Metal Ion–Aromatic Complexes. IV. Five-Coordinate Silver(I) in $C_6H_6 \cdot AgAlCl_4$

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Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. *Received February 3, 1966.*

Abstract: A new silver(I)–benzene complex ($C_6H_6 \cdot AgAlCl_4$) has been prepared and its crystal structure determined by three-dimensional photographic single-crystal X-ray diffraction techniques. In contrast to the pleated sheet structure of $C_6H_6 \cdot CuAlCl_4$, the structure of $C_6H_6 \cdot AgAlCl_4$ is made up of infinite planar sheets composed of $AlCl_4^-$ tetrahedra connected by Ag–Cl bonds with π-type Ag(I)–aromatic interactions perpendicular to the sheet. This arrangement gives Ag(I) a coordination number of five: four Ag–Cl interactions at 2.59, 2.77, 2.80, and 3.04 A, all ±0.02 A, and one Ag–C_6H_6 interaction with Ag to the center of the nearest C–C bond, a distance of 2.57 ± 0.06 A. Each Ag(I) species is bonded to only one benzene ring such that the dihedral angle between the benzene ring plane and the plane defined by silver with its two nearest carbon neighbors is 98°. However, these shorter Ag–C distances are unequal at 2.92 and 2.47 A, both ±0.06 A. All other interatomic distances correspond to normal van der Waals distances.

The existence of a number of silver(I)–aromatic complexes of varying degrees of stability was demonstrated some time ago by the solubility measurements of Andrews and Keefer.[3] The gross geometrical features of the silver(I)–benzene interaction in the silver perchlorate–benzene complex were predicted by both Mulliken[4] and Dewar[5] and verified by the structure investigation of Smith and Rundle.[6] However, this structure has several unusual features; *e.g.*, either a large anisotropic thermal motion or a statistical disordering of the Ag atoms is required, and the benzene ring shows an unusual distortion. In order to better understand the nature of the binding forces in silver(I)–aromatic complexes as well as to clarify the reported unusual features of the silver perchlorate–benzene complex, we have prepared a number of hitherto unknown crystalline complexes of the type ArAgX, where Ar represents a variable aromatic donor and X a variable anion. This is part of a general program of investigation of the structure of metal ion–aromatic complexes in which the effect of the following factors on complex formation is being investigated: (1) the electronic structure and energy levels of the metal ion and the aromatic system; (2) metal ion–anion interactions; (3) steric factors; and (4) molecular packing, at least in the solid state. As part of this research, we have prepared $C_6H_6 \cdot AgAlCl_4$ and have found no simple relationship in terms of space group or cell dimensions between this compound and $C_6H_6 \cdot CuAlCl_4$[7,8] or $C_6H_6 \cdot AgClO_4$.[6] We undertook a single-crystal X-ray structure analysis to determine the stereochemistry of the $C_6H_6 \cdot AgAlCl_4$ complex and also to further our understanding of the nature of the bonding between the metal ion and the aromatic system. The metal–anion distances would also give more insight into the role of the anion in these complexes.

Experimental Section

$C_6H_6 \cdot AgAlCl_4$ was prepared by treating a slight excess of pure, dried AgCl with 0.03 mole of resublimed $AlCl_3$ and 20 ml of dried benzene. The procedure for the preparation of this compound and growing of single crystals is very similar to that of $C_6H_6 \cdot CuAlCl_4$; for details see ref 8. There were two complications that arose with $C_6H_6 \cdot AgAlCl_4$ that were not present with $C_6H_6 \cdot CuAlCl_4$: (1) the crystals had to be grown in the dark to avoid photochemical decomposition of the silver ion; and (2) it was very difficult to obtain suitable single crystals for diffraction studies. The crystals had a marked tendency to twin, and over a period of 3 years more than 100 crystals were examined until one was found to be sufficiently free of twinning to justify a single-crystal structure analysis. As with $C_6H_6 \cdot CuAlCl_4$, the chemical analyses were only sufficiently accurate to indicate the correct stoichiometry.

A crystal of approximately 0.35 × 0.30 × 0.40 mm was used to collect 496 independent *hkl* observed intensities by standard multiple film equiinclination Weissenberg techniques from *hk*0, *hk*1, ..., *hk*5 levels with Zr-filtered Mo Kα radiation. 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 of the three-dimensional Patterson and electron density calculations. Intensities were measured with a calibrated strip. The linear absorption coefficient (μ) for $C_6H_6 \cdot AgAlCl_4$ with Mo Kα radiation is 28 cm^{-1}. Since some surface decomposition was unavoidable and the absorption due to this decomposition could not be readily calculated, no corrections for absorption were made.

