Metal Ion–Aromatic Complexes. III. The Crystal and Molecular Structure of $C_6H_6{\cdot}CuAlCl_4$

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Abstract: A new benzene complex, $C_6H_6{\cdot}CuAlCl_4$, has been synthesized and its structure determined by three-dimensional, single-crystal X-ray diffraction techniques. Cu(I) is in a distorted tetrahedral environment with three metal-to-chlorine bonds and one π-type metal ion-aromatic interaction. The three Cu–Cl (2.365, 2.398, and 2.555 A, all ±0.006 A) interactions are made with different $AlCl_4^-$ tetrahedra in such a way that a pleated sheet of $CuAlCl_4^-$ is formed with Cu–C_6H_6 linkages protruding from the sheet. The sheets are separated by normal van der Waals distances. The Cu(I) is located almost directly above a C–C bond of the benzene ring with Cu–C distances of 2.15 and 2.30 A, both ±0.03 A. It appears that the anions play an important role in the stability of this complex.

The existence of complexes between silver ions and olefins or aromatic donors has been known for some time.[2] Mulliken[3] and Dewar[4] have formulated theoretical models for the bonding in these complexes. Single-crystal X-ray structure investigations of silver (I)–olefin[5–7] complexes and $C_6H_6{\cdot}AgClO_4$[8] have been carried out and the geometry and bond distances established. However, a thorough understanding of the factors involved in metal ion–olefin or aromatic complexes can be obtained only from a systematic study of complexes with various metal ions, anions, and a number of donors. Baenziger and his co-workers[9] have examined a number of olefin complexes, and we are examining a number of metal–ion aromatic complexes. A preliminary communication has been published on $C_6H_6{\cdot}CuAlCl_4$[10] and we now present synthetic and structure details.

Experimental Section

$C_6H_6{\cdot}CuAlCl_4$ was prepared by treating a slight excess of resublimed CuCl with 0.03 mole of resublimed $AlCl_3$ contained in easily broken Pyrex ampoules with an excess of dried benzene (20 ml) in one side of a dry evacuated H tube (Figure 1).

Upon breaking the tubes, the closed system was heated for 2 hr at 40° by immersing the two legs in dewars filled with warm water. Any HCl formed from residual water adsorbed on the vessel walls was pumped out; then the stopcock was sealed off. Since CuCl is insoluble in benzene, the solution of $C_6H_6{\cdot}CuAlCl_4$ in the left leg was filtered into the right leg. Single crystals were grown from the concentrated solution in the right leg by immersing the left leg in a Dry Ice–acetone bath. After excess benzene had been removed, the lower part of the right leg was cut off; this segment was transferred to a small drybox wherein single crystals were transferred to thin-walled (0.01 mm) glass capillaries. The glass capillaries were sealed off with a torch. The crystals were found to be very sensitive to air and moisture, and it was difficult to avoid some decomposition. Chemical analyses were performed, but they were only sufficiently accurate to confirm the above stoichiometry.

The crystal of approximately 0.3 × 0.3 × 0.6 mm was used for collecting the intensity data. Multiple film equiinclination Weissenberg techniques were used to collect 1200 independent *hkl* observed intensities with Zr-filtered Mo Kα radiation from *hk*0, *hk*1, . . ., *hk*6 levels. In addition, *h*0*l* and 0*kl* precession-timed exposure intensity data were collected with Zr-filtered Mo Kα radiation and used for preliminary scaling purposes. All intensities were visually estimated with a calibrated strip. The linear absorption coefficient (μ) for this compound is 32 cm^{-1} with Mo Kα radiation. Since no adsorption correction could be made for unavoidable surface decomposition, no absorption corrections were made.

Calculations were made with an IBM 7094 computer at New York University.[11] Lorentz polarization corrections were made and intensities reduced to squared structure factors. Fourier calculations were made with the Sly–Shoemaker–Van den Hende program. The full-matrix least-squares refinement was carried out using the Busing and Levy OR FLS program with the Hughes[12] weighting scheme with $4F_{\min} = 10$. We minimized the function $\Sigma w(F_o - F_c)^2$. Atomic scattering factors were taken from the compilation of Ibers[13] for Cu^+, Cl^-, Al^{+3}, and neutral C. The variables were scale factors, atomic coordinates, and individual atom temperature factors for the isotropic refinement. For the anisotropic refinement, the variables were the six β_{ij} for each atom along with the atomic positional coordinates. The anisotropic temperature factors were of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The scale factors were fixed after the isotropic refinement and not allowed to vary further until the refinement was completed.

Results

Unit Cell and Space Group. $C_6H_6{\cdot}CuAlCl_4$ was found to crystallize with four formula units per cell in the monoclinic crystal system. With CuKα_1(1.5405 A) α_2-(1.5443 A), unit cell constants were found to be a = 8.59 ± 0.01, b = 21.59 ± 0.03, c = 6.07 ± 0.01 A, and β = 93° 0′ ± 15′. The systematic extinctions of (for *h*0*l*) $h + l = 2n + 1$ and (for 0*k*0) $k = 2n + 1$ uniquely specify the space group as $P2_1/n$. The calculated crystal density was found to be 1.85 g cm^{-3}

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Table I. Observed and Calculated Structure Factors $F(C) = 10F(\mathrm{Calcd})$

