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The Crystal Structure of $Cu_3Cl_6(H_2O)_2 \cdot 2H_8C_4SO_2$, trans-tetra-$\mu$-[chlorodichlorodiaquocopper(II)]copper(II)bis(tetramethylene sulfone), and the Molecular Structure of the $Cu_3Cl_6(H_2O)_2$ Trimer

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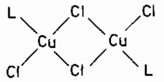
The crystal structure of $Cu_3Cl_6(H_2O)_2 \cdot 2H_8C_4SO_2$ has been determined by single crystal X-ray diffraction methods. The compound contains a new aquo complex of copper chloride, $Cu_3Cl_6(H_2O)_2$. This species exists as a discrete trans planar trimer with halogen bridges and has approximately C_{2h} symmetry. This unusual aquo species is stabilized by hydrogen bonding between the tetramethylene sulfone molecule and the water molecule with an O–H···O distance of 2.70A. The packing of the trimers leads to infinite chains parallel to the crystallographic b-axis of the monoclinic unit cell. The tetramethylene sulfone groups fill in the space between the chains, isolating them from each other.

The structure is monoclinic, C2/c, with a = 23.978 (10) Å, b = 6.142(5) Å, c = 18.956(10) Å, and β = 127.00(2)°. The unit cell contains four formula units with an observed density of 2.27 g/cc (2.23 g/cc calculated). Within the trimer, the bridging Cu–Cl distances (ave. = 2.28 Å) are slightly longer than the terminal Cu–Cl distances (2.24 Å). The Cu–O distance is 1.97 Å and the bridging Cu–Cl–Cu angles are just slightly larger than 90°.

Introduction

Interest in the role that the ligand plays in determining the geometry of $CuX_2 \cdot nL$ compounds has been stimulated by the determination of several unusual structures in recent years. In compounds such as $CuCl_2 \cdot 2H_2O$[1] and $CuCl_2 \cdot 2C_5H_5N$,[2] essentially discrete planar *trans* $CuCl_2L_2$ molecules exist. In complexes such as $CuCl_2 \cdot CH_3CN$,[3] planar dimeric species exist of the type



In the corresponding pyridine-N-oxide compound,[4,5] a $Cu_2Cl_4L_2$ dimer is again formed. However, the ligand now acts as the bridging group with the pyridine rings approximately perpendicular to the Cu_2O_2 plane. The copper coordination geometry is intermediate between tetrahedral and square-planar. Surprisingly, when the $CuCl_2 \cdot 2L$ species is formed (L = pyridine-N-oxide) the compound remains as an oxygen-bridged dimer but the additional pyridine-N-oxide ligand forces itself into the copper coordination sphere to give a square-pyramidal geometry,[6] while in the corresponding bromide species the coordination around the copper ion is trigonal bipyramidal. A decided contrast to the pyridine-N-oxide system is found in the DMSO (DMSO = dimethylsulfoxide) system, where neither $CuCl_2 \cdot$ DMSO nor the $CuCl_2 \cdot$2DMSO exist as dimers.[7,8] $CuCl_2 \cdot$DMSO forms infinite chlorine-bridged chains reminiscent of $CsCuCl_3$.[9] The copper ion has a planar coordination sphere of three chloride ions and a DMSO group bonded through the oxygen atom. In $CuCl_2 \cdot$ 2DMSO, discrete $CuCl_2 \cdot 2L$ molecules exist, but while the O–Cu–O angle is nearly linear (173°) the Cl–Cu–Cl angle is bent to 146°.

All of the above information prompted us to look at the structure of a copper halide species which presumably contained a sulfone group as a ligand. The structure of the compound chosen, $Cu_3Cl_6(H_2O)_2 \cdot$ $2TMSO_2$ ($TMSO_2$ = tetramethylene sulfone) is reported in this paper. While the objective of obtaining information about the nature of a copper–sulfone bond was thwarted by the idiosyncrasies of the chemistry of this compound, the structure has proved to be very interesting and informative.

Preparation, Physical Properties, and Crystallographic Data

$Cu_3Cl_6(H_2O)_2 \cdot 2TMSO_2$ was prepared by dissolving anhydrous copper(II) chloride in ethanol and adding tetramethylene sulfone to the solution. The compound crystallizes out of solution as thin golden-yellow platelets. The density, determined by flotation in a mixture of methyl bromide and methyl iodide, was 2.27(3) g/cc. The calculated density for Z = 4 is 2.23 g/cc.

Systematic X-ray extinctions for the monoclinic crystal [(hkl) for h+k=2n+1, (h0l) for l=2n+1] indicate that the space group is Cc or C2/c. The lattice constants are a = 23.978(10) Å, b = 6.142(5) Å, c = 18.956(10) Å, and β = 127.00(2)°, based on a least squares fit for 16 reflections collected at 2Θ and minus 2Θ on the Picker diffractometer, using a scan rate of 0.5 deg/min, with Mo K_α radiation. A total of 1766 reflections, 556 of which were classified as unobserved, were measured on a Picker diffractometer equipped with a G.E. quarter circle orienter with Zr filtered Mo K_α radiation. A Θ–2Θ scan technique with 60 second (2°) scans and 20 second background measurements preceding and following the scan were used. The crystal size was 0.02 × 0.15 × 0.30 mm. During the data collection, three standard peaks were monitored to assure continued alignment of the crystal. No absorption corrections were made (μ = 43 cm^{-1}). For structure factor calculations, atomic form factors from the literature were used.[10] No dispersion corrections were made. All programs were from the Washington State University Crystallographic Library.[11] The standard deviation of the structure factor for each reflection was calculated by the formula

$$\sigma^2(F) = F/2NC\,[TC + BC + (aNC)^2]$$

where TC = total counts
BC = background counts
NC = net counts = TC – BC
a = 0.07

Reflections were labeled unobserved if the net count was less than $4\sigma(I)$ and assigned a structure factor of $2\sigma(F)$.