Calculations were made with an IBM 7090. Patterson and Fourier calculations were made with the Sly–Shoemaker–Van den Hende program. The refinement was carried out by full-matrix least squares[9] with the Hughes[10] weighting scheme with $4F_{\min} = 15$. We minimized the function $\Sigma w(F_o - F_c)^2$. Atomic scattering factors were taken from the compilation of Ibers[11] for Ag$^+$, Cl$^-$, Al^{3+}, and neutral C.

Results

Unit Cell and Space Group. $C_6H_6 \cdot AgAlCl_4$ was found to crystallize in the monoclinic crystal system. With Mo Kα (0.7107 A), cell constants were obtained from precession photographs: a = 9.09, b = 10.22, c = 12.73 A (all ±0.03 A), and β = 95° 05′ ± 15′. The observed systematic extinctions (for *h*0*l*, $l = 2n + 1$; and for 0*k*0, $k = 2n + 1$) uniquely specify the space group as $P2_1/c$. With four $C_6H_6 \cdot AgAlCl_4$

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[1] In partial fulfillment for the Ph.D. requirements, University of Pittsburgh, 1965.

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Table I. Calculated and Observed Structure Factors, $F(C) = 10F(\text{calcd})$

	FIOI	FICI
0K0		
4	457	484
6	440	-491
8	191	185
1K0		
2	129	-94
3	113	95
4	271	253
5	271	-250
6	303	-305
8	133	138
2K0		
1	327	-204
3	423	448
4	175	-124
5	216	-193
8	68	46
3K0		
1	97	44
3	371	320
4	462	-506
6	86	73
8	141	-133
4K0		
0	462	-381
1	299	308
2	375	354
3	15	57
4	391	-395
5	188	172
6	127	125
7	130	-113
8	186	-198
5K0		
0	250	-216
1	391	426
2	265	235
3	176	-140
4	212	-162
5	201	191
6	81	68
7	188	-199
8	105	-111
6K0		
0	122	108
1	250	245
2	104	-90
3	105	-118
4	102	91
5	100	96
7	110	-99
7K0		
0	130	130
1	87	65
2	221	-203
3	78	60
4	245	280
5	67	52
8	105	105
8K0		
0	127	141
1	116	-102
8K0 (CONT)		
2	130	-123
3	213	212
4	176	174
5	72	-81
8	60	49
9K0		
1	143	-158
3	113	118
5	82	-112
10K0		
0	164	-184
1	91	-100
0K1		
3	71	71
4	130	113
5	312	344
6	162	-145
7	201	-198
9	107	99
10	59	-49
11	80	-78
1K1		
3	75	50
4	275	255
5	269	271
6	245	-246
8	93	79
9	91	87
10	157	-157
-1K1		
3	116	-101
4	47	55
5	109	83
6	130	139
7	235	-234
8	164	-159
2K1		
1	238	-236
3	158	151
4	311	340
5	175	141
6	180	-187
7	156	155
8	139	136
10	171	-203
-2K1		
1	75	-71
2	479	573
3	156	-106
5	210	-158
6	222	191
7	134	-108
8	245	-239
9	62	-53
10	89	112
12	75	-95
3K1.		
1	249	-232
2	141	115
3	211	190
4	235	192
3K1 (CONT)		
5	114	-74
7	163	168
9	165	-205
10	106	-115
-3K1		
2	193	156
4	68	-39
5	289	-238
6	69	49
7	138	95
8	213	-192
9	129	-117
10	67	71
11	100	94
4K1		
0	65	0
1	211	-181
3	77	51
4	114	-89
5	121	-107
6	84	48
7	72	51
8	80	-71
9	142	-166
-4K1		
1	128	75
3	118	99
4	147	-124
5	264	-256
6	140	-105
7	120	92
9	121	-132
11	66	92
5K1		
1	230	-255
2	43	-43
3	93	-67
4	189	-220
6	167	202
7	76	72
8	90	-106
10	101	119
-5K1		
1	244	247
2	92	-57
3	152	127
4	135	134
5	156	-153
6	153	-163
8	99	107
9	67	-68
11	53	49
6K1		
1	156	-136
3	83	-78
4	82	-61
5	210	212
6	153	150
9	78	96
-6K1		
1	181	163
3	83	4
4	139	110
6	60	-73
7	63	-59
8	115	119
7K1		
1	56	65
3	48	-18
4	55	-5
5	156	160
9	74	86
-7K1		
1	86	91
3	94	-83
5	50	57
7	55	-57
8K1		
1	68	70
2	110	-118
3	51	11
5	77	109
6	56	-75
-8K1		
1	43	24
3	62	-92
4	80	-103
7	50	-75
9	62	90
9K1		
2	83	-106
-9K1		
2	54	-45
4	69	-102
5	64	-28
0K2		
3	178	-159
4	313	329