	F(O)	F(C)
0K0		
6	297	259
8	435	-440
12	159	159
18	127	142
20	118	-111
1K0		
5	213	256
8	206	-182
9	241	-311
10	115	128
11	157	153
12	183	-192
13	111	94
14	43	30
15	45	-44
16	102	90
17	87	68
18	50	-37
20	105	114
21	70	-73
2K0		
2	158	113
3	300	299
4	167	-146
5	150	130
6	37	-19
7	99	-83
8	126	112
9	91	72
10	62	-44
11	156	-143
12	52	37
13	75	-64
15	49	44
16	39	44
18	52	-43
19	63	64
20	65	49
3K0		
1	184	-168
2	185	172
3	225	272
4	32	18
5	118	-96
8	225	228
9	190	193
10	259	-273
11	165	-162
13	34	-22
14	112	99
16	84	-75
17	92	-88
18	81	76
19	59	46
20	56	48
21	44	33
4K0		
0	181	-164
1	299	365
3	49	-46
4	68	100
5	213	-255
6	155	-140
7	244	258
8	170	154
9	102	-75
10	100	77
11	150	-136
12	125	-110
13	140	130
16	94	-85
17	74	-79
19	95	103
20	51	-22
5K0		
1	130	-108
2	177	165
3	81	47
4	268	-312
6	98	87
7	93	83
8	93	78
10	55	-47
11	37	25
12	62	45
13	59	-65
14	46	50
15	76	-54
16	74	-76
17	57	55
6K0		
0	75	-53
1	44	-35
4	46	-32
5	50	-25
6	40	24
7	45	-25
10	53	36
11	70	57
12	40	12
14	88	-78
16	62	62
18	63	-50
19	82	-92
7K0		
2	165	-162
3	52	45
4	135	115
7	134	-117
8	73	-63
7K0		
9	81	75
10	83	108
14	91	-99
15	105	96
16	60	65
8K0		
1	118	-102
2	54	46
4	56	60
5	76	113
6	75	-134
7	86	-122
11	106	119
12	104	-116
13	90	-87
14	91	90
9K0		
2	96	-89
3	79	73
4	86	67
8	59	-62
0K1		
6	274	259
7	298	343
8	171	-168
9	182	-189
10	88	71
11	151	155
13	156	-112
14	73	-75
15	217	-224
16	90	77
17	83	125
19	107	-80
21	83	52
23	133	137
1K1		
6	362	375
7	221	-237
8	52	-61
11	238	237
12	112	81
13	126	-101
14	218	-251
15	122	-94
17	199	234
19	166	-189
22	110	113
25	82	-92
-1K1		
5	51	59
6	81	-19
7	165	133
8	113	71
9	48	-54
10	47	30
11	171	-161
12	60	27
13	96	-63
15	86	84
16	95	-96
17	64	-56
18	76	91
19	163	174
20	91	-86
21	66	21
22	75	63
23	77	-92
23	77	-92
2K1		
2	208	-195
4	157	167
5	157	153
6	65	-55
7	94	-81
8	225	-226
9	288	295
10	186	179
12	193	184
13	123	-107
14	177	-195
15	130	95
16	101	97
17	96	-64
20	163	-196
22	62	92
-2K1		
1	99	-103
2	177	127
3	278	299
4	262	247
5	226	-193
6	198	-167
7	211	-172
8	200	181
9	264	272
10	276	-302
11	213	-211
12	185	-161
13	56	35
14	196	179
15	134	121
17	84	-55
18	95	63
20	136	131
3K1		
0	133	101
1	63	51
3	242	-266
4	177	144
5	96	50
6	159	-136
3K1		
7	164	108
8	161	-135
10	128	111
11	185	181
12	106	-100
14	70	71
17	82	-89
18	75	-85
21	75	-115
-3K1		
0	331	-394
1	240	-262
2	292	350
3	200	165
4	132	96
6	317	-307
7	134	-101
8	123	92
9	222	220
11	196	-179
12	125	-116
13	79	-45
14	130	102
15	87	70
16	146	164
17	66	-58
18	142	-152
19	58	24
20	59	55
21	87	100
22	63	-53
23	65	-75
24	82	-123
4K1		
1	179	136
2	167	126
4	232	-228
6	117	-91
8	124	108
9	195	-179
10	75	-54
11	87	86
12	88	72
14	142	123
16	157	-162
17	57	61
18	65	60
22	80	-114
23	82	-105
24	91	116
-4K1		
1	162	142
2	142	-136
3	131	82
4	103	94
5	145	-133
6	41	-40
7	198	-163
8	163	-143
9	74	-36
10	238	245
11	79	57
12	126	-113
14	63	48
15	153	171
16	61	70
18	153	-143
20	81	72
23	100	-128
5K1		
0	213	221
1	44	-33
2	73	-60
3	112	78
4	134	-119
5	167	-145
6	158	142
7	107	96
8	159	-130
9	69	56
10	100	-97
11	205	-216
12	172	173
13	162	162
15	56	-52
18	99	105
22	82	-117
-5K1		
0	268	321
2	193	-191
3	115	-83
4	62	40
6	131	122
8	212	-200
11	95	89
18	66	78
6K1		
1	123	98
2	126	82
3	135	-121
4	93	87
5	50	19
9	101	-93
11	78	-67
12	84	-69
13	173	197
15	95	-110
19	65	137
20	67	42
21	114	-166
-6K1		
1	91	73
2	93	79
3	214	-219
4	205	-213
5	95	78
7	130	99
8	143	144
9	74	-56
10	172	-144
12	195	205
13	90	73
15	103	-104
16	101	-100
7K1		
0	100	-94
1	95	70
2	108	98
4	54	-35
5	85	76
6	93	-67
8	120	117
10	130	-123
12	52	59
13	105	-105
14	62	69
16	104	-115
-7K1		
0	113	-150
1	165	183
2	64	60
3	97	-103
4	75	-53
5	177	-200
6	98	78
7	169	177
8	104	99
9	102	-93
10	104	-131
12	84	78
13	105	130
15	63	-88
16	64	-89
8K1		
1	71	-97
2	58	74
3	162	169
5	120	-125
7	67	74
9	69	74
11	63	-84
-8K1		
3	81	89
4	100	-92
5	92	-107
6	102	105
7	72	64
17	84	-78
9K1		
0	97	-111
4	63	79
7	64	88
10	57	97
-9K1		
5	89	96
7	84	-80
0K2		
6	283	342
7	191	-209
8	226	-240
9	266	315
10	184	-179
12	216	231
13	92	86
17	93	-87
18	159	181
19	147	-125
20	136	-91
21	84	25
22	99	-132
1K2		
4	340	342
5	176	118
6	184	-180
7	122	-94
8	216	-207
9	216	-220
10	284	343
11	113	-83
12	211	-201
13	237	277
15	125	-130
16	156	154
18	137	-137
19	122	157
20	83	60
21	169	-221
-1K2		
4	151	-165
6	195	-183
7	164	141
8	194	178
9	266	-295
10	86	71
