histidine at pD 8.6 and 12.4, where the imidazole ring is nonprotonated. The upfield shift is indicative of an increase in electron density about the ring protons at pD >11, as a result of ionization of the "pyrrole" hydrogen. P.m.r. data support amino coordination in the Zn(II)–histidine complex at pD 11.8, for the alanine resonances lie between those observed for free histidine at pD 8.6 and 12.4, where the amino group is protonated and nonprotonated, respectively. Furthermore, the alanine resonances lie upfield of those observed in the Zn(II) complex at pD 5.0. These facts are consistent with replacement of the proton on the amino group by the less electronegative Zn(II) ion in going from pD 5.0 to 11.8.

In summary, the particular value of the infrared spectral data, and the ancillary p.m.r. data, is that the structures of the coordinated species at a given pD are deducible from correlation of the spectra with the spectra of free ligand as a function of pD. The evaluation of formation constants is not very precise, but the agreement of the results in this area with the expectations based on more precise methods is sufficiently good to lend support to the interpretations placed on the infrared data. In addition, observation of certain frequency shifts in favorable cases, such as the antisymmetric carboxylate stretching mode, yields information which relates closely to the relative enthalpies of coordinate bond formation.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY
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A Redetermination of the Crystal Structure of $CsCuCl_3$[1a]

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The crystal structure of $CsCuCl_3$ has been redetermined by single crystal X-ray diffraction techniques. Data were taken by scintillation counter methods and the atomic parameters were refined by anisotropic least-squares methods. The final parameters are essentially those originally reported by Wells. The structure consists of distorted hexagonally close-packed layers of cesium and chlorine atoms with the copper atoms occupying octahedral holes. The Cu–Cu distance is a very short 3.062 Å., but direct copper–copper bonding is ruled out by overlap integral calculations. The close approach of the coppers is considered to be a result of the copper atoms sharing faces of their chlorine octahedra instead of edges as has been found in all other halogen-bridged copper compounds. This interpretation differs from that of Wells. Several other metal–halogen systems having chain structures similar to that found in $CsCuCl_3$ are considered and the overlap integrals for metal–metal interaction calculated. From the calculations it is apparent that d–d metal–metal bonding for the elements at the right of the transition metal series is unlikely. The implications of this are related to the much discussed $Cu_2(C_2H_3O_2)_4 \cdot 2H_2O$.

Introduction

The structure determination of $CsCuCl_3$ was first attempted by Klug and Sears in 1946,[2a] but they were unsuccessful in solving the structure. Wells[2b] next investigated the problem and obtained a model which gave an agreement factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, of 20% on the basis of 60 reflections.

Because of their interesting structural and magnetic features, several related copper compounds have recently been investigated in this laboratory, namely, $LiCuCl_3 \cdot 2H_2O$,[3,4] $KCuCl_3$, and NH_4CuCl_3.[5] These structures all consisted of $Cu_2Cl_6^{2-}$ dimers associated into chains by long unsymmetric Cu–Cl bridges and are quite different from the $CuCl_3^-$ infinite chain found for $CsCuCl_3$ by Wells. Thus $CsCuCl_3$ should represent a different and particularly simple system to study magnetically because of its essentially one-dimensional character. Preliminary to such a study we decided to carry out a more accurate determination of its structure, which is being reported here. A magnetic investigation of this compound is currently underway, by B. C. Gerstein of this laboratory.

Experimental Section

Dark red-brown crystals of $CsCuCl_3$ were obtained by evaporating to dryness a solution containing copper and cesium chlorides. A molar excess of copper chloride was used to prevent formation of Cs_2CuCl_4. The crystals appeared as hexagonal prisms often capped by hexagonal pyramids.

Weissenberg photographs exhibited 6/mmm Laue symmetry. The only systematic extinction observed was $l \neq 6n$ for $00l$ reflections, indicating the space group $P6_122$ and confirming Wells' observation. The lattice constants were determined by a least-squares extrapolation treatment of twelve reflections in the back-reflection region observed using a single crystal orienter. The orienter was previously aligned with an aluminum single crystal. The lattice constants found are: $a = b = 7.2157 \pm 0.0005$ and $c = 18.1777 \pm 0.0010$ Å.