6	96	-97
8	133	143
11	56	-45
1K2		
3	213	215
4	144	110
5	44	-48
6	206	152
8	136	125
10	53	37
11	82	-84
-1K2		
3	289	-302
4	271	273
5	209	196
6	216	-229
7	99	-100
10	86	-120
2K2		
0	223	-147
1	299	-326
2	435	431
3	287	265
4	180	-138
5	104	-88
6	239	240
7	150	155
10	60	86
-2K2		
0	136	120
3	280	-307
5	295	360
6	184	-169
7	73	-70
10	101	-86
3K2		
0	270	-296
1	178	-153
2	462	523
3	123	-84
4	337	-347
5	153	-114
6	249	225
7	55	45
8	82	-73
-3K2		
0	327	-327
3	187	-138
5	260	205
7	71	-68
4K2		
0	350	-378
2	224	198
4	300	-287
6	154	143
-4K2		
0	379	-319
1	78	-41
2	231	200
6	189	152
8	72	-51
5K2		
0	125	-73
1	255	212
2	184	-135
3	240	-223
4	141	-96
5	89	78
-5K2		
0	201	-183
1	289	-253
2	328	308
3	216	189
4	82	-56
5	211	-174
6	181	150
-5K2 (CONT)		
7	107	103
8	80	-70
9	80	-53
6K2		
0	212	196
1	107	90
2	211	-220
3	108	-95
4	70	61
5	141	90
6	128	-122
8	55	63
-6K2		
0	152	131
1	225	-242
2	125	78
3	267	257
4	69	57
5	130	-130
6	43	-29
7	117	118
8	67	-66
7K2		
0	307	325
1	46	-34
2	167	-163
4	153	156
5	63	-45
6	153	-166
-7K2		
0	102	98
1	96	-65
2	104	-101
3	179	178
4	60	67
6	76	-68
8K2		
0	178	197
1	140	-150
3	126	75
4	63	58
5	170	-131
6	69	-76
-8K2		
0	82	67
1	76	52
2	148	-168
4	94	78
9K2		
1	99	-107
5	71	-104
-9K2		
1	92	115
2	46	-50
3	94	-115
10K2		
2	94	106
-10K2		
1	81	103
3	58	-97
11K2		
2	53	75
0K3		
3	146	-181
4	81	82
5	66	63
6	71	-83
7	58	-45
8	60	55
9	86	91
1K3		
2	27	19
4	175	116
6	86	-96
8	77	86
9	43	33
-1K3		
3	135	-166
4	87	-74
5	67	55
7	52	-63
9	76	98
11	49	-64
2K3		
1	125	122
2	33	-26
3	81	76
4	88	52
6	96	-90
7	51	66
8	47	57
-2K3		
1	85	85
2	32	33
3	81	-83
4	100	-104
6	63	48
7	43	-28
8	57	-67
9	48	34
10	51	48
3K3		
1	37	39
2	27	-5
4	130	-81
5	68	-68
6	42	-39
7	75	82
9	45	-55
-3K3		
2	85	75
3	68	49
5	61	-39
6	111	101
7	69	45
8	70	-66
4K3		
2	42	34
4	145	-104
7	48	52
4K3 (CONT)		
8	44	-60
10	49	75
-4K3		
3	40	41
5	65	-59
6	68	61
7	144	143
5K3		
1	33	-46
2	57	64
4	43	-37
6	69	76
8	46	-70
10	51	51
-5K3		
3	78	60
4	73	44
5	67	-40
6	52	-36
7	93	84
6K3		
2	43	50
7	74	-111
-6K3		
2	36	-39
4	43	46
7K3		
7	56	-73
0K4		
3	103	97
4	31	27
5	78	-66
7	48	44
1K4		
2	67	55
3	149	162
4	47	-36
5	111	-95
7	78	84
8	88	-68
-1K4		
2	126	-175
3	74	-63
4	97	96
7	53	-52
2K4		
0	157	-144
1	151	-131
2	175	187
3	66	43
4	75	-76
5	120	-117
6	58	53
7	54	60
8	73	-78
-2K4		
0	42	51
1	140	171
2	102	-81
3	155	-182
4	110	114
5	37	43
7	82	-83
9	50	49
3K4		
0	126	-110
1	58	-45
2	143	130
3	48	-37
4	61	-58
6	81	80
-3K4		
1	161	173
2	76	64
5	84	86
6	47	42
7	69	-83
9	63	59
4K4		
0	38	-31
1	93	105
2	81	66
3	93	-83
5	65	79
-4K4		
0	87	-76
1	121	112
2	95	78
5	69	38
6	58	58
7	47	-32
5K4		
0	119	119
1	108	90
2	45	-41
3	71	-71
4	66	59
5	80	70
6	53	-47
-5K4		
0	132	-141
2	38	41
3	83	64
4	51	-54
6	91	64
6K4		
0	120	113
1	43	27
2	91	-96
3	52	-44
4	47	58
6	87	-81
-6K4		
1	84	-82
3	94	96
5	102	-88
7K4		
0	47	51
1	47	-46
2	91	-90
6	54	-56
-7K4		
3	57	74
8K4		
3	37	55
0K5		
4	60	56
7	87	-91
8	46	52
1K5		
1	36	24
2	54	-48
5	84	-100
6	40	-49
-1K5		
3	53	-50
5	36	37
6	28	20
7	62	-63
2K5		
2	49	-40
5	100	-92
-2K5		
2	43	-56
4	69	-79
5	53	68
6	35	34
7	44	-34
9	51	48
3K5		
2	56	49
3	19	40
5	64	-70
-3K5		
1	43	48
2	51	-40
3	47	45
4	85	-101
6	51	49
4K5		
1	71	61
2	69	64
-4K5		
1	40	0
2	42	-33
3	42	48
4	38	-46
6	38	55
5K5		
1	69	67
2	40	37

