1469
11	998	1002
13	537	564
15	537	605
17	696	814
19	816	763
21	-435	430
K= 3 L= 5		
1	663	695
3	405	409
5	-255	313
7	551	546
9	814	747
11	468	509
13	-286	270
15	-304	346
17	-394	530
19	680	522
K= 4 L= 5		
2	462	-420
3	402	-342
4	467	-501
5	-287	-14
6	445	-435
K= 5 L= 5		
1	1130	1192
3	1072	1064
5	1036	1011
7	983	1019
9	906	970
11	749	802
13	808	627
15	764	574
17	657	563
19	601	471
K= 0 L= 6		
0	1353	1188
2	696	733
8	771	820
9	469	-525
10	911	1020
12	588	586
14	521	247
16	-332	405
18	739	677
20	682	643
K= 1 L= 6		
1	761	791
3	725	745
5	660	680
7	586	610
9	491	549
11	-274	423
K= 2 L= 6		
0	1512	1591
2	1183	1230
4	639	670
6	670	701
8	1157	1102
10	1155	1169
12	748	729
14	-343	358
16	-439	422
18	595	586
20	-440	520
K= 3 L= 6		
1	636	-610
3	618	-630
5	603	-607
7	514	-507
9	485	-394
K= 4 L= 6		
0	762	803
2	621	654
4	437	349
6	-274	382
8	548	644
10	601	700
12	580	506
14	-375	318
16	-397	372
18	-418	464
K= 6 L= 6		
0	733	460
K= 1 L= 7		
1	608	675
3	520	489
5	-293	407
7	522	587
9	577	632
11	490	516
13	-415	364
K= 3 L= 7		
1	1026	1049
9	791	869
11	726	718
13	702	558
15	-404	503
17	-423	523
K= 0 L= 8		
0	721	767
2	572	596
4	448	378
6	-393	355
8	658	563
10	717	627
K= 1 L= 8		
1	562	-588
3	529	-565
5	607	-538
K= 2 L= 8		
0	714	715
2	677	594
4	507	407
6	519	403
8	658	591
10	676	648
12	-447	463
K= 1 L= 9		
1	649	558
3	-399	481
5	-404	462

[a] The columns are h, $10|F_o|$, and $10\ F_c$. An unobserved reflection is denoted by a negative $10|F_o|$.

bon atoms were placed in these four sites with occupational factors of ¼. Refinement of the positional parameters only for these atoms yielded a final value of $R_1 = 0.081$. No attempt was made to refine their thermal parameters since the high standard deviations made the values so obtained meaningless. Again, no unusual shifts occurred during the refinement and the bond distances and angles were reasonable although not as accurate as desired. The occupational parametes of these atoms were not refined either. The difference Fourier synthsis showed no further features above background.

Discussion of Structure

The three-dimensional structure determination has shown that the square planar $CuCl_4^{2-}$ ion does exist in this compound. This is only the second instance that this ion has been found, the other being in $(NH_3)_2CuCl_4$, although it has been postulated to exist in $Pt(NH_3)_4CuCl_4$.[12] The independent Cu–Cl bond lengths are 2.277 ± 0.066 Å and 2.285 ± 0.004 Å and thus are equal within experimental error. The Cl(1)–Cu–Cl(2) bond angle is 90.0 ± 0.3°. The (4+2) distorted octahedral arrangement is completed by sharing two chlorine atoms, from neighboring $CuCl_4^{2-}$ ions. This ties the $CuCl_4^{2-}$ ions into an infinite, two-dimensional framework lying in the yz plane, as shown in Figure 1. These two additional chlorine atoms are perpendicular to the $CuCl_4^{2-}$ plane (90.3 ± 0.3°) and at a distance of 2.975 ± 0.005 Å. The plane of these ions is approximately perpendicular to the layer or sheetlike structure of the compound. Each Cu–Cl(1) is tipped 7.3° away from the a-axis while each Cu–Cl(2) is tipped 5.1° out of the yz plane.

In comparison with the bond distances found in $(NH_4)_2CuCl_4$, the significant feature seems to be a slight shortening of the four equatorial copper-clorine bonds and a considerable lengthening of the

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[12] M. Bukowska and M. A. Porai-Koshits, *Crystallography*, 5, 127 (1960) translated from *Kristallografiya*, 5, 137 (1960).