Complete three-dimensional data to $\sin \theta/\lambda = 0.904$ were taken with zirconium-filtered molybdenum $K\alpha$ radiation using a General

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[1] (a) Work was performed at the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1780. (b) Deceased, Oct. 9, 1963.

[2] (a) H. P. Klug and G. W. Sears, Jr., *J. Am. Chem. Soc.*, **68**, 1133 (1946); (b) A. F. Wells, *J. Chem. Soc.*, 1662 (1947).

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[4] P. H. Vossos, D. R. Fitzwater, and R. E. Rundle, *Acta Cryst.*, **16**, 1037 (1963).

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (L, $10F_o$, $10F_c$)

L	$10F_o$	$10F_c$
0 0 L		
18	876	897
24	1051	1076
30	0	48
1 0 L		
0	722	728
1	316	312
2	212	216
3	1653	1820
4	480	463
5	591	559
6	1844	1952
7	203	172
8	177	73
9	1312	1336
10	364	359
11	125	109
12	495	404
13	333	301
14	97	85
15	799	802
16	294	290
17	442	433
18	810	777
19	58	35
20	89	96
21	420	414
22	178	161
23	151	152
24	276	271
25	136	124
26	103	100
27	177	195
28	82	92
29	178	203
30	241	229
31	44	35
32	54	51
1 1 L		
1	757	740
2	144	131
3	122	86
4	321	290
5	272	213
6	741	725
7	309	251
8	167	158
9	129	97
10	198	174
11	543	504
12	1960	1904
13	412	380
14	365	351
15	144	133
16	249	242
17	124	120
18	203	166
19	199	190
20	249	239
21	96	89
22	105	99
23	170	169
24	650	628
25	108	101
26	223	225
27	49	68
28	65	74
29	59	73
30	60	38
31	119	97
32	94	104
2 0 L		
0	872	982
1	443	442
2	1168	1237
4	957	947
5	1342	1337
7	1268	1220
8	680	662
10	834	814
11	183	184
12	394	371
13	154	156
14	535	520
15	1409	1443
16	384	385
17	555	550
18	1023	1021
19	495	493
20	183	188
21	740	733
22	262	269
23	0	15
24	59	26
25	38	2
26	141	138
27	300	304
28	71	83
29	169	161
30	262	264
31	164	141
32	54	24
2 1 L		
0	65	114
1	249	211
2	343	346
3	1224	1268
4	430	439
5	921	857
6	1554	1541
7	1139	1081
8	451	448
9	952	945
10	245	234
11	335	305
12	132	113
13	227	225
14	234	232
15	610	562
16	180	164
17	290	277
18	735	720
19	570	566
20	191	196
21	271	270
22	136	117
23	247	247
24	85	75
25	78	95
26	109	106
27	126	116
28	51	45
29	74	86
30	251	245
31	187	180
2 2 L		
1	1864	2135
2	812	786
3	148	137
4	294	282
5	807	814
6	1626	1649
7	787	797
8	264	250
9	136	100
10	549	534
11	1339	1331
12	1767	1734
13	1314	1276
14	467	467
15	117	87
16	115	111
17	229	243
18	550	536
19	249	249
20	94	84
21	83	47
22	189	203
23	430	438
24	488	490
25	406	414
26	180	165
27	0	34
28	0	18
29	52	7
30	43	25
31	44	7
3 0 L		
0	1726	2017
1	1111	1181
2	589	578
3	290	192
4	293	278
5	189	127
6	578	568
7	102	68
8	73	56
9	190	178
10	629	615
11	665	642
12	1256	1228
13	858	843
14	134	120
15	158	157
16	241	243
17	196	195
18	152	122
19	46	42
20	170	177
21	145	143
22	270	296
23	187	200
24	400	390
25	331	341
26	40	22
27	100	99
28	42	75
29	141	105
30	43	38
31	62	13
3 1 L		
0	251	286
1	368	289
2	812	792
3	1228	1244
4	327	328
5	897	854
6	1069	1045
7	742	695
8	283	285
9	1004	997
10	623	620
11	224	180
12	194	200
13	344	321
14	394	399
15	638	635
16	130	145
17	466	483
18	488	489
19	252	270
20	135	136
21	394	395
22	225	244
23	148	144