entities per cell, the calculated crystal density was found to be 2.01 g cm^{-3}. No density determination was made, but the cell volume of 1176 A^3 is very close to the 1123 A^3 found for $C_6H_6 \cdot CuAlCl_4$, which has been shown to have four molecules per cell.

Determination of the Structure. The observed intensities were corrected for Lorentz and polarization factors and reduced to squared structure factors for input to the three-dimensional Patterson function.

From the three-dimensional Patterson function it was found that the Ag, four Cl, and Al atoms were in the general positions of $P2_1/c$, $\pm(x, y, z: x, {}^1/_2 - y, {}^1/_2 + z)$.[12] The carbon atoms were located from three-dimensional electron density sections with phases based upon the Ag, four Cl, and Al atom coordinates. The structure was refined by least squares until the maximum shift of position coordinates for the last refinement cycle was found to be 0.0003 of the cell edges for the heavier atoms and 0.002 for carbon. The variables were the atomic coordinates, individual isotropic atomic temperature factors, and the scale factors for the isotropic refinement. For the anisotropic refinement, the Ag and Cl atoms had variable anisotropic temperature factors of the form exp $-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)$, but the carbon atoms had only an individual isotropic variable temperature factor. The scale factors were not varied after the isotropic refinement. A final three-dimensional difference map did not indicate any unusual features. The final disagreement index, R ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$), after refinement was found to be 0.132, and the final weighted disagreement index was 0.168. The standard error of an individual reflection $\{[\Sigma_i w_i(F_c - F_o)^2/(m - n)]^{1/2}$, where m = 496 observations and n = 78 variables$\}$ upon completion of the refinement was found to be 2.07. Although the value of the disagreement index is somewhat high by modern standards, as are the errors, the stability of the compound and the nature of the crystals are such that we feel that we have done the best analysis possible with the best data we have been able to obtain. Hence, no physical interpretation should be made of the anisotropic temperature factors. The final observed and calculated structure factors are listed in Table I. Final atomic parameters and standard

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(12) Reference 11, Vol. I, 1952, p 99.

Table II

Positional and Temperature Parameters and Errors[a]

Atom	x/a	y/b	z/c	$\sigma(x)/a$	$\sigma(y)/b$	$\sigma(z)/c$
Ag	0.1382	0.2297	0.0323	0.0003	0.0003	0.0008
Cl(1)	0.8527	0 5069	0.6290	0.0014	0.0015	0.0030
Cl(2)	0.2300	0.4385	0.6753	0.0014	0.0015	0.0029
Cl(3)	0.0472	0.6076	0.8651	0.0016	0.0013	0.0031
Cl(4)	0.0996	0.7547	0.6215	0.0018	0.0011	0.0030
Al	0.0574	0.5767	0.6998	0.0016	0.0013	0.0036
C(1)	0.5422	0.2504	0.1120	0.0055	0.0048	0.0110
C(2)	0.4895	0.3554	0.1548	0.0052	0.0050	0.0101
C(3)	0.3532	0.4289	0.1081	0.0056	0.0056	0.0115
C(4)	0.3478	0.3747	0.0007	0.0055	0.0054	0.0107
C(5)	0.4458	0.2884	0.9466	0.0054	0.0053	0.0106
C(6)	0.5144	0.2908	0.4805	0.0058	0.0052	0.0102

