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DV Xα Molecular Orbital Studies of the Bonding in Benzene Complexes of Univalent Gallium Salts

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The electronic structures of the benzene/gallium(I) model complexes $[(C_6H_6)Ga]^+$ (C_{6v} symmetry), $[(C_6H_6)_2Ga]^+$ (D_{6h}), $[(C_6H_6)_2Ga]^+$ (C_{2v}), and $[(C_6H_6)_2Ga(GaCl_4)]$ (C_{2v}) have been calculated by using the discrete variation Xα (DV Xα) molecular orbital method. The results show that a weak dative bond is formed between the C_6H_6 molecule and the Ga^I atom in these species, electronic charge being transferred from the π orbitals of the benzene molecule to the three 4p orbitals of the Ga^I atom. The total amount of charge transfer to the Ga^I atom increases from 0.13e to 0.24e in this series, but the amount of charge transfer from a single C_6H_6 molecule decreases from 0.13e to 0.04e. These amounts are comparable to those estimated for charge-transfer complexes of benzene and substituted benzenes with other electron acceptors. The results for $[(C_6H_6)_2Ga]^+$ suggest that there is a slight strengthening of the C_6H_6–Ga^I dative bond in going from the "flat sandwich" structure (D_{6h}) to the "bent sandwich" structure (C_{2v}). However, the results for $[(C_6H_6)_2Ga(GaCl_4)]$ indicate that there is also a significant covalent interaction between the Ga^I center and the $[GaCl_4]^-$ counterion. This is therefore also expected to be a factor in determining the frequently observed "bent sandwich" arrangement in complexes of benzene and substituted benzenes with $Ga[GaCl_4]$. Although K^+ has an ionic radius similar to that of Ga^+, there is no charge-transfer interaction between C_6H_6 and K^+, due to the fact that the potassium 4s and 4p orbitals are too high in energy to allow a significant bonding interaction with benzene. This agrees with the experimental observation that potassium salts do not form stable complexes with benzene.

Introduction

It has been known for some time that many salts of the monovalent cations of Ga, In, and Tl are surprisingly easily soluble in aromatic solvents,[1-5] whereas the corresponding salts of alkali metals are insoluble. For example, $Ga[GaCl_4]$ dissolves in benzene to yield a 7 wt % solution, whereas $K[GaCl_4]$ is insoluble in benzene. Since the ionic radii of Ga^+, In^+, and Tl^+ are comparable to those of the corresponding alkali-metal ions K^+, Rb^+, and Cs^+,[5] it seems unlikely that differences in the electrostatic interaction between the aromatic molecule and the cations or differences in the lattice energies are responsible for these differences in solubility behavior. It therefore appears to be more likely that some metal-specific factor is responsible for this phenomenon.

It was pointed out some years ago that specific molecular complexes involving aromatic hydrocarbons and Ga^+, In^+, or Tl^+ may exist.[6] It was proposed that these complexes involve a charge-transfer interaction in which electronic charge is transferred from the aromatic molecule to the monovalent metal ion. For the above metal ions, the lowest energy acceptor orbitals available are the p orbitals. The specific case of complexes with benzene was considered, and it was pointed out that if the metal ion lies on the 6-fold axis of the benzene molecule, then the metal p_x, p_y orbitals have the same symmetry as the highest energy donor orbital of benzene (e_1 in C_{6v} symmetry), so a charge-transfer interaction can take place without a lowering of symmetry. This contrasts with the case of metal ions such as Ag^+, in which the lowest energy acceptor orbital is an s orbital whose symmetry (a_1 in C_{6v}) does not match that of the highest energy benzene donor orbital. A charge-transfer bonding interaction can only occur in this case if the symmetry of the complex is lowered by displacement of the Ag^+ ion away from the 6-fold axis of the benzene molecule.[6] The fact that Ag^+ forms asymmetric complexes with benzene has been verified experimentally in an X-ray diffraction determination of the structure of the 1:1 complex of benzene with $Ag[AlCl_4]$.[7]