11	221	231
12	85	67
14	118	106
15	78	-62
16	151	-138
2K2		
0	163	-157
2	197	227
4	180	-167
2K2		
5	237	236
6	171	-185
7	184	-214
8	192	186
9	98	-73
10	174	-155
12	81	74
13	186	-207
14	124	127
15	178	178
-2K2		
3	168	-154
4	141	100
6	49	-25
7	52	28
8	129	133
9	126	-123
10	111	104
11	150	129
12	182	-190
17	106	-114
18	120	-112
20	155	148
3K2		
1	155	-123
2	250	246
3	265	308
4	94	-81
5	214	-224
6	184	165
8	225	209
10	256	-261
15	84	69
16	94	-53
18	103	86
-3K2		
1	285	-320
2	142	-134
3	235	211
4	87	-47
5	107	71
6	130	95
7	158	-125
8	136	-97
9	483	494
11	227	-230
12	102	97
13	112	-104
14	157	-153
15	81	88
16	83	76
17	211	-232
18	65	62
19	97	85
20	106	-113
4K2		
0	148	130
1	400	406
2	164	-124
3	77	78
4	107	91
5	285	-327
6	111	90
7	302	344
9	161	-126
10	123	116
11	200	-185
12	180	-175
13	197	206
14	94	-98
15	122	-125
-4K2		
0	268	-296
1	204	-201
2	158	143
3	132	122
4	107	70
5	185	168
6	182	-177
7	145	-121
8	224	206
9	140	-114
10	49	52
11	145	120
12	170	-162
13	62	-61
15	141	-129
17	237	289
18	62	-67
19	110	-122
5K2		
2	228	219
3	267	-285
4	258	-267
5	273	301
6	133	120
7	86	-61
8	64	50
10	184	-178
11	205	197
13	148	-140
14	84	107
15	99	-85
-5K2		
1	121	-85
3	184	158
4	124	111
5	165	-141
6	204	184
7	115	98
8	169	-132
9	101	-96
-5K2		
11	105	76
14	166	-167
16	87	94
17	72	60
18	64	73
6K2		
2	127	-107
6	162	160
7	90	-72
8	79	-88
9	99	84
10	87	57
12	70	61
13	97	-68
14	117	-143
-6K2		
1	202	229
4	82	-41
7	92	73
9	146	-126
11	82	-80
18	106	75
19	69	145
7K2		
2	195	-221
3	84	85
4	180	156
6	118	-97
9	97	61
10	111	103
-7K2		
2	133	116
4	140	-128
6	102	-90
7	117	-120
8	198	229
10	147	-154
14	141	130
8K2		
0	160	-183
1	111	-119
4	98	104
6	162	-188
8	130	137
12	147	-161
14	135	155
-8K2		
5	158	-154
6	99	-79
8	60	-53
9	128	102
10	54	21
12	30	5
9K2		
3	140	179
5	122	-136
0K3		
5	183	184
6	125	93
7	278	-308
10	104	74
11	176	150
13	227	-233
15	80	70
16	83	65
17	86	110
18	103	-117
19	60	-63
20	68	73
22	72	68
1K3		
5	347	352
6	168	177
8	194	-180
10	67	65
11	60	40
12	71	-57
13	101	-91
16	97	109
19	80	-46
-1K3		
5	174	-147
6	195	-197
7	269	276
9	132	-125
10	89	85
11	159	-149
12	114	-89
13	114	88
14	124	102
17	91	65
19	60	41
2K3		
1	121	-100
2	354	-442
3	63	60
4	385	398
6	164	-174
8	161	-162
9	162	158
10	175	179
13	109	-112
14	93	-110
15	82	75
16	87	93
17	86	-91
19	57	-10
21	84	87
22	87	85
23	15	-12
-2K3		
2	233	312
3	387	403
4	179	-167
5	268	-328
7	92	-53
8	233	231
9	132	135
10	271	-287
11	128	-125
12	77	61
13	63	30
14	51	54
15	155	166
16	117	-105
18	80	58
19	70	-68
3K3		
0	147	-132
1	222	-210
2	69	-53
4	129	111
5	109	89
6	110	-104
7	144	-118
8	85	71
9	82	79
10	84	79
11	127	94
12	97	-87
14	95	103
16	90	-97
-3K3		
0	390	-401
1	143	138
2	280	343
3	106	-97
4	102	55
5	121	-121
6	295	-329
7	77	57
8	166	153
9	36	27
10	67	-61
11	77	-46
12	72	-40
13	41	28
14	118	117
15	122	108
17	110	-123
18	60	-76
4K3		
1	76	66
3	60	-45
4	111	-101
6	46	24
7	93	95
9	82	-80
10	68	66
11	64	-46
12	67	30
13	69	36
14	74	54
15	84	-84
16	94	-85
17	90	70
22	91	-104
24	96	101
-4K3		
1	51	29
2	81	-54
3	53	41
4	68	-34
6	66	-52
7	91	-57
9	63	53
10	158	147
11	126	-132
12	76	-66
14	127	100
18	137	-136
5K3		
0	174	162
1	73	42
3	62	-46
4	156	-142
5	116	-93
6	189	191
7	68	47
8	126	-116
10	137	-148
11	56	-60
12	225	270
13	88	94
14	119	-114
18	97	99
-5K3		
1	146	-130
2	181	-185
4	64	-54
5	116	-95
6	162	169
8	147	-123
9	160	146
11	72	-42
12	138	117
13	46	91
14	48	-42
15	60	-47
16	76	-75
17	63	-62
18	84	74
6K3		
1	140	132
2	78	58
3	223	-229
4	59	-31
5	85	69
7	74	85
8	78	56
9	191	-193
11	90	79
13	97	126
14	62	-65
25	81	17
-6K3		
1	123	80
2	63	57
3	240	-281
4	79	-73
5	153	149
6	53	-53
7	173	187
8	89	75
9	211	-217
10	141	-128
11	164	163
12	76	74
15	113	-119
17	66	65
7K3		
0	161	158
1	60	78
2	68	-68
6	82	59
7	89	78
8	55	-61
9	68	-65
-7K3		
0	148	128
1	158	178
2	118	-103
3	80	-79
4	106	-63
5	57	-50
6	185	206
7	130	115
8	76	-59
9	113	-75
14	93	-104
17	15	-12
8K3		
2	117	118
4	103	-95
-8K3		
5	80	76
6	72	85
9K3		
0	75	-60
0K4		
5	201	-200
6	226	219
8	109	91
9	146	138
10	299	-328
12	274	252
13	141	139
14	116	107
16	116	-99
18	135	146
1K4		
4	111	98
5	115	-109
6	120	-99
10	59	65
11	190	-133
12	92	89
13	210	227
14	95	-68
16	93	115
18	129	-116
19	128	153
21	120	-171
22	195	164
-1K4		
4	238	-301
6	88	90
7	253	263
8	162	135
9	196	-150
13	130	115
14	218	209
15	245	-242
16	173	-199
19	91	112
21	10	8