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	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Ag	0.0084	3	0.0081	3	0.0045	7	−0.0004	3	−0.0012	6	−0.0010	7
Cl(1)	0.0099	16	0.0112	15	0.0058	13	−0.0031	13	−0.0029	27	0.0002	25
Cl(2)	0.0130	18	0.0099	14	0.0055	15	0.0064	14	−0.0028	28	−0.0030	25
Cl(3)	0.0129	17	0.0070	13	0.0060	10	0.0021	12	0.0026	30	−0.0013	25
Cl(4)	0.0211	22	0.0033	13	0.0073	21	−0.0009	12	0.0001	30	0.0004	20
Al	0.0095	18	0.0033	12	0.0035	17	0.0015	12	0.0027	31	−0.0014	25

Carbon atom isotropic temperature factors

Atom	B, A^2	Layer	Scale factor	σ
C(1)	3.47	$hk0$	0.3253	0.0053
C(2)	5.71	$hk1$	0.3209	0.0047
C(3)	4.18	$hk2$	0.2745	0.0036
C(4)	5.13	$hk3$	0.1523	0.0048
C(5)	5.82	$hk4$	0.1172	0.0029
C(6)	3.68	$hk5$	0.1042	0.0060

$F(\mathrm{calcd})_{\mathrm{abs}} = F(\mathrm{C})/(10 \times \text{scale factors})$

[a] Numbers in parentheses consistent with subscripts in other tables and figures.

Table III. Distances and Angles for $C_6H_6 \cdot AgAlCl_4$

		Bonded Distances	
$\mathrm{Al{-}Cl_4}$	2.13 ± 0.02	$\mathrm{Ag{-}Cl_4}$	2.80 ± 0.02
$\mathrm{Al{-}Cl_3}$	2.14 ± 0.02	$\mathrm{Ag{-}Cl_3}$	2.77 ± 0.02
$\mathrm{Al{-}Cl_2}$	2.15 ± 0.02	$\mathrm{Ag{-}Cl_2}$	2.59 ± 0.02
$\mathrm{Al{-}Cl_1}$	2.12 ± 0.02	$\mathrm{Ag{-}Cl_1}$	3.04 ± 0.03
$\mathrm{C_1{-}C_2}$	1.31 ± 0.10	$\mathrm{Ag{-}C_3}$	2.92 ± 0.07
$\mathrm{C_2{-}C_3}$	1.52 ± 0.08	$\mathrm{Ag{-}C_4}$	2.47 ± 0.06
$\mathrm{C_3{-}C_4}$	1.47 ± 0.16	Ag-midpoint $\mathrm{C_3{-}C_4}$	2.57 ± 0.06
$\mathrm{C_4{-}C_5}$	1.47 ± 0.12	Nonbonded Intermolecular Distances, A	
$\mathrm{C_5{-}C_6}$	1.21 ± 0.08	$\mathrm{Cl_3{-}Cl_4}$ 3.97 $\mathrm{Cl_2{-}Cl_3}$ 4.18	$\mathrm{Cl_1{-}C_4}$ 3.99
$\mathrm{C_6{-}C_1}$	1.42 ± 0.10	$\mathrm{Cl_1{-}Cl_3}$ 4.02 $\mathrm{Cl_3{-}Cl_3}$ >5.00	$\mathrm{Cl_2{-}C_3}$ 3.88
		Nonbonded Intramolecular Distances, A	
$\mathrm{Cl_1{-}Cl_2}$	3.50 ± 0.02	$\mathrm{Cl_1{-}Cl_4}$	3.39 ± 0.02
$\mathrm{Cl_2{-}Cl_3}$	3.50 ± 0.02	$\mathrm{Cl_3{-}Cl_1}$	3.51 ± 0.02
$\mathrm{Cl_3{-}Cl_4}$	3.51 ± 0.02	$\mathrm{Cl_2{-}Cl_4}$	3.49 ± 0.02
		Bonded Angles for $C_6H_6 \cdot AgAlCl_4$	
		$\mathrm{Cl_4{-}Ag{-}Cl_2}$	137.2 ± 0.6°
$\mathrm{Cl_1{-}Al{-}Cl_2}$	110 ± 1°	$\mathrm{Cl_1{-}Ag{-}Cl_4}$	70.3 ± 0.3°
$\mathrm{Cl_1{-}Al{-}Cl_3}$	111 ± 1°	$\mathrm{Cl_1{-}Ag{-}Cl_3}$	144.0 ± 0.6°
$\mathrm{Cl_2{-}Al{-}Cl_3}$	109 ± 2°	$\mathrm{Cl_2{-}Ag{-}Cl_3}$	103.8 ± 0.6°
$\mathrm{Cl_1{-}Al{-}Cl_4}$	106 ± 2°	$\mathrm{Cl_4{-}Ag{-}Cl_3}$	79.0 ± 0.4°
$\mathrm{Ag{-}Cl_4{-}Al}$	95.0 ± 0.6°	$\mathrm{Cl_1{-}Ag{-}Cl_2}$	87.2 ± 0.5°
$\mathrm{Cl_3{-}Al{-}Cl_4}$	111 ± 1°	$\mathrm{C_4{-}Ag{-}C_3}$	30.0 ± 4°
$\mathrm{Ag{-}Cl_1{-}Al}$	87.7 ± 0.5°	$\mathrm{Cl_1}$-Ag-midpoint $\mathrm{C_3{-}C_4}$	118.9 ± 2°
$\mathrm{Ag{-}Cl_2{-}Al}$	93.9 ± 0.6°	$\mathrm{Cl_2}$-Ag-midpoint $\mathrm{C_3{-}C_4}$	96.6 ± 2°
$\mathrm{Ag{-}Cl_3{-}Al}$	129.1 ± 0.6°	$\mathrm{Cl_4}$-Ag-midpoint $\mathrm{C_3{-}C_4}$	125.9 ± 2°
$\mathrm{C_2{-}C_3{-}Ag}$	98.2 ± 4°	$\mathrm{Cl_3}$-Ag-midpoint $\mathrm{C_3{-}C_4}$	93.8 ± 2°
$\mathrm{C_6{-}C_4{-}Ag}$	95.7 ± 4°		