The crystalline phase obtained from benzene solutions of $Ga[GaCl_4]$ has a 3.5:1 stoichiometry, and the crystal structure of this complex shows that it contains the dimeric units $[(C_6H_6)_2Ga(GaCl_4)]_2$ and three molecules of crystal benzene. In the complex units each gallium atom is associated with two benzene molecules, and the metal atoms lie close to the point where the 6-fold axes of the two benzene molecules intersect at an angle of about 120°.[4] Structures of a number of other complexes of Ga^I salts with substituted benzenes have been determined,[4,8-13] and while the detailed structures vary considerably, they all show the common feature that the Ga^I atom lies close to the 6-fold axis of the benzene ring. This is also the case for several complexes of aromatic molecules with other main-group metal ions that have an outer-shell s^2 configuration (e.g. Sn^{II}, Sb^{III}).[13-17]

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These structural results are thus consistent with the hypothesis that there is a covalent interaction involving a dative bond between the aromatic molecule and the main-group metal ion. A measure of the extent of this interaction is the amount of charge transferred from the aromatic molecule to the metal ion, and one of the aims of the present work was to determine this from molecular orbital calculations. Such calculations should also provide answers to a number of other questions concerning the bonding in these complexes. Thus, in complexes in which two aromatic molecules are associated with the metal ion, the planes of the two aromatic molecules are not parallel but are inclined at an angle to form a "bent sandwich" complex. It has been proposed that such bonding results in a more stable complex because it allows the two valence s electrons on the metal to become involved in the bonding.[5] However, in all cases where such bent-sandwich structures are found, there are always additional contacts between the central metal ion and atoms in the neighboring anions (e.g. the Cl atoms in the $[GaCl_4]^-$ ions in the benzene complex of $Ga[GaCl_4]$[4]). While electrostatic attraction between the anion and the cation is expected to be a factor in stabilizing such structures, it is possible that coordination of the anion through dative covalent bonding to the Ga^+ ion is also important in determining the structure. One way to answer these latter questions would be to determine the potential energy surface of the system as a function of the various parameters (bond angles and bond lengths) involved. However, the total sytem involving the metal ions, aromatic molecules, and counterions is sufficiently large that its study by molecular orbital methods that yield reliable total energies (e.g. LCAO-MO programs involving Gaussian basis sets) would be excessively time-consuming. We have chosen rather to use a minimum basis-set method that yields information about the bonding via an atomic orbital population analysis. In particular, the degree of charge transfer to the central metal ion from the surrounding species (aromatic molecules and counterions) gives an indication of the stabilization of the complex through dative bonding.

In order to answer the questions discussed above, molecular orbital calculations were carried out on the systems $[(C_6H_6)Ga]^+$ (C_{6v} symmetry), $[(C_6H_6)_2Ga]^+$ (D_{6h}), $[(C_6H_6)_2Ga]^+$ (C_{2v}), and $[(C_6H_6)_2Ga(GaCl_4)]$ (C_{2v}). The system $[(C_6H_6)K]^+$ (C_{6v}) was also examined for comparison with the corresponding gallium(I) species.

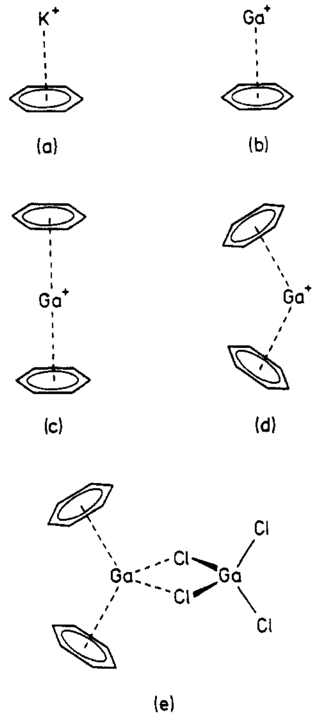

Figure 1. Structures of model complexes used in the calculations: (a) C_{6v} $[(C_6H_6)K]^+$; (b) C_{6v} $[(C_6H_6)Ga]^+$; (c) D_{6h} $[(C_6H_6)_2Ga]^+$; (d) C_{2v} $[(C_6H_6)_2Ga]^+$; (e) C_{2v} $[(C_6H_6)_2Ga(GaCl_4)]$.