23	5	28
2K4		
0	82	-82
2	161	145
3	170	-167
4	149	139
5	94	66
6	297	-335
8	110	97
9	73	-70
11	198	201
12	185	-190
13	189	-182
14	260	267
15	86	56
-2K4		
2	177	-192
4	117	74
5	176	-159
-2K4		
7	157	132
8	186	181
10	112	116
11	133	-135
12	165	-153
13	128	128
14	112	113
16	168	-183
3K4		
1	152	-136
2	176	164
3	270	266
4	130	-132
5	150	-132
6	117	109
7	158	-161
8	88	-50
9	136	134
13	125	-131
15	216	252
20	70	61
22	16	-9
-3K4		
1	76	-58
4	236	224
5	113	83
6	165	-131
7	167	-107
9	186	147
10	225	-198
11	104	-16
12	97	55
13	117	-116
14	10	-10
16	55	11
17	145	-143
18	182	211
4K4		
0	69	63
1	60	36
3	154	157
5	64	-55
7	109	102
8	148	-139
9	58	64
10	205	184
11	215	-215
12	133	-123
13	78	100
14	80	-93
16	221	263
18	146	-170
-4K4		
1	163	-116
3	105	70
4	57	-54
5	271	270
6	184	139
7	98	-55
8	120	-92
9	143	-97
11	128	92
13	148	-145
14	169	-177
15	97	-98
16	177	220
17	177	195
18	171	-138
5K4		
1	91	78
2	68	-72
3	200	-176
4	192	169
5	282	268
6	150	-151
7	161	-141
11	141	134
12	170	-148
13	82	-107
15	61	-48
-5K4		
1	135	138
2	44	32
3	232	-220
4	45	-29
5	126	122
6	272	257
7	131	-102
8	289	-286
9	148	-142
10	161	117
11	196	216
14	196	-203
16	130	127
17	107	91
6K4		
0	123	96
1	204	-186
2	124	-119
3	76	40
4	76	-70
5	151	145
6	142	120
7	231	-257
9	148	128
12	86	78
13	164	-189
15	91	112
-6K4		
0	242	314
2	152	-129
8	166	-154
-6K4		
9	95	-136
14	60	68
7K4		
1	58	-72
2	177	-195
4	182	190
5	103	-93
7	160	128
10	135	119
11	19	-20
-7K4		
5	97	-121
6	80	-95
8	153	156
10	84	-89
8K4		
0	74	-83
-8K4		
0	221	-290
2	103	173
4	60	-8
6	61	-82
8	88	109
9	109	121
9K4		
4	159	-199
12	164	173
-9K4		
9	135	117
10K4		
1	134	176
0K5		
3	112	-141
4	57	83
5	132	151
7	153	-165
13	66	-61
1K5		
0	87	-116
1	130	-163
2	45	43
5	178	230
6	93	-82
7	162	-208
8	19	72
11	80	60
13	172	-158
15	110	125
-1K5		
1	102	156
2	57	-62
3	66	79
4	59	30
5	147	-187
6	73	42
7	191	239
8	171	-165
9	67	-29
10	121	109
11	188	-188
13	209	190
15	145	-127
16	163	167
2K5		
1	150	-173
2	162	-181
3	245	317
4	200	237
5	208	-255
6	43	-25
7	97	95
8	138	-120
9	129	138
10	145	121
11	132	-131
14	93	-96
17	74	-85
-2K5		
2	240	250
3	119	87
4	385	-399
5	107	-92
6	102	86
7	74	-39
8	173	137
10	187	-165
11	101	85
12	105	94
13	120	-96
14	94	63
15	126	133
16	123	-107
19	136	-142
3K5		
0	275	-313
1	111	-85
2	164	140
4	69	68
6	177	-179
8	211	215
9	74	-60
12	127	-121
14	93	100
15	101	-115
16	104	-86
17	100	119
-3K5		
1	227	263
2	75	56
3	136	-137
4	101	94
5	112	-117
6	157	-131
-3K5		
7	158	126
9	98	-80
12	127	-92
14	126	61
15	70	58
4K5		
1	35	-16
2	74	64
4	128	-119
6	128	93
12	101	103
13	44	63
15	47	-43
-4K5		
1	11	-8
2	117	-58
3	20	-47
5	71	38
7	80	7
8	93	61
10	92	40
12	58	34
14	43	-14
5K5		
0	171	164
1	71	71
2	93	-67
3	99	-80
4	80	-60
6	178	163
8	115	-106
10	44	-67
11	139	77
12	142	133
13	47	-40
14	128	-100
-5K5		
0	23	15
1	158	-161
4	144	-125
6	183	191
7	109	-104
9	115	86
10	117	-111
12	153	185
14	130	-127
6K5		
1	133	118
2	75	-83
3	226	-225
5	138	101
8	80	-43
9	176	-163
10	67	86
11	119	117
12	70	-47
-6K5		
3	168	-156
7	169	195
9	186	-186
10	103	81
7K5		
0	155	139
1	155	-131
2	106	-100
6	109	84
7	105	-81
-7K5		
0	165	172
0K6		
2	82	-88
3	75	-116
4	182	-215
5	132	-139
6	271	316
7	212	227
8	126	-93
9	136	-102
10	165	-172
12	263	244
14	201	-195
1K6		
3	166	-126
4	167	-178
5	94	94
7	91	69
8	146	119
9	177	-141
10	107	-99
11	132	106
-1K6		
2	304	316
3	275	-292
4	327	-333
5	159	179
6	144	186
7	139	155
8	119	68
9	147	-129
10	173	-178
13	187	197
15	252	-257
2K6		
4	128	121
5	147	-134
6	129	-136
10	165	182
12	197	-219
14	131	168
-2K6		
5	121	-112
6	119	81
7	126	85
-2K6		
8	111	74
9	101	-45
10	129	-97
11	141	-139
13	169	133
15	131	-114
16	189	-188
3K6		
1	140	-95
4	164	-116
5	123	-90
6	51	23
8	110	94
9	245	262
10	50	-55
12	91	-84
13	133	-104
14	154	158
15	253	225
16	113	-99
-3K6		
2	221	-189
3	111	97
4	318	334
5	147	-118
6	95	-91
7	156	142
10	112	67
12	121	-73
4K6		
1	133	50
3	43	46
5	147	-100
7	20	13
9	127	104
11	133	-170
16	151	135
-4K6		
0	133	99
1	305	-286
4	100	-65
5	385	380
7	345	-347
8	113	-99
11	210	181
12	128	83
13	279	-279
14	33	-39
15	192	137
16	144	110
5K6		
5	133	-133
6	146	-104
-5K6		
2	267	-262
3	202	-211
4	265	279
5	253	254
7	173	-206
8	268	-230
10	268	215
11	108	49
6K6		
3	42	20
7	143	-142
-6K6		
0	179	144
1	231	-201
-7K6		
1	110	-99
3	199	207
4	112	-122
-8K6		
0	208	-285
1	182	178
2	120	144
6	203	-233