Equation of Best Least-Squares Plane for C_6H_6

$0.7063x + 0.6709y - 0.2259z = 1$

Individual Atomic Deviations from this Plane, A

C_1	−0.090	C_4	−0.080
C_2	+0.136	C_5	+0.155
C_3	−0.065	C_6	−0.071

deviations are tabulated in Table II. Interatomic distances, angles,[13] and errors are listed in Table III.

Description of the Structure. The crystal structure is composed of sheets of infinite extent in the bc plane weakly held together by van der Waals forces. These

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[13] W. R. Busing, K. O. Martin, and H. Levy, OR FFE program.

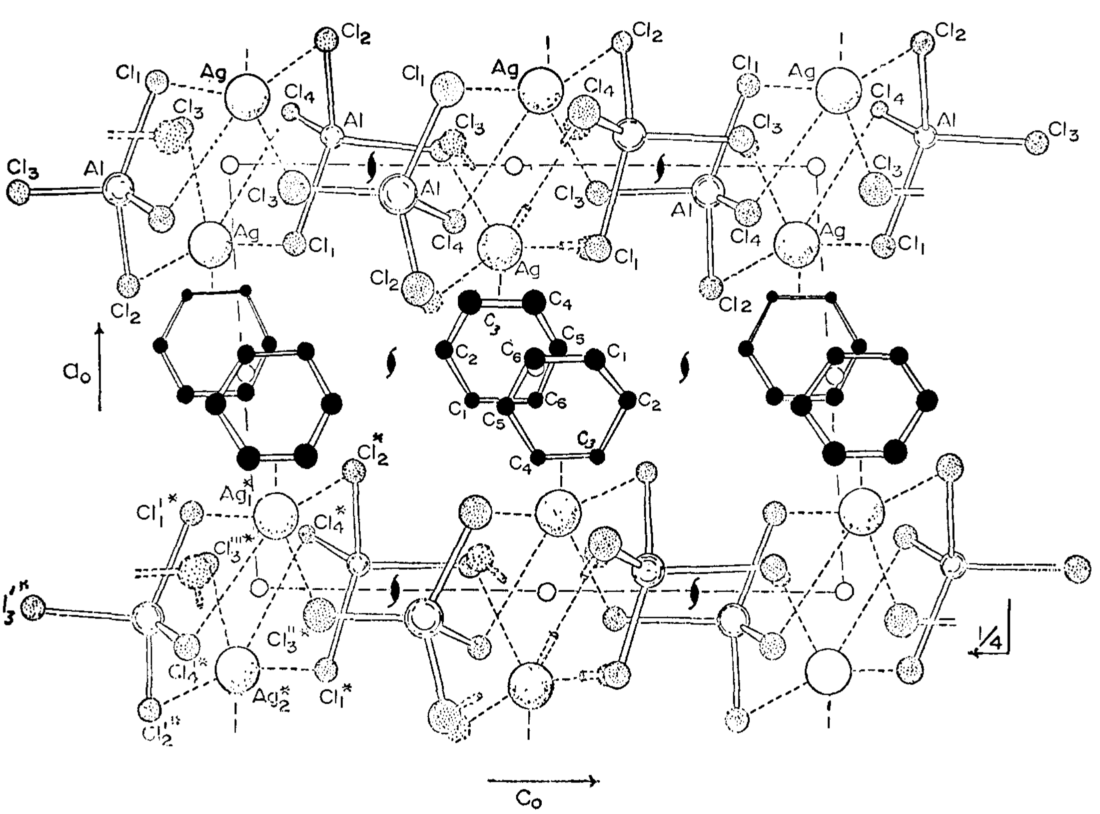

Figure 1. A perspective view down the $b(y)$ axis of the unit cell outlined by dashed lines. Primes denote different $AlCl_4^-$ tetrahedra (b = 10.22 A): Ag_1* at $y \sim b/4$, Ag_2* at $y \sim -b/4$, Cl_2* at $y \sim 0$, Cl_4* at $y \sim -{}^1/_4b$, Cl_1* at $y \sim 0$, Cl_1'* at $y \sim 0$, Cl_4'* at $y \sim {}^1/_4b$, Cl_2'* at $y \sim 0$, Cl_3''* at $y \sim b/3$, Cl_3'''* at $y \sim b/3$.

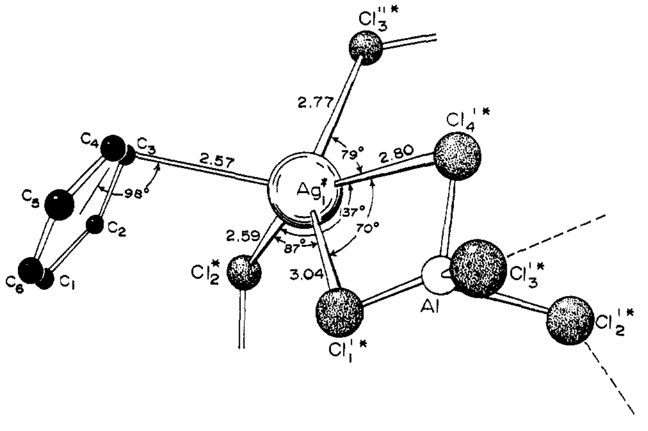

Figure 2. A perspective view of Ag_1* of Figure 1 down the c axis showing the ring coordination geometry and the fivefold coordination of Ag(I). Dotted lines refer to other Ag–Cl interactions.