Determination and Refinement

The three-dimensional Patterson function was calculated and the presence of Harker peaks on the v = 0 section indicated that C2/c was the correct space group. The most reasonable Cu–Cu vectors gave an initial copper location at (0.159, 0.196, 0.392). The R-factor, based on the structure factors calculated for this position, was 0.58. A Fourier synthesis, based on the above position, was calculated and a second independent copper at 1/4, 3/4, 1/2 revealed the existence of a trimeric species molecular unit. A Fourier synthesis based on these two atoms yielded all other non-hydrogen atoms. Complete full-matrix least squares refinement with anisotropic thermal parameters for all atoms yielded an R-factor of 0.093 (observed reflections only). Unobserved reflections were omitted from the refinement if the calculated structure factor was less than $2\sigma(F)$. No attempt was made to locate hydrogen atoms. All peaks on the final difference map were less than 0.5 electron/$Å^3$.

The final positional and thermal parameters with standard deviations are listed in Table I. Observed and calculated structure factors are listed in Table II. The bond lengths and bond angles with standard deviations are listed in Table III.

Discussion

The structure contains a new copper(II) chloride–aquo species, $Cu_3Cl_6(H_2O)_2$. This species exists as discrete planar trimers. These stack above each other to form infinite chains parallel to the b-axis of the crystal, as shown in Figure 1. The closest distances

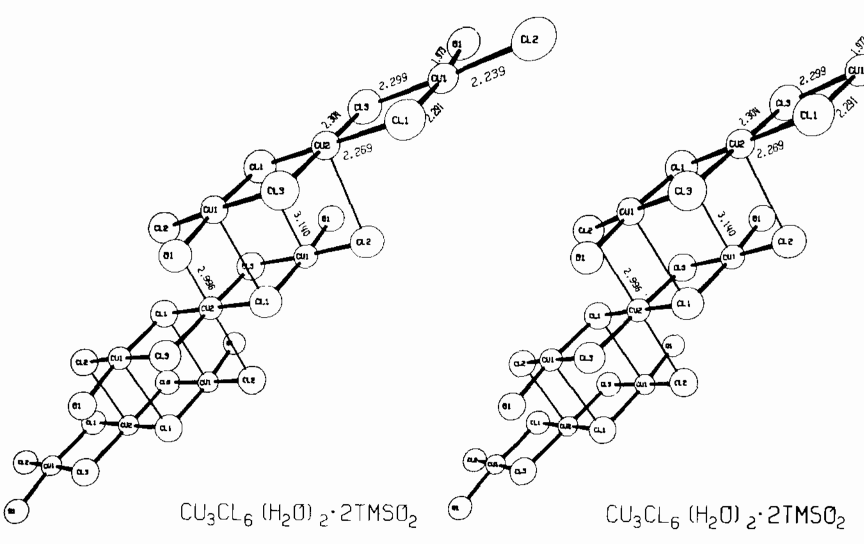


Figure 1. Stereographic illustration of the $[Cu_3Cl_6(H_2O)_2]_n$ chains.

TABLE I. Final positional and thermal parameters for $Cu_3Cl_6(H_2O)_2 \cdot 2(C_4H_8SO_2)$.[a,b]

Atom	X	Y	Z
Cu(1)	0.1556(1)	0.1926(3)	0.3932(1)
Cu(2)	0.2500	−0.2500	0.5000
Cl(1)	0.2570(2)	0.0378(5)	0.4306(2)
Cl(2)	0.1685(2)	0.4853(5)	0.3338(2)
Cl(3)	0.1472(2)	−0.0999(5)	0.4621(2)
S	0.0715(2)	−0.0022(6)	0.1606(2)
O(1)	0.0723(5)	0.3206(17)	0.3750(7)
O(2)	0.0174(6)	0.1517(19)	0.0975(8)
O(3)	0.0812(5)	−0.0200(16)	0.2442(7)
C(1)	0.0567(9)	−0.2670(23)	0.1135(10)
C(2)	0.1195(11)	−0.2933(30)	0.1083(13)
C(3)	0.1790(10)	−0.1713(35)	0.1797(13)
C(4)	0.1521(8)	0.0486(29)	0.1794(13)

U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
0.0241(8)	0.0187(8)	0.0407(9)	0.0022(4)	0.0096(4)	0.0053(4)
0.0322(14)	0.0205(12)	0.0550(16)	0.0052(5)	0.0140(6)	0.0097(5)
0.0286(18)	0.0239(17)	0.0411(19)	0.0027(7)	0.0108(8)	0.0057(7)
0.0383(20)	0.0236(16)	0.0411(20)	0.0022(8)	0.0124(8)	0.0049(7)
0.0288(18)	0.0264(17)	0.0495(21)	0.0035(7)	0.0127(8)	0.0068(8)
0.0295(19)	0.0304(18)	0.0403(19)	0.0026(8)	0.0103(8)	0.0017(8)
0.0459(63)	0.0377(60)	0.0687(71)	0.0151(27)	0.0203(30)	0.0109(28)
0.0652(81)	0.0497(73)	0.0599(77)	0.0130(33)	0.0144(34)	0.0110(30)
0.0457(63)	0.0315(55)	0.0444(59)	0.0018(25)	0.0131(27)	0.0026(23)
0.0702(114)	0.0214(72)	0.0451(87)	−0.0009(36)	0.0191(43)	−0.0049(30)
0.0841(136)	0.0536(109)	0.0779(123)	0.0010(52)	0.0351(59)	−0.0055(49)
0.0598(115)	0.0650(129)	0.0748(130)	0.0059(53)	0.0205(54)	0.0060(55)
0.0409(85)	0.0545(99)	0.0771(132)	−0.0015(41)	0.0203(46)	−0.0047(48)

$$R_1 = \frac{\Sigma \| F_{obs}| - |F_{calc}\|}{\Sigma |F_{obs}|} = .093 \qquad R_3 = \left[\frac{\Sigma W(|F_{obs}| - |F_{calc}|)^2}{\Sigma W |F_{obs}|^2}\right]^{1/2} = .137$$

[a] Thermal parameters are of the from $T=\exp[-2\pi^2\{U_{11}(ha^*)^2+U_{22}(kb^*)^2+U_{33}(lc^*)^2+2U_{12}(ha^*kb^*) +2U_{13}(ha^*lc^*)+2U_{23}(kb^*lc^*)\}]$. [b] Standard deviations are given in parenthesis.

between adjacent trimers in the chain are Cu–Cl distances of 3.00 and 3.14 Å. The $TMSO_2$ molecules, which are hydrogen bonded to the water molecules, pack between the chains, isolating the chains from each other. This can be seen in Figure 2. This is the second trimeric copper halide structure reported, the other being $Cu_3Cl_6(CH_3CN)_2$.[3] The two structures will be compared and contrasted in the following paragraphs.