in good agreement with the observed value of 1.86 g cm^{-3}.

Determination of the Structure. After two false starts with the three-dimensional Patterson function,

Table II[a]

Positional and Temperature Parameters and Errors

Atom	x/a	$\sigma(x)/a$	y/b	$\sigma(y)/b$	z/c	$\sigma(z)/c$
Cu	0.1790	0.0004	0.1703	0.0001	0.0043	0.0004
Cl (1)	0.2319	0.0007	0.2838	0.0002	0.1031	0.0007
Cl (2)	0.3810	0.0009	0.4318	0.0003	0.0692	0.0012
Cl (3)	0.4200	0.0006	0.3270	0.0003	0.6351	0.0006
Cl (4)	0.1381	0.0006	0.1921	0.0002	0.6237	0.0006
Al	0.4145	0.0006	0.3398	0.0002	0.9839	0.0007
C(1)	0.4732	0.0037	0.0896	0.0016	0.8261	0.0053
C(2)	0.4833	0.0032	0.1255	0.0014	0.9892	0.0046
C(3)	0.3789	0.0047	0.1229	0.0019	0.1602	0.0066
C(4)	0.2789	0.0035	0.0796	0.0017	0.1541	0.0051
C(5)	0.2605	0.0035	0.0403	0.0019	0.9699	0.0059
C(6)	0.3606	0.0038	0.0442	0.0013	0.8187	0.0038

Thermal Parameters and Standard Deviations

{Anisotropic temperature factors of the form

$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; $\sigma' = \sigma \times 10^4$}

Atom[a]	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Cu	0.0090	6	0.0020	1	0.0140	11	0.0024	2	−0.0004	5	0.0015	2
Cl(1)	0.0085	7	0.0005	1	0.0119	12	−0.0013	2	0.0067	8	−0.0014	3
Cl(2)	0.0131	13	0.0002	1	0.0353	23	0.0003	3	0.0070	12	−0.0003	4
Cl(3)	0.0027	7	0.0029	2	0.0007	11	−0.0003	3	0.0000	5	0.0000	3
Cl(4)	0.0044	7	0.0015	1	0.0017	10	−0.0015	2	−0.0008	5	0.0000	2
Al	0.0014	8	0.0001	1	0.0016	13	−0.0001	2	0.0001	7	0.0001	2
C(1)	0.0075	43	0.0023	9	0.0358	94	0.0013	18	0.0141	38	0.0008	21
C(2)	0.0071	40	0.0014	10	0.0272	89	0.0000	13	−0.0067	40	0.0042	16
C(3)	0.0165	63	0.0027	11	0.0437	121	0.0026	20	−0.0205	50	−0.0007	29
C(4)	0.0052	46	0.0025	9	0.0323	106	0.0017	17	0.0003	47	−0.0012	24
C(5)	0.0056	45	0.0038	9	0.0443	96	−0.0005	15	−0.0024	46	0.0122	17
C(6)	0.0167	61	0.0012	7	0.0131	64	0.0033	16	−0.0032	43	−0.0005	15

Layer	Scale factor	σ
hk0	0.2321	0.0043
hk1	0.3130	0.0036
hk2	0.3616	0.0042
hk3	0.2923	0.0038
hk4	0.4801	0.0063
hk5	0.3589	0.0059
hk6	0.5427	0.0085

[a] To put structure factors on an absolute scale, F(C) should be multiplied by 1/(scale factors). Numbers in parentheses refer to subscripted numbers in other tables and drawings.

the correct solution was found. The Cu, 4Cl, and Al atoms were all located in the general positions of $P2_1/n$: $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z)$.

The disagreement index R ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) with the coordinates of the heavy atoms from the three-dimensional Patterson function was found to be 0.28. A three-dimensional electron density calculation with phases based on only Cu, Cl, and Al positions located the carbon atoms of the aromatic ring. After six cycles of full-matrix least squares with individual atom isotropic temperature factors of the form $\exp[-(\sin^2 \theta\lambda^{-2})]$, R was found to be 0.19. After eight cycles of full-matrix least squares with individual atom anisotropic temperature factors, R converged to 0.139. The maximum shift of positional coordinates for the last cycle was 0.00002 of the cell edges. A three-dimensional difference map did not indicate any unusual features. The final calculated and observed structure factors are listed in Table I. Final atomic parameters and standard deviations are tabulated in Table II. Interatomic distances, angles, and errors[14] are listed in Table III. The equation for the best least-squares plane through the benzene ring carbons and the deviations of each atom from this plane are also given in Table III.[15]

Since the intensity data were only taken about one axis and no corrections were made for absorption, anomalous dispersion, or extinction, no physical interpretation should be made of the anisotropic temperature factors. For these same reasons our estimates of error may be somewhat optimistic.

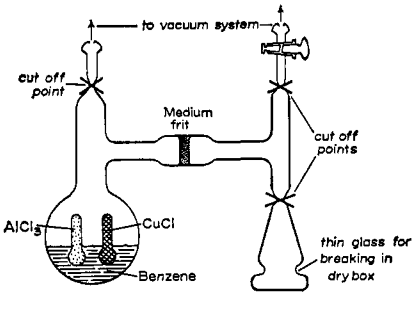

Figure 1. H tube for preparation of metal ion–benzene complexes.

Description of the Structure. The structure is made up of sheets pleated about $y = {}^1/_4, {}^3/_4$, or infinite extent in the a and c directions. These sheets are composed of distorted tetrahedral Cu(I) bonded to chlorine atoms of three different $AlCl_4^-$ species. For example (Figure 2), Cu*, $z \sim {}^1/_2c$ is bonded to Cl_1* and Cl_3*

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(14) W. R. Busing, K. O. Martin, and H. A. Levy, OR FFE program.