24	91	100
25	184	192
26	95	113
27	190	191
28	30	41
29	183	180
30	161	153
31	99	85
3 2 L		
0	274	290
1	634	581
2	609	601
3	737	740
4	898	902
5	509	480
6	637	620
7	390	369
8	549	545
9	568	565
10	601	602
11	409	371
12	121	121
13	478	460
14	284	275
15	421	413
16	583	590
17	285	290
18	226	227
19	156	142
20	147	130
21	206	204
22	272	276
23	147	147
24	92	43
25	232	225
26	113	123
27	170	139
28	211	208
29	92	121
30	0	38
3 3 L		
0	918	913
1	1123	1117
2	330	316
3	325	317
4	280	247
5	330	345
6	795	783
7	219	239
8	156	121
9	0	32
10	141	146
11	859	843
12	638	620
13	658	650
14	308	307
15	349	363
16	199	192
17	146	146
18	377	382
19	51	2
20	58	22
21	75	60
22	90	57
23	326	336
24	216	238
25	213	213
26	172	166
27	190	177
28	68	70
29	31	5
4 0 L		
0	923	946
1	287	235
2	1156	1209
3	1390	1430
4	1676	1746
5	760	722
6	1390	1387
7	800	758
8	1424	1439
9	1081	1072
10	877	888
11	285	258
12	552	542
13	180	154
14	568	570
15	670	651
16	858	855
17	323	319
18	612	594
19	366	370
20	533	540
21	295	295
22	272	264
23	175	164
24	144	109
25	84	111
26	103	97
27	130	111
28	202	222
29	86	103
30	141	142
4 1 L		
0	1024	1031
1	1185	1198
2	428	401
3	118	111
4	462	443
5	191	223
6	636	634
7	229	245
8	255	230
9	220	221
10	314	310
11	833	816
12	681	661
13	798	784
14	281	275
15	55	63
16	353	361
17	103	59
18	255	254
19	129	132
20	95	101
21	162	159
22	148	138
23	296	313
24	218	224
25	293	303
26	127	125
27	51	47
28	144	152
29	0	27
30	0	52
4 2 L		
0	273	272
1	655	665
2	1014	1005
3	978	984
4	804	795
5	1178	1176
6	262	247
7	1106	1100
8	648	632
9	795	785
10	796	808
11	463	464
12	137	146
13	360	360
14	508	509
15	482	484
16	392	390
17	558	568
18	75	70
19	473	484
20	216	229
21	271	264
22	279	286
23	140	143
24	64	12
25	109	88
26	115	130
27	74	104
28	96	84
29	145	151
4 3 L		
0	149	40
1	195	195
2	321	319
3	490	493
4	596	599
5	567	558
6	158	156
7	685	677
8	599	597
9	441	429
10	233	241
11	51	70
12	99	98
13	201	203
14	169	169
15	253	254
16	267	277
17	235	234
18	111	118
19	411	415
20	305	299
21	180	192
22	98	107
23	76	68
24	29	72
25	84	81
26	67	38
27	91	78
4 4 L		
0	220	242
1	835	844
2	766	756
3	306	305
4	388	391
5	445	450
6	489	495
7	462	468
8	362	371
9	192	225
10	538	531
11	534	540
12	137	138
13	538	551
14	503	505
15	225	230
16	184	162
17	146	124
18	237	235
19	163	154
20	149	129
21	131	120
22	197	189
23	161	151
24	42	10
25	165	159
26	173	174
5 0 L		
0	172	191
1	177	221
2	434	422
3	677	690
4	189	162
5	838	836
6	292	296
7	1006	1004
8	297	281
9	539	543
10	411	407
11	62	51
12	136	145
14	167	172
13	230	247
15	307	311
16	77	78
17	288	308
18	171	177
19	554	576
20	209	223
21	170	167
22	159	188
23	110	127
24	74	75
25	86	86
26	92	56
27	66	48
28	60	44
29	96	80
5 1 L		
0	312	318
1	182	142
2	435	427
3	580	576
4	910	925
5	523	509
6	262	259
7	574	563
8	887	901
9	470	469
10	223	222
11	119	110
12	292	281
13	153	152
14	273	264
15	329	327
16	430	445
17	247	248
18	208	205
19	324	321
20	424	443
21	235	197
22	61	9
23	89	87
24	143	153
25	87	76
26	72	59
27	134	109
28	149	140
5 2 L		
0	342	343
1	636	626
2	565	568
3	359	347
4	113	112
5	164	159
6	505	505
7	223	211
8	38	27