The $Cu_3Cl_6(H_2O)_2$ trimer possesses only a crystallographically imposed center of inversion. Nevertheless, it has approximately C_{2h} symmetry, with the water molecules *trans* across the molecule. Each copper ion has basically a square-planar coordination geometry. The two bridging Cu–Cl–Cu angles are 92.7 and 93.8° respectively. The Cu–O bond length is 1.973(9)Å, comparable to the bond length in $CuCl_2 \cdot 2H_2O$ of 1.92 Å(1). The terminal Cu–Cl bond length is 2.239(4)Å, while the bridging Cu–Cl bond lengths range from 2.269(3) to 2.304(4)Å. These compare well with the Cu–Cl bond distance of 2.28Å for the square-planar $CuCl_4^{2-}$ ion in $(C_2H_5NH_3)_2CuCl_4$.[12] The geometry of the trimer is almost identical to the $Cu_3Cl_6(CH_3CN)_2$ trimer. As shown in Figure 3, all corresponding bond distances are equal to within 0.02Å and all corresponding bond angles are equal to within 3°.

The stacking of the trimeric units above each other leads to a stair-step type chain parallel to the b-axis. The packing scheme, dictated by Cl–Cl van der Waals repulsion forces, leads to an interplanar spacing of roughly 3 Å. As shown in Figure 1, the packing is such that the terminal chlorine atom, Cl(2), sits above the middle copper atom, Cu(2) of the preceding trimer. This leads to a b-axis repeat distance of 6.14 Å, very analogous to the repeat distances of 6.14 Å found in $Cu_3Cl_6(CH_3CN)_2$, of 6.04 Å in $Cu_5Cl_{10}(C_3H_7OH)_2$,[3] of 6.08Å in $LiCuCl_3 \cdot 2H_2O$,[13] and of 2 × 6.04Å in

TABLE II. Observed and calculated structure factors for $Cu_3Cl_6(H_2O)_2 \cdot 2(C_4H_8SO_2)$. The values listed under FO and FC are $10|F_o|$ and $10\,F_c$ respectively. A negative sign preceding the value of $10\,F_o$ indicates an unobserved reflection.

H	K	FO	FC
L = 0			
0	2	204	389
0	4	2005	1979
0	6	694	653
1	1	2307	2139
1	3	-170	-251
1	5	366	366
1	7	-240	29
2	0	1946	-2330
2	2	190	189
2	4	938	-809
2	6	497	355
3	3	2764	2245
3	5	-214	-55
3	7	710	735
4	0	1442	-1693
4	2	300	-164
4	4	645	628
4	6	575	-624
5	1	1390	-1174
5	3	1873	-1435
5	5	269	-276
5	7	344	-321
6	0	783	514
6	2	929	749
6	4	1463	-1764
6	6	381	402
7	1	424	507
7	3	2523	-2462
7	5	-230	-104
7	7	746	-732
8	0	559	374
8	2	966	-537
8	4	375	-303
8	6	761	-763
9	1	312	-909
9	3	182	836
9	5	499	-447
10	0	3733	-3536
10	2	535	627
10	4	963	-863
10	6	-223	93
11	1	252	-200
11	3	434	313
11	5	-224	117
12	0	3356	3351
12	2	335	345
12	4	1134	1265
12	6	427	412
13	1	871	534
13	3	427	-592
13	5	411	431
14	0	472	417
14	2	-212	242
14	4	657	-639
15	1	336	561
15	3	1191	1155
15	5	-242	61
16	0	-310	-251
16	2	367	334
16	4	515	513
17	1	1039	-1045
17	3	241	179
18	0	364	-471
18	2	-213	-62
18	4	-226	39
19	1	257	279
19	3	571	-623
20	0	703	647
20	2	530	-631
21	1	-225	-77
22	0	1047	1125
22	2	-218	153
L = 1			
0	2	944	-514
0	4	1052	854
0	6	398	-411
1	1	156	-133
-1	1	1042	-1124
1	3	317	325
-1	3	-172	53
1	5	-257	41
-1	5	-219	472
1	7	981	845
-1	7	1317	-1455
-2	2	617	775
2	4	1354	1230
-2	4	1252	1134
2	6	913	817
-2	6	-213	-153
3	1	2593	1533
-3	1	372	-527
3	3	2246	-2022
-3	3	1726	1516
3	5	220	142
-3	5	-207	104
3	7	-235	130
-3	7	826	832
4	2	763	-505
-4	2	383	412
4	4	653	592
-4	4	2229	-2173
4	6	-225	-247
-4	6	532	594
5	1	1431	-1594
-5	1	1597	1161
-5	3	2403	-2212
5	5	-210	-33
-5	5	384	-274
5	7	273	-232
-5	7	-230	55
6	2	716	-534
-6	2	845	-572
6	4	1555	1355
-6	4	541	402
6	6	430	-472
-6	6	232	214
7	1	434	313
-7	1	2129	-2046
7	3	1393	-1284
-7	3	1645	1530
7	5	-210	-21
-7	5	456	-391
8	2	597	-406
-8	2	1947	-731
8	4	1054	-1017
-8	4	1060	574
8	6	296	234
-8	6	887	-508
9	1	299	69
-9	1	1424	1465
9	3	-196	-49
-9	3	243	-316
9	5	-211	17
-9	5	-214	221
10	2	-195	49
-10	2	912	532
10	4	-213	-393
-10	4	675	-612
10	6	365	302
-10	6	552	521
11	1	330	-422
-11	1	712	575
11	3	244	-223
-11	3	-197	-131
11	5	-216	82
-11	5	425	-359
12	2	-201	-74
-12	2	422	-279
12	4	1080	1140
-12	4	655	-671
12	6	376	-391