(15) Program courtesy of L. Dahl.

Table III. Distances and Angles for $C_6H_6 \cdot CuAlCl_4$

Bonded Distances and Angles

$Al-Cl_1$	2.136 ± 0.007 A	$Cu-Cl_1$	2.555 ± 0.066 A	$Cu-C_3$	2.15 ± 0.03 A
$Al-Cl_2$	2.078 ± 0.008 A	$Cu-Cl_3$	2.398 ± 0.006 A	$Cu-C_4$	2.30 ± 0.03 A
$Al-Cl_3$	2.141 ± 0.007 A	$Cu-Cl_4$	2.365 ± 0.004 A	Cu-midpoint (C_3-C_4)	2.13 ± 0.03 A
$Al-Cl_4$	2.153 ± 0.007 A				
$Cl_1-Al-Cl_2$	109.9 ± 0.3°	C_1-C_2	1.25 ± 0.04 A	$C_1-C_2-C_3$	123 ± 3°
$Cl_1-Al-Cl_3$	109.0 ± 0.2°	C_2-C_3	1.41 ± 0.05 A	$C_2-C_3-C_4$	119 ± 3°
$Cl_1-Al-Cl_4$	109.4 ± 0.3°	C_3-C_4	1.26 ± 0.05 A	$C_3-C_4-C_5$	121 ± 3°
$Cl_2-Al-Cl_3$	112.4 ± 0.3°	C_4-C_5	1.40 ± 0.05 A	$C_4-C_5-C_6$	119 ± 3°
$Cl_2-Al-Cl_4$	109.9 ± 0.3°	C_5-C_6	1.29 ± 0.04 A	$C_5-C_6-C_1$	121 ± 3°
$Cl_3-Al-Cl_4$	107.7 ± 0.3°	C_6-C_1	1.37 ± 0.04 A	$C_6-C_1-C_2$	119 ± 3°
$Cu-Cl_1-Al$	125.8 ± 0.2°	Midpoint of $C_3-C_4-Cu-Cl_1$	118.1 ± 0.5°		
$Cu-Cl_3-Al$	113.8 ± 0.2°	Midpoint of $C_3-C_4-Cu-Cl_3$	114.3 ± 0.5°		
$Cu-Cl_4-Al$	113.1 ± 0.2°	Midpoint of $C_3-C_4-Cu-Cl_4$	127.6 ± 0.5°		
$Cl_1-Cu-Cl_3$	92.9 ± 0.2°	C_3-Cu-C_4	33 ± 1°		
$Cl_1-Cu-Cl_4$	92.9 ± 0.2°	C_1-C_3-Cu	97 ± 1°		
$Cl_3-Cu-Cl_4$	101.7 ± 0.2°	C_6-C_4-Cu	94 ± 1°		

Nonbonded Intermolecular Distances (A)

Cl_1-Cl_3	3.639 ± 0.006	C_1-Cl_1	3.81 ± 0.03	C_1-C_3	4.13 ± 0.05
Cl_1-Cl_4	3.571 ± 0.006	C_2-Cl_1	3.80 ± 0.02	C_1-C_4	4.31 ± 0.04
Cl_2-Cl_3	4.113 ± 0.009	C_4-Cl_3	3.66 ± 0.02	C_3-C_6	4.36 ± 0.05
Cl_3-Cl_4	3.776 ± 0.008	C_1-Cl_4	3.74 ± 0.03	C_4-C_6	4.12 ± 0.03
All others >4.5		C_3-Cl_1	3.70 ± 0.03	All others >4.5	
		C_4-Cl_3	3.66 ± 0.02		
		C_1-Cl_1	3.81 ± 0.03		
		C_2-Cl_1	3.85 ± 0.02		
		All others >3.85			

Nonbonded Intramolecular Distances (A) and Angles on $AlCl_4^-$

Cl_1-Cl_2	3.451 ± 0.008
Cl_1-Cl_3	3.596 ± 0.006
Cl_1-Cl_4	3.501 ± 0.008
Cl_2-Cl_4	3.465 ± 0.008
Cl_2-Cl_3	3.508 ± 0.008
Cl_3-Cl_4	3.427 ± 0.006

Dihedral Angle between Planes Each Defined by Three Atoms for Benzene Ring

$C_4-C_1-C_6$ $C_6-C_5-C_4$	5 ± 3°	$C_6-C_1-C_4$ $C_3-C_4-C_6$	1 ± 3°
$C_4-C_1-C_6$ $C_1-C_4-C_3$	2 ± 3°	$C_6-C_1-C_4$ $C_1-C_3-C_6$	1 ± 3°
$C_6-C_1-C_4$ $C_1-C_2-C_3$	1 ± 3°	Ring is planar within experimental error	

Equation of Best Least-Squares Plane through Benzene Ring

$$-0.6019x + 0.6338y - 0.4859z = 1$$

Deviations from This Plane (A)

C_1 +0.006	C_4 −0.030
C_2 −0.004	C_5 +0.035
C_3 +0.029	C_6 −0.013

both at $z \sim {}^2/_3c$ and also to Cl_4* at $z \sim {}^1/_{10}c$ which is on the $AlCl_4^-$ tetrahedron below the one containing Cl_3*. The Cl_4 on the tetrahedron with Cl_3* is then bonded to the Cu atom in the unit cell above. Extension of the sheet in the [100] direction is generated by the glide plane at $y = {}^1/_4$. The coordination number of 4 for Cu(I) is completed by a π-type aromatic ring interaction (Figure 3). The Cu–Cl interactions with a particular $AlCl_4^-$ ion is shown in Figure 4. Inasmuch as the sum of the tetrahedral single bond covalent radius of Cu[16] and Cl is 2.34 A, Cu–Cl distances of 2.365, 2.398, and 2.555 A (all ±0.006 A) indicate a substantial Cu–Cl covalent interaction. These distances are also in good agreement with tabulated[17] Cu(I)–Cl distances of 2.31–2.48 found in fourfold coordinated Cu(I) compounds. It is to be noted that the "free" Al–Cl distance is significantly shorter (0.07 A) than the Al–Cl distances, wherein the Cl is also bonded to a Cu atom. This value of 2.07 A is in good agreement with the terminal Al–Cl distance found in Al_2Cl_6[18] (2.07 A) vapor and the non-Co-bonded Al–Cl distance in $Co(AlCl_4)_2$[19] (2.10 A). On the other hand, the remaining Al–Cl distances are the values expected for externally Cl-coordinated Al–Cl distances, *e.g.*, in $Co(AlCl_4)_2$, ~2.15 A. All Cl–Cl, Cl–C, and C–C distances between sheets are at least 3.6 A; hence, only van der Waals interactions exist between sheets. The aromatic ring is bound to only one Cu(I) atom, and the rings are back-to-back. The neighborhood of a particular Cu(I) species with bond distances, angles, and errors is shown in Figure 5. Since a value of 2.12 A is expected for a Cu–C "single" bond, the Cu–C closest distances of 2.15 and 2.30 A are indicative of a strong interaction. The distance of Cu to the center of the nearest C–C bond was found to be 2.13 A.