9	273	285
10	499	497
11	349	350
12	225	222
13	495	510
14	329	336
15	176	185
16	126	118
17	174	156
18	240	246
19	92	110
20	81	63
21	117	124
22	220	251
23	125	119
24	58	65
25	207	217
26	120	124
27	30	59
5 3 L		
0	245	238
1	290	295
2	605	603
3	307	312
4	381	376
5	555	555
6	135	102
7	457	473
8	379	365
9	363	364
10	445	449
11	237	254
12	218	218
13	132	144
14	382	397
15	173	156
16	186	169
17	315	331
18	125	129
19	207	211
20	164	171
21	231	231
22	173	177
23	97	106
24	73	123
25	30	43
5 4 L		
0	456	450
1	228	230
2	237	248
3	272	296
4	336	350
5	315	330
6	125	114
7	254	251
8	217	217
9	168	186
10	245	259
11	225	219
12	326	322
13	109	91
14	151	147
15	239	258
16	230	255
17	174	204
18	0	39
19	76	88
20	58	62
21	65	81
22	111	131
23	84	95
5 5 L		
0	219	242
1	369	386
2	260	241
3	269	279
4	171	162
5	332	339
6	78	48
7	285	292
8	109	123
9	122	123
10	195	205
11	295	314
12	159	176
13	247	229
14	160	166
15	282	282
16	134	119
17	186	185
18	50	52
19	83	122
20	0	53
21	0	35
6 0 L		
0	551	550
1	1230	1251
2	764	769
3	508	489
4	76	85
5	653	657
6	637	628
7	646	663
8	124	106
9	389	392
10	525	541
11	813	816
12	341	323
13	803	819
14	498	508
15	317	299
16	55	35
17	226	212
18	257	249
19	229	229
20	38	4
21	172	156
22	192	205
23	250	249
24	0	54
25	245	254
26	181	179
27	52	101
6 1 L		
0	383	362
1	321	317
2	695	709
3	196	187
4	264	244
5	608	618
6	136	108
7	480	474
8	153	141
9	115	96
10	596	610
11	282	297
12	262	251
13	102	115
14	420	432
15	209	202
16	174	174
17	364	373
18	83	54
19	184	170
20	27	48
21	88	65
22	279	291
23	122	114
24	92	95
25	59	48
26	167	168
6 2 L		
0	596	582
1	271	263
2	500	506
3	213	203
4	915	933
5	364	357
6	268	259
7	364	352
8	795	801
9	180	185
10	373	371
11	199	207
12	417	407
13	133	145
14	244	221
15	116	128
16	468	487
17	186	175
18	109	98
19	175	171
20	317	322
21	107	102
22	77	72
23	114	78
24	168	150
25	60	28
6 3 L		
0	164	158
1	362	377
2	398	403
3	284	288
4	147	133
5	277	282
6	147	142
7	256	258
8	141	144
9	263	282
10	233	239
11	281	279
12	154	155
13	258	258
14	317	319
15	148	161
16	129	100
17	157	155
18	102	108
19	118	116
20	91	60
21	143	160
22	93	72
23	111	113
6 4 L		
0	95	87
1	443	445
2	339	349
3	245	261
4	284	277
5	403	407
6	176	174
7	356	354
8	238	229
9	241	252
10	280	295
11	340	336
12	82	87
13	263	254
14	178	176
15	161	167
16	136	131
17	203	197
18	100	99
19	149	127
20	106	85
21	157	144
6 5 L		
0	0	2
1	111	96
2	214	218
3	167	171
4	235	227
5	154	135
6	210	209
7	103	94
8	226	228
9	220	225
10	153	152
11	80	95
12	0	27
13	76	53
14	168	153
15	96	77
16	143	118
17	51	87
6 6 L		
0	98	81
1	160	164
2	248	239
3	177	157
4	278	286
5	195	181
6	99	81
7	190	194
8	261	270
9	122	98
10	156	152
11	96	104
12	50	54
13	131	107
7 0 L		
0	614	605
1	227	216
2	44	40
3	229	224
4	662	678
5	32	27
6	314	300
7	89	33
8	447	450
9	190	178
10	157	145
11	231	219
12	415	413
13	154	132
14	142	136
15	166	162
16	456	478
17	37	48
18	117	108
19	67	35
20	152	151
21	75	82
22	81	67
23	148	118
24	153	140
25	73	64
7 1 L		
0	135	93
1	530	544
2	478	498
3	141	141
4	121	99
5	418	425
6	179	173
7	351	354
8	125	101
9	54	24
10	316	342
11	421	436
12	104	90