H	K	FO	FC
-12	6	-234	153
13	1	993	-1033
-13	1	403	-478
13	3	1103	1130
-13	3	535	-544
13	5	-219	114
-13	5	-223	258
14	2	-234	23
-14	2	-203	-126
14	4	636	-668
-14	4	1280	1245
15	1	872	799
-15	1	252	-354
15	3	1026	-1078
-15	3	1134	1102
15	5	-217	-12
-15	5	-220	172
16	2	-211	25
-16	2	563	613
16	4	307	-333
17	1	295	-331
-17	1	1308	1247
17	3	429	482
-17	3	743	-797
18	2	393	-255
-18	2	-218	196
18	4	531	597
-18	4	-233	-225
19	1	-222	-24
-19	1	786	-839
19	3	-226	-38
-19	3	-226	132
20	2	-222	29
-20	2	592	-503
21	1	319	245
-21	1	-234	44
-22	2	401	362
L = 2			
0	0	1180	1576
0	2	2054	-1859
0	4	-197	-215
0	6	954	-921
1	1	-143	-53
-1	1	-146	-173
1	3	2477	-2119
-1	3	593	746
1	5	-213	-47
-1	5	634	-556
1	7	707	-722
-1	7	445	422
2	0	3553	-3787
2	2	925	-795
-2	2	1169	1023
2	4	1072	-1123
-2	4	645	-571
2	6	733	741
-2	6	-218	4
3	1	2585	-2548
-3	1	922	662
3	3	1552	-1207
-3	3	1551	1155
3	5	393	-331
-3	5	311	315
3	7	263	-294
-3	7	391	381
4	0	1672	-1431
-4	0	4696	4762
4	2	-161	-131
-4	2	752	693
4	4	460	287
-4	4	2515	2313
4	6	699	-613
-4	6	553	567
5	1	511	413
-5	1	1257	946
5	3	2524	2393
-5	3	1945	-1674
5	5	397	-324
-5	5	1057	1003
5	7	461	465
-5	7	-211	-133
6	0	2091	-1743
-6	0	903	1224
6	2	633	542
-6	2	677	411
6	4	797	913
-6	4	727	-853
6	6	-218	23
-6	6	413	435
7	1	606	503
-7	1	3601	3413
7	3	1163	-973
-7	3	1386	1413
7	5	-213	113
-7	5	255	253
7	7	463	382
8	0	4173	4375
-8	0	273	311
8	2	272	185
-8	2	313	263
8	4	1342	1293
-8	4	328	255
8	6	330	343
-8	6	681	-651
9	1	1022	-941
-9	1	2193	-2363
9	3	-194	-12
-9	3	-197	133
9	5	561	540
-9	5	672	-926
-10	0	575	-372
10	2	352	355
-10	2	-180	71
10	4	267	-337
-10	4	211	-263
10	6	-235	272
-10	6	674	683
11	1	-196	-123
-11	1	244	-312
11	3	1263	1393
-11	3	1364	-1224
11	5	-220	144
-11	5	362	351
12	0	232	-215
-12	0	1295	1325
12	2	-193	383
-12	2	2536	-2533
12	4	756	791
-12	4	484	-503
-12	6	382	-395
13	1	-207	-107
-13	1	-199	-93
13	3	353	-323
-13	3	539	-853
13	5	-224	-152
-13	5	462	-465
14	0	523	565
-14	0	1971	-1725
14	2	450	-477
-14	2	897	823
14	4	429	-511
-14	4	1189	-1153
15	1	-216	-186
-15	1	-201	-29
15	3	937	-968
-15	3	595	675
15	5	-215	-77
-15	5	615	-473
16	0	-216	49
-16	0	271	360
16	2	466	-471

H	K	FO	FC
-16	2	434	427
16	4	-221	-20
-16	4	1122	1068
17	1	397	-441
-17	1	-215	-140
17	3	727	791
-17	3	513	-418
18	0	1661	-1609
-18	0	672	697
18	2	-221	91
-18	2	-212	-20
-18	4	-223	-37
19	1	251	-285
-19	1	1524	1464
19	3	-231	-120
-19	3	330	337
20	0	1145	1238
-20	0	522	527
20	2	-229	-25
-20	2	-223	180
21	1	330	339
-21	1	401	-439
-22	0	386	-383
22	2	759	753
L = 3			
0	2	1321	-1330
0	4	939	937
0	6	1322	-1216
1	1	3525	-3267
-1	1	1486	1661
1	3	742	989
-1	3	411	-409
1	5	-208	-12
-1	5	763	669
1	7	323	-393
-1	7	542	-579
2	2	-166	-321
-2	2	1113	1154
2	4	225	224
-2	4	514	-475
2	6	651	796
-2	6	454	474
3	1	724	824
-3	1	469	671
3	3	2183	-1876
-3	3	518	-407
3	5	267	215
-3	5	400	-491
3	7	-233	39
-3	7	764	833
4	2	699	419
-4	2	1233	-1343
4	4	1897	-1736
-4	4	614	-518
4	6	-222	135
-4	6	251	318
5	1	587	-322
-5	1	1093	-912
5	3	1345	1289
-5	3	1040	-905
5	5	-215	-213
-5	5	725	636
-5	7	278	-405
6	2	-175	13
-6	2	821	-1015
6	4	1182	1190
-6	4	1959	1990
6	6	-227	-137
-6	6	-241	-134
7	1	794	-650
-7	1	1342	-1104
7	3	-136	-11
-7	3	1800	1693
7	5	-220	173
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8	2	333	-331
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8	4	-218	44
-8	4	1611	1559
-8	6	341	359
9	1	-226	-163
-9	1	184	106
9	3	-227	-119
-9	3	1292	1457
-9	5	321	-321
10	0	320	-252
-10	0	1074	-896
10	2	839	852
-10	2	1003	1024
-10	4	952	-582
-10	6	-223	124
11	1	-230	-205
-11	1	652	652
-11	3	-189	-33
-11	5	-216	-94
12	0	387	-408
-12	0	1662	1822
-12	2	1324	-1303
-12	4	-207	1
-12	6	-230	-145
-13	1	-189	86
-13	3	806	864
-13	5	506	515
-14	0	1741	-1552
-14	2	398	351
-14	4	-197	-99
-15	1	1766	-1523
-15	3	303	-232
-15	5	681	-709
-16	0	1294	-1206
-16	2	294	-327
-16	4	-200	-67
-17	1	1039	958
-17	3	332	440
-18	0	-202	273
-18	2	-208	-130
-18	4	673	-722
-19	1	-221	14
-19	3	973	-985
-20	0	1378	1397
-20	2	-210	54
-21	1	-213	-61
-22	0	1721	-1671
-22	2	603	598
L = 11			
0	2	293	-343
0	4	960	1019
1	1	305	-207
-1	1	625	-513
1	3	-201	461
-1	3	238	-203
-1	5	475	424
2	2	456	393
-2	2	407	-475
2	4	825	-845
-2	4	267	-241
-2	6	-231	-9
3	1	779	832
-3	1	-196	138
3	3	638	-646
-3	3	228	-197
3	5	-212	-12
-3	5	534	-531
4	2	-216	49