Discussion

Mulliken[3] considered the use of the empty 5s orbital of silver as the electron acceptor and the e_1 filled molecular orbital of benzene as the donor. In addition, he considered the use of excited states of Ag(I) of the proper symmetry to give a possible C_6 complex but rejected them on energetic grounds. Dewar[4] maintained that not only is the $e_1 \rightarrow 5s$ interaction important but the use of a filled d orbital donating electrons to the empty e_2 molecular orbital is also important to the binding. This latter interaction, back bonding, is generally accepted as being important in platinum(II)–olefin complexes. Either or both of these interactions led to the correct gross geometry for the crystalline

[16] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

[17] H. Ondik and D. Smith, ref 13, p 260.

[18] K. J. Palmer and N. Elliott, *J. Am. Chem. Soc.*, **60**, 1852 (1938).

[19] J. A. Ibers, *Acta Crys.*, **15**, 967 (1962).

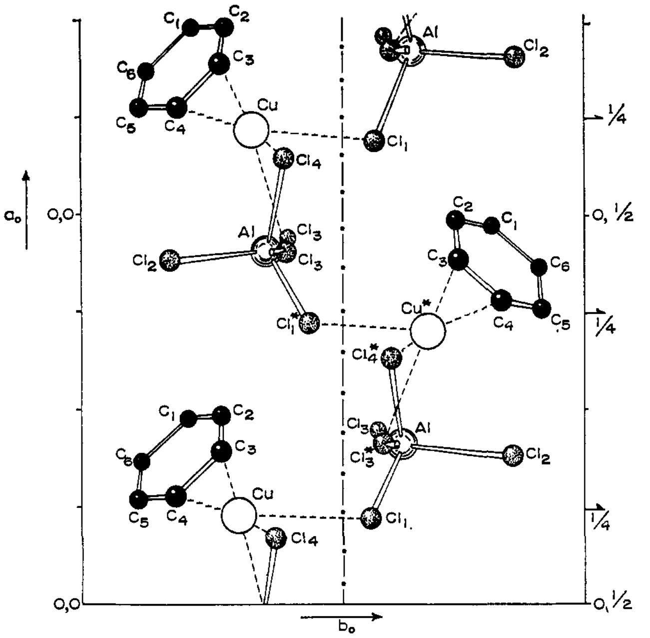

Figure 2. View of the $C_6H_6\cdot CuAlCl_4$ sheet structure down the *c* axis. Dotted lines represent nearest neighbor Cu-X interactions. Dot-dash line represents *n* glide at $y = {}^1/_4$. Cu* at $z \sim {}^1/_2c$; Cl₁* at $z \sim {}^2/_3c$; Cl₃* at $z \sim {}^2/_3c$; Cl₄* at $z \sim {}^1/_{10}c$; and c = 6.07 A. Cl₃ and Cl₃* are in reality superposed, but they are displaced here for clarity.

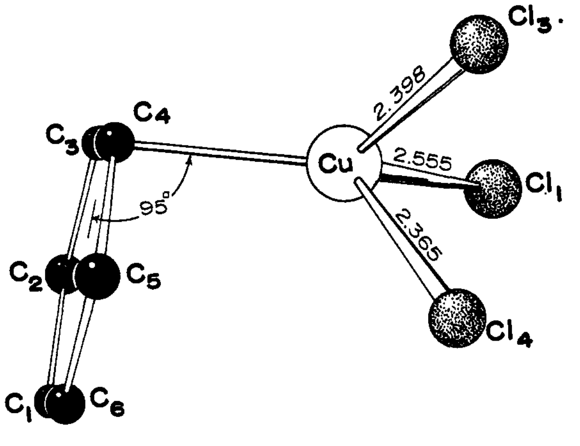

Figure 3. Local geometry around Cu(I) indicating the "π" nature of the complex.

$C_6H_6\cdot AgClO_4$ complex,[8] and they also correctly predict the gross features of the $Cu(I)\cdot C_6H_6$ bonding in $C_6H_6\cdot CuAlCl_4$, *i.e.*, the metal ion above and approximately between two C-C bonds of the benzene ring. Although the $C_6H_6\cdot AgClO_4$ complex is not a 1:1 metal-aromatic complex as predicted by the theory but rather ∞ : ∞ and each Ag(I) is bonded to two benzene rings, the Ag-O distances are sufficiently long (2.70 A) that the neglect of cation-anion interactions seems reasonable and the theoretical framework is justified. However, in our present investigation the Cu-Cl interactions are far from negligible and must contribute substantially to the stability of the complex.

The excited states of Ag(I) that could be used as acceptors for complex formation are ~4 ev above the ground state, but in Cu(I) the lowest-energy excited state is only 1.5 ev[20] above the ground state. Whether

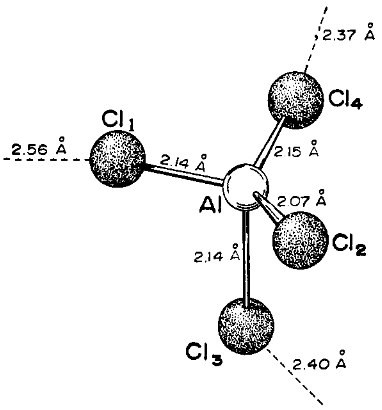

Figure 4. Bond lengths and bonding about a particular $AlCl_4^-$ species. Dotted lines indicate Cu-Cl interactions.