13	318	330
14	357	381
15	178	189
16	96	96
17	243	239
18	110	111
19	143	138
20	49	49
21	41	50
22	136	142
23	161	182
24	84	51
7 2 L		
0	42	13
1	219	227
2	333	326
3	348	352
4	167	171
5	195	195
6	224	231
7	252	250
8	220	222
9	317	331
10	318	334
11	116	119
12	46	37
13	186	192
14	157	162
15	193	193
16	87	80
17	84	63
18	94	113
19	165	155
20	166	166
21	166	168
22	139	175
7 3 L		
0	172	153
1	143	86
2	251	249
3	226	231
4	416	435
5	149	132
6	114	97
7	123	142
8	413	429
9	217	234
10	159	152
11	0	44
12	159	154
13	87	75
14	172	172
15	113	131
16	233	234
17	81	70
18	96	97
19	105	85
20	220	226
7 4 L		
0	90	86
1	173	188
2	158	152
3	220	224
4	182	163
5	179	172
6	106	110
7	208	218
8	175	174
9	160	172
10	74	86
11	144	128
12	85	86
13	164	153
14	111	122
15	159	161
16	82	77
17	88	70
7 5 L		
0	102	59
1	174	188
2	176	154
3	170	169
4	49	74
5	121	111
6	187	196
7	128	114
8	86	64
9	186	174
10	153	138
11	120	142
12	65	60
7 6 L		
0	29	33
1	145	141
2	109	99
3	127	117
8 0 L		
0	182	177
1	462	488
2	570	576
3	261	256
4	167	148
5	477	483
6	397	395
7	424	423
8	79	52
9	230	224
10	497	516
11	354	355
12	124	110
13	258	259
14	311	323
15	123	126
16	98	72
17	205	215
18	196	205
19	130	146
20	86	48
21	82	92
22	228	233
23	94	95
8 1 L		
0	75	52
1	120	94
2	210	206
3	112	89
4	481	510
5	149	162
6	165	165
7	133	114
8	509	519
9	135	112
10	69	93
11	106	94
12	125	92
13	85	53
14	166	150
15	68	44
16	250	265
17	133	114
18	118	114
19	87	49
20	285	282
21	51	75
8 2 L		
0	125	112
1	331	323
2	345	361
3	281	278
4	168	168
5	369	374
6	70	72
7	365	377
8	163	163
9	204	210
10	233	239
11	221	196
12	103	82
13	207	212
14	237	249
15	173	176
16	107	94
17	173	172
18	51	56
19	188	174
8 3 L		
0	54	45
1	268	290
2	125	86
3	152	166
4	91	78
5	184	187
6	120	100
7	127	118
8	108	83
9	101	92
10	69	88
11	270	268
12	64	41
13	146	152
14	64	53
15	154	155
16	0	47
8 4 L		
0	157	137
1	160	130
2	228	238
3	136	141
4	250	259
5	180	187
6	57	27
7	146	155
8	240	230
9	132	135
10	189	179
11	77	89
9 0 L		
0	118	108
1	165	168
2	266	294
3	251	240
4	69	52
5	221	205
6	274	264
7	302	293
8	92	33
9	181	183
10	230	236
11	98	27
12	87	80
13	186	181
14	207	217
15	155	141
16	57	54
17	70	54
18	164	159
19	178	186
20	0	28
9 1 L		
0	107	111
1	305	316
2	207	199
3	54	70
4	0	84
5	196	211
6	241	226
7	154	145
8	95	64
9	126	102
10	152	167
11	286	287
12	69	89
13	168	175
14	140	142
15	0	44
16	112	70
17	149	130
9 2 L		
0	217	214
1	159	128
2	96	80
3	48	90
4	254	276
5	153	149
6	134	110
7	116	111
8	211	200
9	0	67
10	99	96
11	90	79
12	144	156
13	119	115
14	0	13
9 3 L		
0	180	183
1	57	78
2	124	139
3	161	155
4	99	103
5	137	139
6	128	106
7	119	115
8	0	75
9	108	109
10 0 L		
0	180	185
1	102	92
2	216	201
3	198	202
4	382	411
5	96	89
6	104	93
7	48	32
8	357	365
9	191	172
10	136	133
11	57	44
12	121	125
13	91	109
14	150	100
15	130	97
10 1 L		
0	146	114
1	74	48
2	222	238
3	89	87
4	80	78
5	175	155
6	70	71
7	128	123
8	107	107
9	91	82
10	163	160
11	50	24
12	105	90
10 2 L		
0	175	185
1	247	265
2	147	129
3	81	48
4	41	34
5	104	121
6	181	180
11 0 L		
0	128	129
1	216	212
2	137	138
3	128	84
4	70	35
5	0	49
6	115	115
7	77	50
8	50	25