H	K	FO	FC
-4	2	865	785
4	4	-216	72
-4	4	400	-362
-4	6	434	454
5	1	1020	-959
-5	1	1174	1264
5	3	227	213
-5	3	-194	-179
-5	5	425	372
6	2	509	-559
-6	2	287	-371
6	4	-222	209
-6	4	379	399
-6	6	509	-571
7	1	-226	94
-7	1	1565	-1445
7	3	-228	212
-7	3	1067	1197
-7	5	-217	-63
8	2	315	285
-8	2	-173	-280
-8	4	944	987
-8	6	-233	204
9	1	224	260
-9	1	541	731
9	3	-226	-50
-9	3	564	-1050
-9	5	-217	-173
10	2	-235	100
-10	2	530	441
-10	4	1614	-1639
-10	6	-231	236
11	1	-230	-56
-11	1	-136	35
-11	3	401	499
-11	5	-219	-233
-12	2	563	466
-12	4	323	359
-12	6	-224	-148
-13	1	565	-566
-13	3	-193	178
-13	5	323	260
-14	2	-203	-278
-14	4	336	381
-15	1	402	-344
-15	3	271	282
-15	5	-225	-226
-16	2	-201	285
-16	4	525	-557
-17	1	1467	1481
-17	3	1133	-1144
-18	2	-205	-83
-18	4	225	-243
-19	1	575	-551
-19	3	1005	1043
-20	2	-212	3
-21	1	-214	144
-22	2	-214	9
L = 12			
0	0	952	839
0	2	743	723
0	4	1101	1206
1	1	-216	107
-1	1	-215	131
1	3	-225	-245
-1	3	694	673
1	5	450	503
-1	5	-205	-34
2	0	494	417
-2	0	1364	-1343
2	2	-217	75
-2	2	570	536
2	4	253	-339
-2	4	667	-644
3	1	1171	1219
-3	1	-203	214
3	3	-238	237
-3	3	-206	-53
-3	5	293	-263
4	0	252	136
-4	0	1596	1416
4	2	-221	174
4	4	-223	-100
-4	4	252	-171
-4	6	243	-345
5	1	795	-769
-5	1	-232	-51
5	3	-224	93
-5	3	1115	-1202
-5	5	-222	102
6	0	651	-671
-6	0	558	-590
6	2	-234	244
-6	2	461	-453
-6	4	294	-307
-6	6	-248	163
7	1	249	-259
-7	1	1700	-1685
7	3	-233	-137
-7	3	-203	-83
-7	5	689	-702
8	0	279	173
-8	0	590	-705
8	2	757	-779
-8	2	-199	-171
-8	4	-193	175
-8	6	417	-476
9	1	-226	-41
-9	1	764	754
-9	3	688	729
-9	5	-216	-59
10	0	237	-209
-10	0	443	343
-10	2	245	-295
-10	4	882	-893
-10	6	-231	213
-11	1	643	659
-11	3	802	-901
-11	5	-218	291
-12	0	2516	3013
-12	2	459	444
-12	4	1093	1315
-12	6	378	360
-13	1	411	465
-13	3	564	564
-13	5	335	366
-14	0	2313	-2519
-14	4	320	-303
-15	1	233	245
-15	3	947	929
-15	5	-223	169
-16	0	1944	810
-16	2	-206	-59
-16	4	-212	110
-17	1	263	300
-17	3	1208	-1291
-18	0	495	394
-18	2	510	-539
-18	4	623	-635
-19	1	664	-732
-19	3	337	-401
-20	0	553	-601
-20	2	341	-333
-21	1	534	-464
-22	0	1209	-1174
-22	2	-216	-150
L = 13			
0	2	261	-190
0	4	716	764

H	K	FO	FC
1	1	735	-735
-1	1	424	346
1	3	725	721
-1	3	703	-757
-1	5	-209	-115
2	2	-217	-91
-2	2	-217	-123
2	4	-217	83
-2	4	807	-854
3	1	419	381
-3	1	427	348
3	3	-231	-253
-3	3	-215	19
-3	5	-209	72
4	2	292	280
-4	2	-213	-122
4	4	290	-314
-4	4	394	333
5	1	-222	-100
-5	1	-210	-256
5	3	-225	-25
-5	3	-209	-104
-5	5	-221	126
6	2	-234	-180
-6	2	303	-231
-6	4	477	535
7	1	340	-298
-7	1	694	-712
-7	3	569	548
-7	5	-221	-99
-8	2	-204	71
-8	4	429	-503
-8	6	313	272
-9	1	917	846
-9	3	1076	-1153
-9	5	-219	134
-10	2	-198	65
-10	4	382	-444
-10	6	-231	184
-11	1	687	-752
-11	3	1052	1082
-11	5	-221	118
-12	2	-202	-37
-12	4	1019	1151
-12	6	306	-327
-13	1	-202	-221
-13	3	-211	-76
-13	5	-229	-127
-14	2	-206	27
-14	4	428	-475
-15	1	790	253
-15	3	-206	92
-15	5	-220	-47
-16	2	-211	-76
-16	4	526	-570
-17	1	415	398
-17	3	599	-705
-18	2	223	-136
-18	4	765	812
-19	1	630	-635
-19	3	1002	962
-20	2	-210	16
-21	1	747	658
-22	2	256	250
L = 14			
0	0	868	-752
0	2	254	259
0	4	311	277
1	1	694	-720
-1	1	249	214
1	3	-228	97
-1	3	436	503
2	0	378	-308
-2	0	-222	-189
2	2	-222	-128
-2	2	-214	-22
2	4	-227	-134
-2	4	527	-565
3	0	644	531
3	1	-223	45
-3	1	777	679
-3	3	273	-262
-3	5	251	272
4	0	522	483
-4	0	2395	2423
4	2	447	-421
-4	2	471	454
-4	4	864	925
5	1	-224	-39
-5	1	-209	80
-5	3	297	355
-5	5	-212	41
6	0	963	-926
-6	0	1897	-1723
6	2	-233	59
-6	2	483	458
-6	4	-213	-190
7	1	-240	-230
-7	1	-206	-46
-7	3	1006	1064
-7	5	-198	54
-8	0	227	253
-8	2	310	-311
-8	4	-210	54
-9	1	-203	-76
-9	3	1395	-1423
-9	5	-223	-25
-10	0	260	353
-10	2	422	-477
-10	4	477	-531
-11	0	404	253
-11	1	251	-311
-11	3	633	-570
-11	5	399	-408
-12	0	635	-552
-12	2	440	-428
-12	4	253	219
-13	1	586	-637
-13	3	494	641
-13	5	-229	-219
-14	0	1607	-1569
-14	2	-209	-80
-14	4	466	-567
-15	1	373	311
-15	3	-218	-196
-15	5	-213	217
-16	0	2891	2851
-16	2	-214	248
-16	4	702	733
-17	1	752	696
-17	3	333	-338
-18	0	511	-469
-18	2	612	535
-18	4	302	-323
-19	1	594	496
-19	3	1216	1352
-20	0	238	-199
-20	2	217	158
-21	1	573	-643
-22	0	-216	197
-22	2	-214	-180
L = 15			
0	2	-220	22
0	4	260	-209
1	1	357	-289
-1	1	435	475
1	3	546	532
-1	3	675	-636
2	2	-722	-20

