Metal Ion-Aromatic Complexes. IV. Five-Coordinate Silver(I) in $C_{6}H_{6} \cdot AgAlCl_{4}$

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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 . CuAlCl₄, the structure of C_6H_6 . AgAlCl₄ is made up of infinite planar sheets composed of AlCl₄tetrahedra 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 \pm 0.02 A, and one Ag–C₆H₆ interaction with Ag to the center of the nearest C–C bond, a distance of 2.57 \pm 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 Mulliken⁴ and Dewar⁵ 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 AgAlCl₄ and have found no simple relationship in terms of space group or cell dimensions between this compound and C₆H₆·CuAlCl₄^{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-

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anion distances would also give more insight into the role of the anion in these complexes.

Experimental Section

C₆H₆·AgAlCl₄ was prepared by treating a slight excess of pure, dried AgCl with 0.03 mole of resublimed AlCl₃ 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 C6H6 ·CuAlCl4; 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 $0.35 \times 0.30 \times 0.40$ mm was used to collect 496 independent hkl observed intensities by standard multiple film equiinclination Weissenberg techniques from hk0, hk1, . hk5 levels with Zr-filtered Mo K α radiation. In addition, h01 and 0kl precession-timed exposure intensity data were collected with Zr-filtered Mo K α 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 C₆H₆·AgAlCl₄ with Mo K α 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 squares⁹ with the Hughes¹⁰ 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 Ibers11 for Ag+, Cl-, Al³⁺, and neutral C.

Results

Unit Cell and Space Group. C₆H₆·AgAlCl₄ was found to crystallize in the monoclinic crystal system. With Mo K α (0.7107 A), cell constants were obtained from precession photographs: a = 9.09, b = 10.22,c = 12.73 A (all ± 0.03 Å), and $\beta = 95^{\circ} 05' \pm 15'$. The observed systematic extinctions (for h0l, l = 2n+ 1; and for 0k0, k = 2n + 1) uniquely specify the space group as $P2_1/c$. With four $C_6H_6 \cdot AgAlCl_4$

(9) W. R. Busing, K. O. Martin, and H. Levy, OR FLS program.

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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(calcd)
~ ~~ ~		o obor rou bri uoruro		$c_{j} = 101 (c_{m}c_{m})$