* 0·0·6, 289.4(345.2); 0·0·12, 321.7(381.0); 1·1·0, 227.3(332.0); 2·0·3, 262.0(359.4); 2·0·6, 249.0(273.7); 2·0·9, 237.6(255.5); 2·2·0, 243.5(293.5)

These reflections affected by extinction, F_o (F_c), are not on an absolute scale.

Electric XRD-5 X-ray unit equipped with a single crystal orienter. For each of the 1092 reflections a total count was obtained from a 100-sec. scan using a scan rate of 1°/min. A correction for background and streak was made from the recorder trace for each reflection. The recorder was calibrated and zeroed frequently to obtain good accuracy. An absorption correction was made using Busing's polyhedral absorption correction program rewritten for the IBM 7074 computer.

Structural Refinement

The parameters of Wells were tested and an agreement factor of $R = 45\%$ was obtained. Using a full-matrix least-squares program two cycles of refinement reduced the R factor to 35%. A model constructed at this point indicated that the cesium atom, on the basis of a hexagonal close-packed arrangement, was displaced by 0.2 Å. and too close to two chlorine atoms. It was shifted to a more nearly close-packed position. Further isotropic refinement yielded an R factor of 11%. At this point seven of the strongest, low-order reflections, suspected of being strongly affected by extinction, were removed. Anisotropic refinement lowered the R factor for the 1062 nonzero reflections to a final agreement factor, $R = 5.05\%$. The final parameters and standard deviations are given in Table II. In Table I the values of $10F_o$ and $10F_c$ are listed on an absolute scale.

Discussion

The $CsCuCl_3$ structure consists of distorted hexagonally close-packed layers of cesium ions and chlorine atoms, with the copper atoms, located on twofold axes, occupying all the octahedral holes which have six chlorine nearest neighbors. Two chlorines are at a distance of 2.35 Å., two at 2.28 Å., and two at 2.78 Å. from the coppers (Figure 1). The distortion from perfect close packing is slight with Cl(2′) 0.149 Å. above the plane and Cl(2) the same distance below (Figure 2). The copper atoms are 0.42 Å. from the 6_1 *c* axis and are oriented to form spiraling chains by sharing faces of the

TABLE II

Final Atom Positional Parameters with Standard Deviations

Atom	x/a	y/b	z/c	σ_x	σ_y	σ_z
Cs[a]	0.35458 (0.345)[b]	0.70916	0.25000	0.0001	0.0002	...
Cu	0.0616 (0.07)	0.0000	0.0000	0.0003	...	...
Cl(1)[a]	0.8877 (0.90)	0.7754	0.2500	0.0003	0.0006	...
Cl(2)	0.3540 (0.35)	0.2095 (0.22)	0.2418 (0.25)	0.0005	0.0005	0.0002

Final Thermal Parameters with Deviations

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	0.01311 (14)	0.01113 (7)	0.00222 (2)	0.00570 (3)	−0.00094 (3)	0
Cu	0.01026 (22)	0.01123 (11)	0.00101 (2)	0.00562 (6)	0.00020 (2)	0.00040 (4)
Cl(1)	0.0125 (4)	0.0094 (2)	0.0012 (1)	0.0047 (1)	0.0001 (1)	0
Cl(2)	0.0097 (2)	0.0128 (3)	0.0014 (1)	0.0051 (2)	−0.0006 (1)	−0.0002 (1)

[a] Special positions: $y = 2x, z = {}^1/_4$. [b] Wells' parameters in parentheses.