sheets are composed of $AlCl_4^-$ tetrahedra interconnected by silver to chlorine bonds with π-type Ag–C_6H_6 interactions extending out of the sheets (Figure 1). It can be seen from Figure 1 that each Ag(I) species is linked to chlorine atoms of three different tetrahedra in such a manner that each halogen of every $AlCl_4^-$ entity is involved in a silver–chlorine interaction. For example, Ag_1* connects Cl_1'* and Cl_4'* of one tetrahedron with Cl_3''* and Cl_2* of two other $AlCl_4^-$ entities, and Ag_2* connects Cl_1* and Cl_4* of the Cl_2* tetrahedron with Cl_2'* and Cl_3'''* of two tetrahedra. Thus, each silver has four halogen interactions with Cl_2 at 2.59 A, Cl_3 at 2.77 A, Cl_4 at 2.80 A, and Cl_1 at 3.04 A. These interactions, along with the Ag–C_6H_6 π interaction, give Ag(I) the unusual coordination number of five (Figure 2). All other Ag–Cl interactions are greater than 5 A. However, as the angles indicate, this is a rather irregular fivefold geometry. Inspection of Table III shows that all other distances correspond to only van der Waals interactions. The nearest Ag–C distances are 2.47 and 2.92 A; and the Ag-to-center of nearest C–C bond is 2.57 A, all ±0.06 A. In contrast to $C_6H_6 \cdot AgClO_4$, each Ag is bonded to only one aromatic ring. Within the relatively large experimental error, the aromatic ring is planar. All the Al–Cl distances are equal within a standard deviation, 2.13 ± 0.02 A.