F(U) F(C) OKC 4 457 484 6 440 -491	SKO (CONT) 3KI (CONT) 2 130 -123 5 114 -74 3 213 212 7 163 168 4 176 174 9 165 -205	-6K1 2K2 1 181 163 0 223 -147 3 83 4 1 299 -326 4 139 110 2 635 (31)	-5K2 (CONT) 1 7 107 103 2 8 80 -70	1K2 53 75 0K3	4K3 (CONT) 8 44 -6C 10 49 75	-2K4 C 42 51 1 140 171	-6K4 1 84 -82 3 94 96
8 191 185 1K0 2 129 -94	5 72 -81 10 106 -115 8 60 49 -3K1 9KC 2 193 156 1 143 -158 4 68 -39	6 60 -73 3 287 265 7 63 -59 4 180 -138 8 115 119 5 104 -88	6K2 4 0 212 196 5 1 107 90 6	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	3 40 41 5 65 -59 6 68 61	3 155 -182	5 102 -88 7K4 0 47 51
4 271 253 5 271 -250 6 303 -305	3 113 118 5 289 -238 5 82 -112 6 69 49 10K0 7 138 95	1 56 65 7 150 155 3 48 -18 10 60 86 4 55 -5	2 211 -220 7 3 108 -95 8 4 70 61 9 5 141 90	58 -45 60 55 86 91	7 144 143 5K3 1 33 -46	5 37 43 7 82 -83 9 50 49	1 47 -46 2 91 -90
8 133 138 2KG 1 327 -204 3 423 448	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 156 160 -2K2 9 74 86 0 136 120 -7K1 3 280 -307	6 128 -122 2 8 55 63 4 -6K2 6	27 19 175 116 86 -96	2 57 64 4 43 -37 6 69 76	3K4 C 126 -110 1 58 -45 2 143 130	6 54 -56 -7K4 3 57 74
4 175 -124 5 216 -193 8 68 46	4 130 113 5 312 344 4K1 6 162 -145 0 65 0	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0 152 131 8 1 225 -242 9 2 125 78 3 267 257 -	77 86 43 33 1K3	8 46 -70 10 51 51 -5K3	3 48 -37 4 61 -58 6 81 80	8K4 3 37 55 0K5 4 60 56
3K0 1 97 44 3 371 320 4 462 -506	7 2C1 -198 1 211 -181 9 1C7 99 3 77 51 10 59 -49 4 114 -89 11 80 -78 5 121 -1C7	3K2 8K1 0 270 -296 1 68 70 1 178 -153 1 68 70 2 462 523	4 69 57 3 5 130 -130 4 6 43 -29 5	135 - 166 87 - 74 67 - 55	3 78 60 4 73 44 5 67 -40	-3K4 1 161 173	7 87 -91 8 40 52 1X5
6 86 73 8 141 -133 4KC	IKI 6 84 48 3 75 50 7 72 51 4 275 255 8 80 -71 5 248 271 9 142 -146	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8 67 -66 9 7K2 11 0 307 325	52 -83 76 98 49 -64	6K3 2 43 50	5 84 86 6 47 42 7 69 -83	2 54 -48 5 84 -100 6 40 -49
1 299 308 2 375 354 3 15 57	6 245 - 246 - 4K1 8 93 79 1 128 75 9 91 87 3 118 99	6 249 225 -8K1 7 55 45 1 43 24 8 82 -73 3 62 -92	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2K3 125 122 33 -26 81 76	7 74 -111 -6K3	9 63 59 4K4 0 38 -31 1 93 105	-1K5 3 53 -50 5 36 37
4 391 -395 5 188 172 6 127 125 7 130 -113	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	4 80 -103 -3K2 ; 7 50 -75 0 327 -327 9 62 90 3 187 -138 5 260 205	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	88 52 96 -90 51 66 47 57	2 33 37 4 43 46 7K3 7 56 -73	2 81 66 3 93 -83 5 85 79	6 28 20 7 62 -63 2K5 2 69 -60
B 186 -198 5K0 0 250 -216	5 109 83 9 121 -132 6 130 139 11 66 92 7 235 -234	9K1 7 71 ~68 2 63 -106 4K2 -9K1 0 350 -378	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2K3 85 85	0K4 3 103 97 4 31 27	-4K4 0 87 -76 1 121 112	5 100 -92 -2K5 2 43 -56
2 265 235 3 176 -140 4 212 -162	2K1 1 230 -255 1 238 -236 2 43 -43 3 158 151 3 93 -67	2 54 -45 2 224 198 4 69 -102 4 300 -287 5 64 -28 6 154 143	6 76 -68 2 3 8K2 4 1 0 178 197 6	32 33 81 -83 100 -104 63 48	5 78 -66 7 48 44	2 95 78 5 69 38 6 58 58 7 47 -32	4 69 -79 5 53 68 6 35 34 7 44 -34
5 201 191 6 81 68 7 188 -199 6 105 -111	4 311 340 4 189 -220 5 175 141 6 167 202 6 180 -187 7 76 72 7 156 155 8 90 -106	CK2 -4K2 3 178 -159 0 379 -319 4 313 329 1 78 -41	1 140 -150 7 3 126 75 8 4 63 58 9 5 170 -131 10	43 -28 57 +67 48 34	1K4 2 67 55 3 149 162 4 47 -36	5K4 0 119 119	9 51 48 3K5 2 56 49
6KC C 122 108 1 25C 245	8 139 136 10 101 119 10 171 -203 -5K1 -2K1 1 244 247	6 96 -97 2 231 200 8 133 143 6 189 152 11 56 -45 8 72 -51 182	6 69 - 76 -8K2 1 0 82 67 2	3K3 37 39	5 111 -95 7 78 84 8 88 -68	1 108 90 2 45 -41 3 71 -71 4 66 59	5 59 40 5 54 -70 -3K5 1 43 48
2 104 -90 3 105 -118 4 102 91 5 100 96	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3 213 215 5K2 4 144 110 0 125 -73 5 44 -48 1 255 212 6 20 16 16 125	1 76 52 4 1 2 148 -168 5 4 94 78 6	130 -81 68 -68 42 -39	-1K4 2 126 -175 3 74 -63	5 80 70 6 53 -47	2 51 -40 3 47 45 4 85 -101 6 51 49
7 110 -99 7KG C 130 13C 1 87 65	6 222 191 6 153 -163 7 134 -108 8 99 107 8 245 -239 9 67 -68 9 62 -53 11 53 49	6 136 125 3 246 -223 10 53 37 4 141 -96 11 82 -84 5 89 78	9K2 7 1 99 -107 9 5 71 -104 -3 2	75 82 45 -55 3K3 85 75	7 53 -52 2K4	-5K4 0 132 -141 2 38 41 3 83 64	4K5 1 71 61 2 69 64
2 221 -203 3 78 60 4 245 280	10 K9 112 12 75 -95 6K1 1 156 -136	-5K2 -1K2 0 201 -183 3 269 -302 1 289 -253	-9K2 3 1 92 115 5 2 46 -50 6 1 3 94 -115 7	$\begin{array}{cccc} 68 & 49 \\ 61 & -39 \\ 111 & 101 \\ 69 & 45 \\ \end{array}$	0 157 -144 1 151 -131 2 175 187 3 66 43	4 51 -54 6 91 64 6K4 0 120 113	-4K5 1 40 C 2 42 -33 3 42 49
5 67 52 8 105 105 8K0 0 127 141	3K1. 3 83 -70 1 249 -232 4 62 -61 2 141 115 5 210 212 3 211 190 6 153 150	4 271 273 2 328 308 5 209 196 3 216 189 6 216 -229 4 82 -56 7 49 -100 5 211 -174	10K2 8 2 94 106 4 10K2 2 1 81 103 (1)	70 -66 K3 42 34	4 75 -76 5 120 -117 6 58 53	1 43 27 2 91 -96 3 52 -44	4 38 -46 6 38 55 5K5
1 116 -102	4 235 192 9 78 96	10 86 -120 6 181 150	3 58 -97 7	48 52	8 73 -78		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 A³ is very close to the 1123 A³ found for C₆H₆·CuAlCl₄, 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 P2₁/c, $\pm (x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z)$.¹² The carbon atoms were located from threedimensional 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