H	K	FC	FC
-2	2	-215	1
-2	4	463	-452
3	1	-227	-93
-3	1	434	-374
3	3	-239	-126
-3	3	333	349
4	2	-232	-66
-4	2	222	-191
-4	4	673	672
5	1	-238	176
-5	1	238	-192
-5	3	-213	10
-5	5	-217	44
-6	2	307	287
-6	4	-220	-74
-7	1	-214	239
-7	3	-215	137
-7	5	-217	155
-8	2	-208	-114
-8	4	670	-695
-9	1	-204	128
-9	3	911	-947
-9	5	-204	40
-10	2	265	-346
-10	4	623	667
-11	1	811	-682
-11	3	826	836
-11	5	-202	-44
-12	2	-209	-185
-12	4	221	292
13	1	844	924
-13	3	469	-490
-13	5	-208	41
-14	2	262	278
-14	4	580	-553
-15	1	485	-401
-15	3	-210	6
-15	5	230	105
-16	2	493	-543
-16	4	-211	154
-17	1	649	-605
-17	3	-212	35
-18	2	355	325
-18	4	465	509
-19	1	-211	105
-19	3	711	725
-20	2	262	264
-21	1	482	487
-22	2	-226	-255
L = 16			
0	0	-246	-161
0	2	245	-240
1	1	-238	-32
-1	1	427	-385
1	3	666	663
-1	3	663	-663
2	0	682	-685
-2	0	-228	197
2	2	-225	51
-2	2	-226	-199
-2	4	310	-250
3	1	-235	-104
-3	1	-220	-4
-3	3	-231	-222
4	0	890	920
-4	0	-223	-185
-4	2	-215	-30
-4	4	-219	67
-5	1	247	-216
-5	3	515	500
-6	0	1704	-1226
-6	2	421	374
-6	4	246	-221
-7	1	-220	222
-7	3	230	182
-8	0	1653	1524
-8	2	-214	150
-8	4	653	646
-9	1	-219	254
-9	3	541	-631
-9	5	-230	237
-10	0	-215	-248
-10	2	490	384
-10	4	247	-211
-11	1	594	660
-11	3	1234	1203
-11	5	-211	-43
-12	0	424	-465
-12	2	-209	65
-12	4	-224	235
-13	1	1001	-969
-13	3	291	-316
-13	5	-215	-165
-14	0	-215	228
-14	2	289	-315
-14	4	-216	-28
-15	3	544	-580
-15	5	-230	-57
-16	0	495	477
-16	2	1095	-1075
-16	4	313	-257
-17	1	324	-254
-17	3	-214	52
-18	0	1459	-1395
-18	2	592	614
-19	1	-215	-86
-19	3	407	401
-20	0	728	612
-20	2	-217	38
-21	1	-218	68
-22	0	547	432
-22	2	-222	123
L = 17			
0	2	-227	2
1	1	255	206
-1	1	-234	6
-2	2	-225	-38
-3	1	514	-515
-3	3	495	473
-4	2	-218	3
-5	1	583	512
-5	3	-226	-87
-6	2	124	378
-6	4	291	-312
-7	1	-214	-28
-7	3	-223	-160
-8	2	569	-493
-8	4	-223	63
-9	1	239	-260
-9	3	-219	-131
-10	2	-215	106
-10	4	413	423
-11	1	-216	146
-11	3	544	530
-12	2	-214	200
-12	4	419	-427
-13	1	715	706
-13	3	697	-707
-14	2	-214	-82
-14	4	-222	158
-15	1	888	-884
-15	3	-220	113
-16	2	555	-509
-16	4	-221	113
-17	1	-225	104
-17	3	-218	223
-18	2	593	650
-18	4	-218	-161
-19	1	-216	148