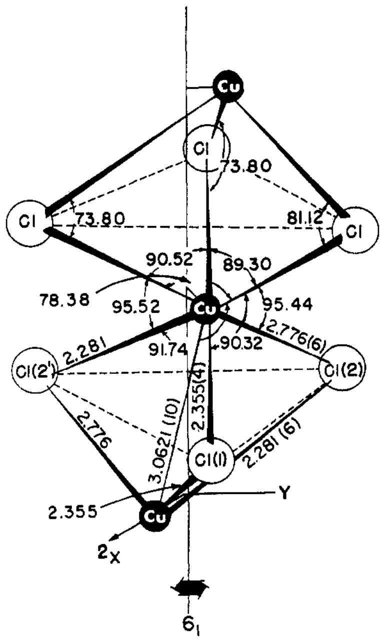
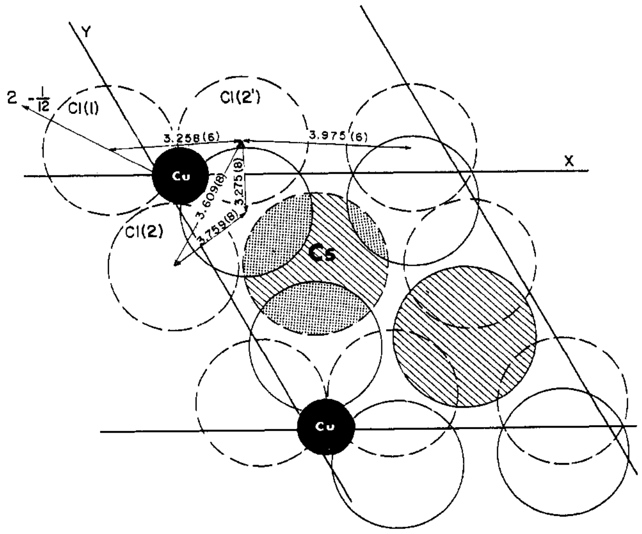


Figure 1.—The molecular structure of $CuCl_3^-$ in $CsCuCl_3$.



AVERAGE Cs-Cl DISTANCE 3.629 (2)

Figure 2.—The hexagonal close packing in $CsCuCl_3$.

TABLE III

DISTANCES AND ANGLES IN COPPER CHLORIDE COMPOUNDS

Formula	Cu–Cu, Å.	Av. angle Cl–Cu–Cl, deg.	Av. angle Cu–Cl–Cu, deg.
$KCuCl_3$	3.443	84.1	95.9
$LiCuCl_3 \cdot 2H_2O$	3.47	85.	95.
NH_4CuCl_3	3.42	84.9	
$Cu_2Cl_4(CH_3CN)_2$	3.39	86.	94.
$Cu_3Cl_6(CH_3CN)_2$	3.346	88.	94.2
$Cu_5Cl_{10}(C_3H_7OH)_2$	3.310	87.	92.8
$CuCl_2 \cdot 2H_2O$	3.73		92.9
$CuCl_2$	3.30	87.	
$CsCuCl_3$	3.0621	90.2	76.2

chlorine octahedra about them. One of the bridging chlorines, Cl(1), is bound symmetrically to two coppers —a feature that has been found in all the garnet-colored copper compounds.[4,5] The three-dimensional character of the compound can be considered to be infinite parallel chains held together by cesium ions. The more important bond distances and angles along with their standard deviations can be seen in Figures 1 and 2.

A very interesting feature of the structure is the very short copper–copper distance. As can be seen in Table III this distance is much shorter than that found in any other halogen-bridged copper compound. Two possible explanations for this short distance can be proposed: (1) The copper atoms form copper–copper bonds along the chain axis. Thus each copper is bonded strongly to four chlorines and weakly to two others and to two neighboring copper atoms. (2) In this compound the copper octahedra are connected together by sharing faces while in the other compounds listed in Table III the octahedra are connected together by sharing edges. The sharing of faces would force the copper–copper distance to be shorter than in the other compounds previously investigated. In this description no direct copper–copper bonding is suggested.