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

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

Positional and Temperature Parameters and Errors ^a												
I	Atom	x/c	2	y/b		z/c	$\sigma(x)_i$	a	$\sigma(y)/b$		$\sigma(z)/c$	
	١q	0.13	82	0.2297		0.0323	0.00	03	0.0003		0.0008	
Ċ	C(1) 0.8527		527	0 5069 0.6290		0.00	14	0.0015	5 0.0030			
Ċ	(2)	0.23	300	0.4385	5 0,6753		0.00	0.0014		0.0015 0.4		
Ċ		0.04	72	0.6076		0.8651	0.0016		0.0013 0.003		0.0031	
Ċ		0.0	996	0.7547		0.6215	0.0018		0.0011 0.0030		0.0030	
Å		0.0	574	0.5767		0,6998	0.00	0.0016			0.0036	
ć	2(1)	0.54	22	0.2504	0,1120		0.00	0.0055 0.0048		0.0110		
Ċ	$\Gamma(2)$	0.48	395	0.3554		0.1548	0.0052 0.4		0.0050		0.0101	
č	$\overline{\mathbf{x}}(3)$	0.35	532	0.4289		0.1081	0.00	0.0056 0.0056			0.0115	
Ċ	(4)	0.34	78	0.3747	1	0.0007	0.00	55	0.0054		0.0107	
Ċ		0.44	58	0.2884		0.9466	0.00	54	0.0053		0.0106	
Ċ	C(6)	0.51	.44	0.2908		0.4805	0.00	58	0.0052		0.0102	
Thermal Parameters and Standard Deviations												
[Ani:	sotropic Ten	neratur	e Factors of	the Forn	$n \exp -(\beta_{11})$	$h^2 + \beta_{22}$	$k^2 + \beta_{33}l^2 + 2$	$2\beta_{12}hk$ -	$+ 2\beta_{13}hl + 2\beta_{13}hl$	$3_{23}kD$:	$\sigma' = \sigma \times 10$	4]
Atom	β_{11}	σ΄	β_{22}	σ'	β_{33}	σ'	β_{12}	σ	β_{13}	σ'	β_{23}	- σ'
Δσ	0.0084	3	0.0081	3	0.0045	7	-0.0004	3	-0.0012	6	-0.0010	7
	0.0099	16	0.0112	15	0.0058	13	-0.0031	13	-0.0029	27	0.0002	25
$\mathbf{C}(2)$	0 0130	18	0 0099	14	0.0055	15	0.0064	14	-0.0028	28	-0.0030	25
C(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 isotronic											
	temperature factors Scale											
Atom B. A ²			Layer fa		fact	ctor σ						
C(1) 3.47			hk0		0.3253		0.0053					
C(2) 5.71		5.71		hk1		0.3209		0.0047				
C(3) 4.18		4.18		hk2		0.2745		0.0036				
C	C(4) 5.13			hk3			0.1523			0.0048		
С	C(5) 5.82			hk4 0.1172		72	0.0029					
C(6) 3.68 $hk5$ 0.1042				0.0060								
F	$F(\text{calcd})_{\text{abs}} = F(C)/(10 \times \text{scale factors})$											