H	K	FO	FC
-19	3	-219	10
-20	2	-232	-173
-21	1	-215	-69
-22	2	444	-425
L = 18			
0	0	544	621
-1	1	-227	-62
-2	0	-226	25
-2	2	-227	28
-3	1	354	312
-4	0	699	-607
-4	2	-220	-77
-5	1	622	-616
-5	3	291	-294
-6	0	-235	9
-6	2	-223	70
-7	1	-220	42
-7	3	383	-389
-8	0	-228	240
-8	2	615	-647
-8	4	-223	-104
-9	1	-216	58
-9	3	-227	227
-10	0	732	-628
-10	2	719	688
-10	4	-231	-246
-11	1	-215	-30
-11	3	520	524
-12	0	310	345
-12	2	-216	44
-12	4	420	446
-13	1	-218	-102
-13	3	492	-514
-14	0	333	370
-14	2	-220	80
-14	4	-219	81
-15	1	779	761
-15	3	583	582
-16	0	333	-219
-16	2	-219	-86
-16	4	-216	-53
-17	1	528	-508
-17	3	-217	20
-18	0	-279	-157
-18	2	515	546
-18	4	-221	93
-19	1	242	-227
-19	3	418	-396
-20	0	269	-164
-20	2	1276	-1171
-21	1	-218	-19
-22	0	365	-254
-22	2	476	438
L = 19			
-3	1	-234	-27
-4	2	285	196
-5	1	-248	469
-6	2	-225	105
-7	1	492	-457
-7	3	-226	-11
-8	2	421	-472
-9	1	-224	30
-9	3	-231	224
-10	2	533	506
-11	1	234	222
-11	3	-222	46
-12	2	-234	181
-13	1	-221	1
-13	3	257	-260
-14	2	378	-395
-14	4	-233	219
-15	1	604	-507
-15	3	-227	136
-16	2	-223	21
-17	1	966	909
-17	3	-224	-54
-18	2	657	549
-19	1	303	-220
-19	3	-222	-64
-20	2	623	-604
-21	1	372	-296
-22	2	-237	-79
L = 20			
-5	1	-234	-95
-6	0	-236	184
-7	1	-235	168
-8	0	279	-304
-8	2	392	-351
-9	1	304	-291
-10	0	-259	75
-10	2	527	514
-11	1	253	-199
-11	3	284	-251
-12	0	-219	-170
-12	2	824	-768
-13	1	-226	187
-13	3	-223	-68
-14	0	-225	-215
-14	2	460	469
-15	1	-225	6
-15	3	233	172
-16	0	-225	107
-16	2	376	354
-17	1	-236	158
-17	3	-224	29
-18	0	328	338
-18	2	-228	35
-19	1	-235	173
-19	3	-230	133
-20	0	-247	-88
-20	2	612	-568
-21	1	236	-189
-22	0	-226	-1
-22	2	851	788
L = 21			
-9	1	495	395
-11	1	-229	-102
-12	2	274	-232
-13	1	-232	-243
-14	2	-235	-122
-15	1	-225	13
-16	2	386	355
-18	2	-230	-105
-19	1	504	-487
-20	2	256	-279
L = 22			
-12	0	-239	-203
-13	1	245	-199
-14	0	-236	-153
-15	1	259	-262
-16	0	-226	-21
-17	1	434	374
-18	0	-226	-6
-19	1	286	-337
-20	0	-228	120
-21	1	369	304
-22	0	-241	143

TABLE III. Bond distances and angles for $Cu_3Cl_6(H_2O)_2 \cdot 2(C_4H_8SO_2)$.

Distances		Angles		Angles	
Cu(1)–Cl(1)	2.291(4)Å	Cl(1)–Cu(1)–Cl(2)	92.7(2)°	Cu(1)–Cl(1)–Cu(2)	93.8(2)°
Cu(1)–Cl(2)	2.239(4)	Cl(1)–Cu(1)–Cl(3)	86.5(2)	Cu(1)–Cl(3)–Cu(2)	92.7(2)
Cu(1)–Cl(3)	2.299(4)	Cl(1)–Cu(1)–O(1)	173.5(3)	Cu(2)–Cl(1)–Cu(1)^{f}	91.7(1)
Cu(1)–Cl(1)^{a}	3.140(7)	Cl(1)–Cu(1)–O(3)	92.0(3)	Cu(1)–Cl(1)–Cu(2)^{g}	96.2(1)
Cu(1)–O(1)	1.973(9)	Cl(1)–Cu(1)–Cl(1)^{a}	89.2(2)	O(2)–S–O(3)	114.7(7)
Cu(1)–O(3)	2.608(11)	Cl(2)–Cu(1)–Cl(1)^{a}	84.6(1)	O(2)–S–C(1)	111.6(8)
Cu(1)Cu(2)	3.331(4)	Cl(2)–Cu(1)–Cl(3)	176.7(1)	O(2)–S–C(4)	112.0(8)
Cu(2)–Cl(1)	2.269(3)	Cl(2)–Cu(1)–O(3)	94.0(2)	O(3)–S–C(1)	109.2(7)
Cu(2)–Cl(3)	2.304(4)	Cl(2)–Cu(1)–O(1)	91.3(3)	O(3)–S–C(4)	110.7(8)
Cu(2)–Cl(2)^{a}	2.996(7)	Cl(3)–Cu(1)–O(1)	89.2(3)	C(1)–S–C(4)	97.2(8)
S–O(2)	1.462(11)	O(1)–Cu(1)–Cl(1)^{a}	86.2(4)	S–C(1)–C(2)	102.4(11)
S–O(3)	1.462(11)	O(1)–Cu(1)–O(3)	92.8(4)	C(1)–C(2)–C(3)	109.2(14)
S–C(1)	1.786(14)	Cl(3)–Cu(1)–Cl(1)^{a}	92.2(1)	C(2)–C(3)–C(4)	106.5(15)
S–C(4)	1.769(15)	Cl(3)–Cu(1)–O(3)	89.2(2)	C(3)–C(4)–S	104.9(12)
C(1)–C(2)	1.574(24)	Cl(1)–Cu(2)–Cl(2)^{d}	92.4(1)		
C(2)–C(3)	1.451(27)	Cl(3)–Cu(2)–Cl(2)^{d}	89.4(2)		
C(3)–C(4)	1.495(25)	Cl(1)–Cu(2)–Cl(3)	86.9(1)		
O(1)–O(2)^{b}	2.707(16)	Cl(1)–Cu(2)–Cl(3)^{e}	93.1(1)		
Cu(1)–Cu(2)^{c}	3.928(2)				

^{a}Atom transformed by ($^1/_2$–x, $^1/_2$–y, 1–z). ^{b}Atom transformed by (–x, y, $^1/_2$–z). ^{c}Atom in adjacent trimer. ^{d}Atom transformed by (x, y–1, z). ^{e}Atom transformed by ($^1/_2$–x, –$^1/_2$–y, 1–z). ^{f}Atom transformed by ($^1/_2$–x, $^1/_2$–y, 1–z). ^{g}Atom transformed by (x, 1+y, z).