Table III. Interatomic bond distances and angles in $(C_2H_5NH_3)_2CuCl_4$ ^{a}

Bond Distances			
Bond	Distance	Bond	Distance
Cu—Cl(1)	2.277±0.006	N—Cl(1) ^{b}	3.85±0.05
Cu—Cl(2)	2.975±0.005	N—Cl(2)	3.33±0.03
Cu—Cl(2) ^{b}	2.285±0.004	N—Cl(2) ^{b}	3.47±0.03
Cl(1)—Cl(2)	3.75 ±0.01	N—Cl(2) ^{e}	3.26±0.03
Cl(1)—Cl(2) ^{b}	3.23 ±0.01	N—Cl(2) ^{g}	3.05±0.03
N—C(1)	1.49 ±0.07	C(1)—C(1,2)	1.33±0.13
N—C(1′)	1.66 ±0.07	C(1)—C(1,2′)	1.38±0.13
N—Cl(1)	3.33 ±0.02	C(1′)—C(1′,2)	1.47±0.14
N—Cl(1) ^{c}	3.52 ±0.05	C(1′)—C(1′,2)	1.43±0.13
N—Cl(1) ^{d}	4.16 ±0.02	C(1)—C(1′)	0.68±0.06

Bond Angles			
Angle	Value	Angle	Value
Cu—Cl(2)—Cu ^{f}	169.6±0.2°	N—C(1)—C(1,2)	119±6°
Cl(1)—Cu—Cl(2)	90.3±0.3°	N—C(1)—C(1,2′)	127±6°
Cl(1)—Cu—Cl(2) ^{b}	90.0±0.3°	N—C(1′)—C(1′,2)	144±6°
Cu—Cl(2)—Cu ^{c}	169.7±0.2°	N—C(1′)—C(1′,2′)	117±7°
Cl(2)—Cu—Cl(2) ^{b}	88.7±0.1°	Cl(2) ^{g}—N—C(1)	121±2°
		Cl(2) ^{g}—N—C(1′) ^{b}	101±2°

^{a} Superscripts indicate symmetry transformations:

^{b} = +x, 0.5—y, —0.5+z
^{c} = +x, 0.5—y 0.5+z
^{d} = +x, —1.0+y, 0.0+z
^{e} = —x, 0.5+y, 0.5—z
^{f} = +x, 0.5+y, 0.5+z
^{g} = —x, 0.5—y, 0.0—z

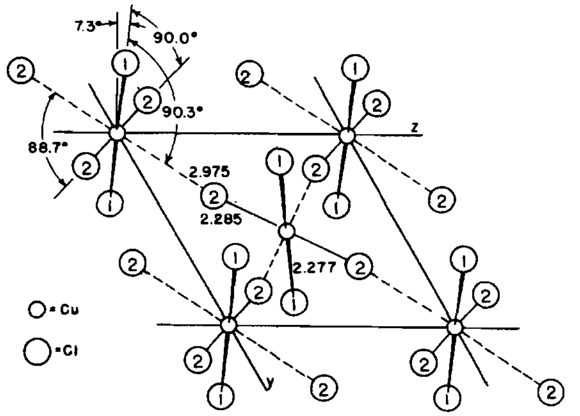

Figure 1. The $CuCl_4^{2-}$ Ion and Its Packing in $(C_2H_5NH_3)_2CuCl_4$.

two axial copper-chlorine bonds. While the equatorial bonds changed by .02 to .05 Å, the axial bonds are lengthened from 2.79 to 2.97 Å. This is consistent with a series of complex copper(II) chlorides whose structures have been determined where the short Cu—Cl bonds range from 2.25-2.34 Å while the long Cu—Cl bonds cover a range from 2.64 Å in $Cu_5Cl_{10}(C_3H_7OH)_2$[13] to 3.18 Å in $Cu_3Cl_6(CH_3CN)_2$.[13] If a van der Waals radius of 1.8 Å is assumed for the chloride ion, and a value of 2.3 Å for the length of the four Cu—Cl bonds in the equatorial plane, then the axial copper-chlorine distance is 2.77 Å if this distance is determined by van der Waals contact between chlorine atoms. This would indicate that the $CuCl_4^{2-}$ ion, as it exists in this compound, may be considered as a discrete species with the coordination to the fifth and sixth octahedral sites being largely determined by ionic and van der Waals interactions. This view is supported by the recent determination of the structure of $(CH_3)_2NH_2CuCl_3$ where each copper has an approximate square-pyramidal configuration (four chlorine atoms at 2.25-2.33 Å and a fifth at 2.73 Å)[14] with the closest approach in the direction of the sixth octahedral site being made by a methyl group.