^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	
Al-Cl ₄	2.13 ± 0.02	Ag–Cl ₄	2.80 ± 0.02
Al–Cl ₃	2.14 ± 0.02	Ag–Cl ₃	2.77 ± 0.02
$Al-Cl_2$	2.15 ± 0.02	$Ag-Cl_2$	2.59 ± 0.02
Al–Cl ₁	2.12 ± 0.02	$Ag-Cl_1$	3.04 ± 0.03
$C_1 - C_2$	1.31 ± 0.10	Ag–C ₃	2.92 ± 0.07
$C_2 - C_3$	1.52 ± 0.08	Ag–C ₄	2.47 ± 0.06
C3-C4	1.47 ± 0.16	Ag-midpoint C_3 - C_4	2.57 ± 0.06
C4-C5	1.47 ± 0.12	Nonbonded Intermolecular Dis	stances, A
C₅C6	1.21 ± 0.08	Cl_3-Cl_4 3.97 Cl_2-Cl_3 4.18	$Cl_1 - C_4 = 3.99$
C_6-C_1	1.42 ± 0.10	Cl_1-Cl_3 4.02 Cl_3-Cl_3 >5.00	$Cl_2 - C_3 = 3.88$
	Nonbo	nded Intramolecular Distances, A	
Cl_1-Cl_2	3.50 ± 0.02	Cl_1-Cl_4	3.39 ± 0.02
Cl_2-Cl_3	3.50 ± 0.02	Cl_3-Cl_1	3.51 ± 0.02
Cl ₃ -Cl ₄	3.51 ± 0.02	Cl_2 - Cl_4	3.49 ± 0.02
	Bon	ded Angles for C ₆ H ₆ ·AgAlCl ₄	
		Cl_4 -Ag- Cl_2	$137.2 \pm 0.6^{\circ}$
$Cl_1-Al-Cl_2$	$110 \pm 1^{\circ}$	Cl ₁ -Ag-Cl ₄	$70.3 \pm 0.3^{\circ}$
Cl_1 - Al - Cl_3	$111 \pm 1^{\circ}$	$Cl_1 - Ag - Cl_3$	$144.0 \pm 0.6^{\circ}$
Cl ₂ -Al-Cl ₃	$109 \pm 2^{\circ}$	$Cl_2 - Ag - Cl_3$	$103.8 \pm 0.6^{\circ}$
$Cl_1-Al-Cl_4$	$106 \pm 2^{\circ}$	Cl ₄ -Ag-Cl ₃	$79.0 \pm 0.4^{\circ}$
Ag–Cl₄–Al	$95.0 \pm 0.6^{\circ}$	Cl_1 -Ag- Cl_2	$87.2 \pm 0.5^{\circ}$
Cl ₃ -Al-Cl ₄	$111 \pm 1^{\circ}$	C_4 -Ag- C_3	$30.0 \pm 4^{\circ}$
Ag-Cl ₁ -Al	$87.7 \pm 0.5^{\circ}$	Cl_1 -Ag-midpoint C_3 - C_4	$118.9 \pm 2^{\circ}$
Ag–Cl ₂ –Al	$93.9 \pm 0.6^{\circ}$	Cl_2 -Ag-midpoint C_3 - C_4	$96.6 \pm 2^{\circ}$
AgCl ₃ -Al	$129.1 \pm 0.6^{\circ}$	Cl_4 -Ag-midpoint C_3 - C_4	$125.9 \pm 2^{\circ}$
C ₂ –C ₃ –Ag	$98.2 \pm 4^{\circ}$	$Cl_3-Ag-midpoint C_3-C_4$	$93.8 \pm 2^{\circ}$
C₅−C₄−Ag	95.7 ± 4°		
Equation of Best L	east-Squares Plane for C ₆ H	H ₆ Individual Atomic Deviation	is from this Plane, A
0.7063x + 0.000x	.6709y - 0.2259z = 1	$C_1 - 0.090$	$C_4 - 0.080$
		$C_2 + 0.136$	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. (13) W. R. Busing, K. O. Martin, and H. Levy, OR FFE program. **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