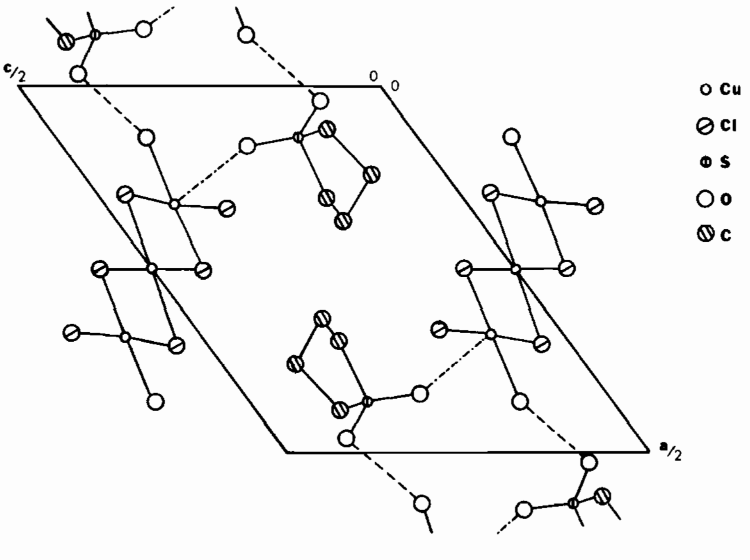


Figure 2. Unit cell packing diagram shown from the <010> direction. Hydrogen bonds are shown by ----. The shortest contact between the copper ions and the $TMSO_2$ group is shown by -.-.-.

$(CH_3)_2NH_2CuCl_3$.[14] The unique Cu–Cl distances between layers are 3.00 and 3.14 Å. This is almost exactly the same as in $Cu_3Cl_6(CH_3CN)_2$, where the respective distances are 3.01 and 3.18 Å. The stacking of the trimers as described here leaves a packing site above (or below) the terminal copper atoms of each trimer. In $Cu_3Cl_6(CH_3CN)_2$ this site is occupied by a chlorine atom from a trimer in another chain. In the structure described in this paper, the $TMSO_2$ group fills this role, as illustrated in Figure 2. Thus, one of the oxygen atoms sits above the copper atom at a distance of 2.61(1)Å. This is 0.05 Å longer than predicted for the Cu–O distance if this distance is assumed to be governed solely by O–Cl van der Waals repulsive forces.[16] Thus, while it does not coordinate to the copper ions, one of the roles of the $TMSO_2$ groups in this structure

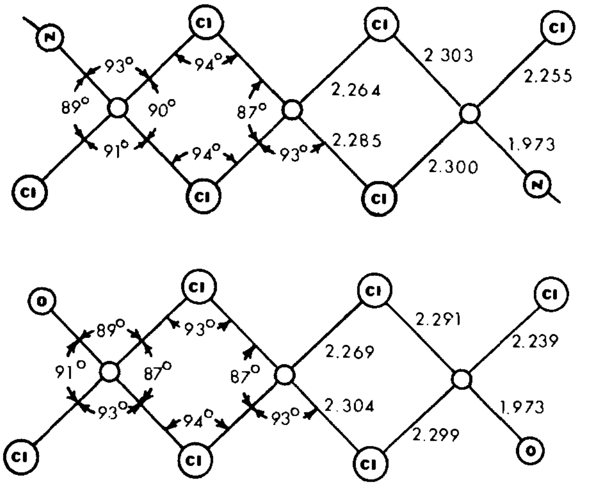


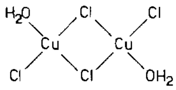
Figure 3. A comparison of the structure of the $Cu_3Cl_6(CH_3CN)_2$ trimer and the $Cu_3Cl_6(H_2O)_2$ trimer.

is to pack between the chains of trimers and isolate them from each other. This factor should have significant effects on the magnetic properties of these two compounds. In $Cu_3Cl_6(CH_3CN)_2$, the interchain interactions will effectively lead to a two-dimensional magnetic network.[15] In $Cu_3Cl_6(H_2O)_2 \cdot 2TMSO_2$, the chains of trimers should act as isolated one-dimensional magnetic systems. The other role played by the $TMSO_2$ molecules is to stabilize the structure by hydrogen bonding to the water moleculer of the trimeric species. The $O(1)\text{–}H\cdots O(2)$ distance is 2.71(2) Å, compared with the O–O distance of 2.76Å in ice.[16] The geometry of the $TMSO_2$ molecule is as expected, with considerable pucker to the five-membered ring. Distances are all normal (S–O = 1.46(1) Å, S–C = 1.77(1), and C–C = 1.51(5) Å) as are the bond angles (O–S–O = 115°(1), O–S–C = 111°(1), C–S–C = 97°(1), S–C–C = 104(1)°, and C–C–C = 108(1)°).

The structure of one other complex with the empirical formula $Cu_3Cl_6L_2(H_2O)_2$ has been reported by Sager and Watson[17] where L = 2-picoline-N-oxide. In contrast to the structure reported here, however, the N-oxide structure contains linear chains composed of alternating $Cu_2Cl_4L_2$ dimers and $CuCl_2(H_2O)_2$ molecules. This emphasizes the uncertainty in predicting structures of copper halide species from empirical formulae.

The mull spectrum of a powdered sample of $Cu_3Cl_6(H_2O)_2 \cdot 2TMSO$ was taken on a Cary–14 equipped with reverse optics. Peaks are observed at 9650 Å (sh) and 8150 Å for the d–d transitions and at 4000A(sh) and 3100A for the charge transfer bands. This is indicative of a square planar coordination geometry.[18]

Finally, it is of interest to speculate on the possible existance of a compound containing a $Cu_2Cl_4(H_2O)_2$ dimer of the type



This would then give a series of species of the type $(CuCl_2)_n\ (H_2O)_2$ for n = 1, 2, and 3. An analogous series exists for the acetonitrile complexes, where the compounds $CuCl_2(CH_3CN)_2$, $Cu_2Cl_4(CH_3CN)_2$, and $Cu_3Cl_6(CH_3CN)_2$ are known.[19,3] The latter two have been shown to be planar polymers[3] and the monomer probably exists as a planar four-coordinate species, although the structure has not been determined. Since the dimeric aquo species cannot be obtained from aqueous solution, its existence must be sought under similar conditions that yielded the $Cu_3Cl_6(H_2O)_2$ trimer. That is, it should be searched for in non-aqueous solutions in the presence of poor-coordinating ligand which can hydrogen bond to the water molecule. If the normal sequence of events in copper chloride chemistry occurs in carrying out this search, the searcher will be rewarded with many unusual compounds, none of them the desired product (although perhaps they can isolate the tetramer!).

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