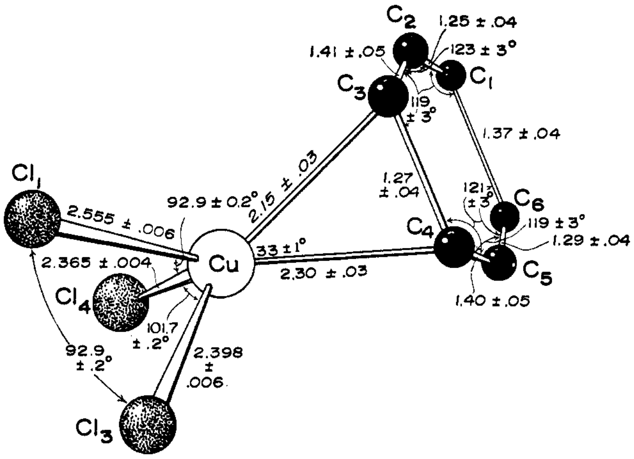

Figure 5. Bond lengths, angles, and errors about a particular Cu(I) atom.

this excited state plays a significant role in complex formation is difficult to decide since the true symmetry of the Cu(I) environment is low. We prefer to describe the Cu(I) as a distorted tetrahedron with an sp³-hybrid orbital acting as an acceptor for the aromatic electrons (see Cl-Cu-Cl and midpoint C_3-C_4-Cu-Cl angles). Since some of the angles are <109°, an alternative description might be to consider the Cu-Cl bonds as made up from Cu 4p orbitals and the 4s orbital being used as an acceptor.

The Cu-C distances are worthy of attention, particularly since a Cu-C single bond length[16] would be 2.12 A, and we observe distances of 2.15 and 2.30 A. This indicates a substantial metal ion-aromatic interaction in comparison with the shortest Ag-C distance, 2.5 A (~1 A > sum of covalent radii), in $C_6H_6\cdot AgClO_4$ and $C_6H_6\cdot AgAlCl_4$. This is in accord with gross observations that it is more difficult to remove benzene from $C_6H_6\cdot CuAlCl_4$ than from $C_6H_6\cdot AgClO_4$ or $C_6H_6\cdot AgAlCl_4$.[21] Unfortunately, the error of ±0.03 A makes the difference of 0.15-A Cu-C distances only five standard deviations. We believe this is a real difference in bond lengths, because not only is it greater than three standard deviations, but also it is consistent with similar results found in $C_6H_6\cdot AgClO_4$ and in

(20) C. E. Moore, "Atomic Energy Levels," Vol. II, No. 467, National Bureau of Standards, Washington 25, D. C., 1952, p 112.

(21) R. W. Turner and E. L. Amma, to be published.

$C_6H_6 \cdot AgClAl_4$.[21] In the former, this asymmetry manifested itself in statistically disordered Ag positions, but it is unambiguous in the latter. It is not likely that molecular packing would be the cause of this asymmetry in metal–carbon distances, because the the packing is quite different in $C_3H_6 \cdot AgClO_4$, $C_6H_6 \cdot CuAlCl_4$ and $C_6H_6 \cdot AgAlCl_4$. A similar asymmetry in Cu–C distances has been observed in a copper(I)–olefin complex.[9f]

We suggest that this asymmetry between the closest carbon-to-metal distances is a fundamental property of metal ion–aromatic complexes. Further, we suggest that the reason for this asymmetry is a compromise between the acceptor properties of the metal ion, or coordinated metal ion, and the donor properties of this same ion. That is, if the acceptor orbital were a 4s- or an sp^3-hybrid orbital, the most advantageous position would be at the point of greatest electron density of the ring, directly above one of the carbon atoms. On the other hand, using inner d orbitals for the metal ion as donor, the most likely position would be above and symmetrically between two carbon atoms of the aromatic system. Hence, a compromise between these two effects is reached and unequal metal–carbon distances result. However, in platinum- and palladium–olefin complexes, there has been no evidence for different metal-to-carbon distances, but it is quite likely that details of the bonding may be quite different for olefin complexes.

Although the bond distances alternate in lengths around the ring and suggest a cyclohexatriene system, the errors are sufficiently large that this variation of bond distances may not be real and caution should be applied to any interpretations based on C–C distances in this complex.

It is, in fact, an interesting question as to why the complex forms at all. In the presence of chlorine donors it is surprising tht the metal–aromatic bond is preferred to M–Cl interactions. The answer may be that in the packing of anhydrous $CuAlCl_4$ large voids remain, and it becomes energetically favorable to form metal ion–aromatic bonds over metal ion–chlorine bonds. We plan to investigate the crystal structure of anhydrous $CuAlCl_4$ in the near future.

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Cage Compounds Containing the Trirhenium(III) Cluster: $Re_3Br_3(AsO_4)_2(DMSO)_3$[1]

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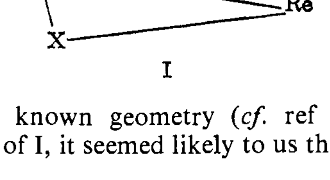
Abstract: The preparation and molecular structure of $Re_3Br_3(AsO_4)_2(DMSO)_3$, a representative member of the new class of compounds $Re_3X_3(MO_{3\text{ or }4})_2L_n$, are discussed. From the visible spectrum, it is apparent that the trirhenium(III) metal atom cluster occurs in this compound. Further insights into its structure are obtained from a detailed analysis of the infrared spectrum. Apparently, two tridentate arsenate ions have replaced the six axial halide ions in the Re_3Br_9 molecule to form a cage which incorporates the cluster. The solvent (DMSO) molecules are thought to occupy nonbridging equatorial sites in the cluster.

The existence of the trirhenium(III) metal atom cluster in complexes prepared from rhenium(III) chloride and rhenium(III) bromide has been well established.[3–11] Studies by Robinson and Fergusson[11] have shown that, of the twelve halogen atoms (six axial, three equatorial bridging, and three equatorial nonbridging) in the $Re_3X_{12}^{3-}$ ion, only three, presumably the equatorial bridging ones, are not subject to exchange with thiocyanate or radioactively labeled halide ions. Apparently, then, the stable structural unit in the trirhenium(III) metal atom cluster compounds is the Re_3X_3 group (I).



I

From the known geometry (*cf.* ref 3–8) and net charge (+6) of I, it seemed likely to us that anions such

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[1] Supported by the U. S. Atomic Energy Commission.

[2] National Science Foundation Postdoctoral Fellow, 1965–1966.

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