Figure 1. A perspective view down the b(y) axis of the unit cell outlined by dashed lines. Primes denote different AlCl₄⁻ tetrahedra (b = 10.22 A): Ag₁* at $y \sim b/4$, Ag₂* at $y \sim -b/4$, Cl₂* at $y \sim 0$, Cl₄* at $y \sim -1/4b$, Cl₁* at $y \sim 0$, Cl₁/* at $y \sim 0$, Cl₄'* at $y \sim 1/4b$, Cl₂'* at $y \sim 0$, Cl₃''* at $y \sim b/3$, Cl₃''* 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 AlCl₄⁻ tetrahedra interconnected by silver to chlorine bonds with π -type Ag-C₆H₆ 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 AlCl₄entity is involved in a silver-chlorine interaction. For example, Ag₁* connects Cl₁'* and Cl₄'* of one tetrahedron with Cl₃''* and Cl₂* of two other AlCl₄entities, and Ag₂* connects Cl₁* and Cl₄* of the Cl₂* tetrahedron with Cl₂'* and Cl₃'''* of two tetrahedra. Thus, each silver has four halogen interactions with Cl₂ at 2.59 A, Cl₃ at 2.77 A, Cl₄ at 2.80 A, and Cl₁ at 3.04 A. These interactions, along with the Ag-C₆H₆ 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 C₆H₆·AgClO₄, 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(NH₃)₂⁺ and Ag(CN)₂⁻;¹⁶ tetrahedral, e.g., Ag[SC(CH₃)NH₂]₄Cl;¹⁷ or octahedral, e.g., Ag·3(O₂C₄H₈)·ClO₄.¹⁸ 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-Cl₁ 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 CuAlCl₄^{7,8} (3) we have observed a similarly long Ag-Cl distance of 3.036 ± 0.005 A in bis(thiourea)silver(I) chloride²² 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 · CuAlCl₄^{7,8} and the 2.07 \pm 0.02 Al-Cl terminal distance in Al₂Cl₆.²³ 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 CuAlCl₄. 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.

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Similar results were noted for the cuprous-benzene complex as well. Although using Mulliken's⁴ and/or Dewar's⁵ theoretical models for the binding in Ag⁺. 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 ·AgClO₄ 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 ·Cu-AlCl₄.

The asymmetry in nearest metal-carbon distances of 2.92 and 2.47 A, both ± 0.06 A, is similar to that found in C₆H₆·CuAlCl₄ (2.15 and 2.30, both ± 0.03 A) and in C₆H₆·AgClO₄ (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⁺·C₆H₆ 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 . CuAlCl₄ and a recent refinement of C_6H_6 ·AgClO₄,²⁴ cast considerable doubt on nuclear magnetic resonance interpretations²⁵ in which the benzene ring is allowed free rotation about its sixfold axis in C_6H_6 ·AgClO₄.

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