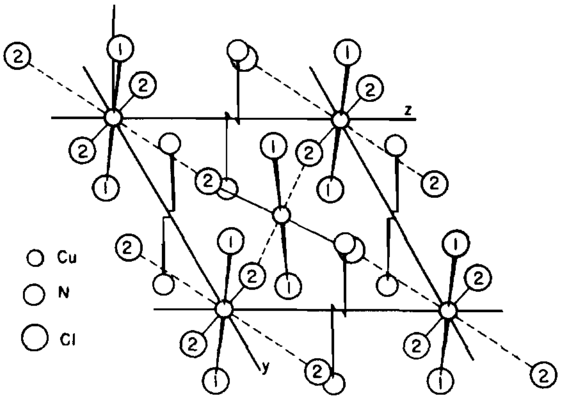

Figure 2. The Environment of the Nitrogen Atom.

The nitrogen atom lies particularly close to one chlorine atom in the yz plane (3.05 Å+0.03 Å) and is in contact with seven more chlorine atoms at a distance of 3.26 to 4.16 Å. These eight chlorine atoms form a « hole » in which the nitrogen sits, as shown in Figure 2. The short N—Cl distance is indicative of a strong N—H– – –Cl type hydrogen bond. This is substantiated by the Cl(2)—N—C(1) and Cl(2)—N—C(1′) bond angles which are close to the value of 109° expected if the N—H– – –Cl bond were linear. It appears that the stability of this type of structure for complex copper(II) halides is dependent upon the formation of these N—H—Cl hydrogen bonds. All of the compounds which assume this structure have cations of the type RNH_3^+ (R = H, CH_3, C_2H_5, $CH(CH_3)_2$) in which the $RNH^+{}_3$ moieties are able to sit down in the holes formed by the chlorine atoms Cl(1).[1] Although K^+ and Rb^+ have essentially the same ionic radii as the $-NH_3^+$ group, they do not form tetrachlorocuprates, while Cs^+, with a larger ionic radius, forms a distinctly different structure. Also, $R_2NH_2^+$ and R_3NH^+ ions do not assume this structure presumably because the $-NH_2^+$ or $-NH^+$ moiety does not fit into the holes between the chlorine atoms.

The ethylammonium ions lie approximately parallel to the a-axis, so that each Cu—Cl—N layer illustrated in Figure 2 is sandwiched between two layers of ethyl groups, forming neutral layers. These neutral layers are then stacked along the a-axis so that the only interactions between adjacent layers are non-bonded

(13) Roger D. Willett and R. E. Rundle, *J. Chem. Phys.*, *40*, 838 (1964).

(14) Roger D. Willett, *J. Chem. Phys.*, *44*, 39 (1966).

interactions between ethyl groups. This arrangement is shown schematically in Figure 3. This explains the excellent cleavage properties perpendicular to the a-axis which are observed for this compound. It is found that a disordering of the ethyl groups occurs in this compounds, with C(1) twofold disordered and C(2) four-fold disordered, as illustrated in Figure 4. The two N–C and the four C–C distances show considerable deviation from the accepted values of 1·47 Å and 1.54 Å respectively, although, because of the large standard deviations associated with these distances, the discrepancies cannot be considered significant. The large standard deviations are the product of two circumstances: The dominant of the scattering power of the crystal by the heavier copper and chlorine atoms and the disorders of the ethyl groups. Since the role of the ethyl groups in this structure is of secondary importance, the inaccuracies in the determination of their positions is not particularly significant.

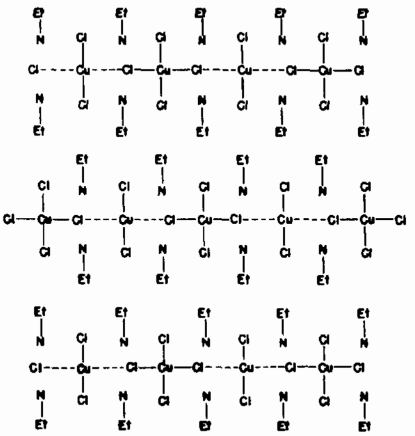

Figure 3. Schematic Packing Picture. Ethylammonium groups lie in front and behind the Cu—Cl chains illustrated.

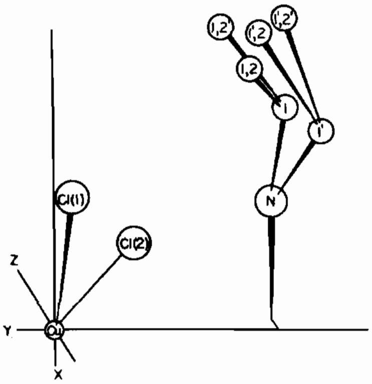

Figure 4. Disorder of Carbon Atoms in $(C_2H_5NH_3)_2CuCl_4$.

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