Discussion

Although there have been several authenticated cases of fivefold coordinated metal ions in the third transition series,[14,15] these have been generally stabilized by phosphines and/or sterically blocked from further coordination. The most widely known geometries for Ag(I) compounds are: linear, *e.g.*, $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$;[16] tetrahedral, *e.g.*, $Ag[SC(CH_3)NH_2]_4Cl$;[17] or octahedral, *e.g.*, $Ag \cdot 3(O_2C_4H_8) \cdot ClO_4$.[18] However, a number of distorted arrangements of atoms about Ag(I) are also known.[19,20] We know of no previous

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report of a five-coordinate Ag(I) species. From Ag and Cl covalent radii[21a] a "normal" Ag–Cl single bond would be expected to be 2.51 A. On the other hand, from ionic radii[21b] one would expect an interatomic separation between Ag(I) and Cl^- of 3.06 A. Hence, we feel that the bond distances of 2.59, 2.77, and 2.80 A correspond to varying amounts of covalent character. Although the 3.04-A Ag–Cl_1 distance is long compared to 2.59 A, we feel that this must be considered as something besides a Ag-to-Cl van der Waals interaction for the following reasons: (1) after the Ag–Cl_1 distance of 3.04 A, the next-nearest Ag–Cl distance is greater than 5 A; (2) a more or less tetrahedral environment about the Ag(I) entity would be expected as appears about Cu(I) in $C_6H_6 \cdot CuAlCl_4$;[7,8] (3) we have observed a similarly long Ag–Cl distance of 3.036 ± 0.005 A in bis(thiourea)silver(I) chloride[22] where there is no doubt that this Cl belongs in the coordination sphere; (4) all the Al–Cl distances are bracketed by 2.13 ± 0.02 A in contrast to the "free" Al–Cl distance of 2.078 ± 0.008 found in $C_6H_6 \cdot CuAlCl_4$[7,8] and the 2.07 ± 0.02 Al–Cl terminal distance in Al_2Cl_6.[23] However, the 2.13 A compares favorably with the Al–Cl distances of 2.136, 2.141, and 2.153 (all ±0.007 A) in which the halogen is also bonded to the metal atom in $C_6H_6 \cdot CuAlCl_4$. Although our estimates of bond length errors in both $C_6H_6 \cdot CuAlCl_4$ and $C_6H_6 \cdot AgAlCl_4$ may be somewhat optimistic, and hence the statistical significance of these differences may be marginal, this consistency is striking.

It is clear from the results of this structure analysis that cation–anion interactions must be important in determining the stability of the crystalline complex. Similar results were noted for the cuprous–benzene complex as well. Although using Mulliken's[4] and/or Dewar's[5] theoretical models for the binding in $Ag^+ \cdot C_6H_6$ complexes gives the correct orientation of the aromatic ring relative to the Ag(I) ion, this must be only fortuitous. Both of these formulations consider isolated Ag(I) and benzene species. This might be a reasonable approximation in $C_6H_6 \cdot AgClO_4$ where the Ag–O distance is 2.7 A, but not in this complex where the shortest Ag–Cl distance of 2.59 A is essentially a Ag–Cl single bond (2.51 A). Further, the local environment about the Ag(I) species is of sufficiently low symmetry that no simple hybrid metal orbital can be considered the acceptor as was the case in $C_6H_6 \cdot CuAlCl_4$.

The asymmetry in nearest metal–carbon distances of 2.92 and 2.47 A, both ±0.06 A, is similar to that found in $C_6H_6 \cdot CuAlCl_4$ (2.15 and 2.30, both ±0.03 A) and in $C_6H_6 \cdot AgClO_4$ (2.40 and 2.63, both ±0.01 A), but is more pronounced. We believe that this asymmetry, although variable in magnitude, is a characteristic of $M^+ \cdot C_6H_6$ complexes. The wide variability may be due to packing considerations, but further structural investigation is necessary to establish this feature conclusively.

The present results, coupled with those from $C_6H_6 \cdot CuAlCl_4$ and a recent refinement of $C_6H_6 \cdot AgClO_4$,[24] cast considerable doubt on nuclear magnetic resonance interpretations[25] in which the benzene ring is allowed free rotation about its sixfold axis in $C_6H_6 \cdot AgClO_4$.

Acknowledgment. We wish to acknowledge financial support from the National Science Foundation (GP-1575).

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