Evidence seems to support the latter explanation. As can be seen from Table III, the angles in $CsCuCl_3$ are distorted from the angles observed in the other copper compounds in such a way as to suggest the sharing of faces. Further evidence for the latter explanation is found in overlap integral calculations. In order to consider the likelihood of the formation of a metal–metal bond, D_{3d} symmetry was assumed at a copper atom. Under this symmetry the representation for σ bonding by copper breaks down into the irreducible representations: $2A_{1g} + E_g + 2A_{2u} + E_u$. Considering only the chlorine atoms the σ bonds transform as

$A_{1g} + E_g + A_{2u} + E_u$. This leaves A_{1g} and A_{2u} for metal–metal bonding in this simple treatment. The A_{1g} transforms as d_{z^2} which is directed right at the coppers along the chain while A_{2u} is a nonbonding orbital. Thus metal–metal bonds could possibly be formed by σ overlap of $3d_{z^2}$ orbitals along the chain axis. However, the value of the overlap integral for σ $3d_{z^2}$ overlap on copper atoms 3.062 Å. apart is less than 10^{-5}. (This value and the values to follow were determined using the improved orbital exponents calculated by Clementi.[6]) It must be realized of course that these calculations only give an approximate value of the overlap because of the uncertainty in the orbital exponent for the isolated atom and more important the unknown change in the exponent in considering a complexed metal. Nevertheless the value of the overlap in the above case is so extremely small that the metal–metal bond order is essentially zero. This result is confirmed by the magnitude of the magnetic moment for $CsCuCl_3$, which is normal for one unpaired electron down to 80°K.[7]

Similar calculations for other metal–halogen systems lend credence to this type of approach. Thus for $CsNiCl_3$, which crystallizes in a close-packed structure isomorphous with $CsCuCl_3$ with a nickel–nickel distance of 2.96 Å.,[8] the overlap integral for $3d_{z^2}$ orbitals between nickel atoms is less than 10^{-4}, and $CsNiCl_3$ also has a normal moment for two unpaired electrons.[9] Overlap calculations have also been performed for $TiCl_3$ and $ZrCl_3$, the structures of which have recently been deduced from powder diffraction studies.[10] The compounds have D_{3d} symmetry at the metal and form chains similar to $CsCuCl_3$ by sharing faces of chlorine octahedra. The metal–metal distance in both of these isomorphous compounds is 3.07 Å.[10] The calculation of the overlap integrals for σ d_{z^2} overlap gave a value of approximately 0.01 for the titanium–titanium bonds and 0.10, almost the maximum possible overlap for $4d_{z^2}$ orbitals, for the zirconium–zirconium bonds. Subnormal magnetic moments have been observed for these substances. $TiCl_3$ has a moment of 1.3 B.M.[11] (compared to the normal moment for one unpaired electron of 1.75 B.M.) indicating some interaction between the metals, and $ZrCl_3$ is almost diamagnetic with a moment of only 0.4 B.M.[11] In the latter case the fourteen σ-bonding electrons (1 from Zr^{3+}, 12 from six chlorines and $^1/_2 \times 2$ from two neighboring zirconium atoms) enter the A_{1g}, E_g, E_u, A_{1u}, and A_{1g}' bonding orbitals, the last being the metal–metal d_{z^2}–d_{z^2} bonding orbital.

This treatment thus consistently explains the magnetic properties of the above materials and also gives evidence that no direct metal–metal bonding occurs in $CsCuCl_3$. In fact from these overlap calculations it was found that for the metals at the right of the first transition series the single bond length for d_{z^2}–d_{z^2} σ bonding is so extremely short that such metal–metal bonding cannot possibly occur unless there are gross changes in the orbital exponent of the combined metal.

The orbital exponents of Clementi were used in these calculations rather than those determined using Slater's rules. The difference between these values is quite significant (for copper $\mu = 2.7$ by Slater's rules and $\mu = 4.4$ as calculated by Clementi), with Clementi's values indicating much more compact d orbitals for the atoms on the right of the transition metal series.

The choice of orbital exponents also has a strong bearing on any discussion of the bonding in copper acetate monohydrate where many approaches have been used to attempt to explain the short copper–copper distance.[12–18] All until recently have invoked some sort of direct 3d–3d bonding, the δ bond being very popular; however, none has been completely successful in explaining all the observed data. Our calculations of overlap rule out any direct 3d–3d bonding. Since our calculations were made, Kokoszka[19,20] and Hansen and Ballhausen[21] have given consistent interpretations of the available data assuming no direct copper–copper interaction. These results are consistent with our work and further indicate that overlap integrals obtained using the improved orbital exponents present a reliable method of evaluating the existence of direct metal–metal interactions.

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