Table I. Valence Orbital Energies and Orbital Compositions for C_{6v} $[(C_6H_6)K]^+$

		composition, %				
		K		C		H
orbital	$-E$, eV	4s	4p	2s	2p	1s
$1a_1$	26.46	−0.3	−0.7	87.0	8.1	6.0
$1e_1$	24.00			68.1	22.8	9.2
$1e_2$	20.27			33.1	52.4	14.5
$2a_1$	17.55			1.6	74.7	23.9
b_1	16.71			23.0	35.3	41.6
b_2	16.39				100.0	
$2e_1$	15.47				73.0	27.0
$2e_2$	13.91			0.5	70.0	29.5
$3a_1$	13.67	0.5	−0.2	0.2	99.5	
$3e_1$	11.27		0.3	0.1	99.6	

Method of Calculation

The structures of the systems studied are shown in Figure 1. The geometry of the benzene molecule was taken to be the same as that of the free molecule in the gas phase.[18] The distance of the gallium atom from the center of the benzene molecule was taken to be the average of the two distances (2.929, 2.764 Å) observed in the $[(C_6H_6)_2Ga(GaCl_4)]_2$ dimer.[4] The angle between the normals to the planes of the two benzene molecules in C_{2v} $[(C_6H_6)_2Ga]^+$ and $[(C_6H_6)_2Ga(GaCl_4)]$ was taken to be 120°, which is close to the experimentally observed value of 124.4° in the $[(C_6H_6)_2Ga(GaCl_4)]_2$ dimer.[4] The orientation of the benzene rings in the C_{2v} species is such that the plane containing the normals to the two benzene rings bisects the rings through the centers of two C–C bonds on opposite sides of the rings. The other geometrical parameters for $[(C_6H_6)_2Ga(GaCl_4)]$ are as follows: $Ga^I\cdots Cl_b$ = 3.29 Å; $Ga^{III}–Cl_b$ = 2.18 Å; $Ga^{III}–Cl_t$ = 2.15 Å; $Cl_b–Ga^{III}–Cl_b$ = 108.3°; $Cl_t–Ga^{III}–Cl_t$ = 110.5° (Cl_b and Cl_t represent the bridging and terminal Cl atoms, respectively). The source of the above parameters is discussed in more detail below.

The molecular orbital calculations were carried out by using the discrete variation Xα (DV Xα) method,[19] a self-consistent LCAO-MO method within the framework of density function theory.[20] Symmetrized molecular orbitals were formed from atomic orbitals, and the atomic configurations for the atoms in the molecule (self-consistent within the framework of a Mulliken population analysis) were determined numerically.[19] The DV Xα method takes all electrons into account, but only the valence electrons are included in the self-consistent process. The 3d electrons of the Ga atom were considered to be part of the valence shell for the purposes of these calculations. The program uses a Fermi distribution of sampling points about each atom for the numerical calculations. The parameter β in the Fermi distribution was set equal to 1.0 and the Fermi radius to 2.0 au for all atoms. The distribution of points at each atom was adjusted so that their numbers were in the ratio of approximately 1.0:0.6:0.2:0.1 for Ga, Cl, C, and H, respectively. However, test calculations showed that the density of points used was sufficiently large that the results

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Table II. Valence Orbital Energies and Orbital Compositions for C_{6v} [$(C_6H_6)Ga]^+$

		composition, %					
		Ga			C		H
orbital	$-E$, eV	3d	4s	4p	2s	2p	1s
$1a_1$	26.56	0.6		−0.2	86.0	7.8	5.8
$1e_2$	25.68	100.0					
$1e_1$	25.66	99.8			0.1	0.1	
$2a_1$	25.64	99.4			0.5		0.1
$2e_1$	24.12	0.2			68.0	22.7	9.2
$2e_2$	20.38				33.2	52.4	14.4
$3a_1$	17.66		0.1		1.6	74.5	23.9
b_1	16.82				23.1	35.4	41.6
b_2	16.51					100.0	
$3e_1$	15.59					73.0	27.0
$4a_1$	14.63		48.7	0.3	0.3	50.7	
$3e_2$	14.03				0.5	70.0	29.5
$5a_1$	12.98		50.6	2.9		46.6	
$4e_1$	11.45			2.2	0.1	97.7	

Table III. Valence Orbital Energies and Orbital Compositions for D_{6h} [$(C_6H_6)_2Ga]^+$

		composition, %			
		Ga		C	
orbital[a]	$-E$, eV	4s	4p	2s	2p
$4a_{1g}$	14.33	35.1		0.3	64.6
$3a_{2u}$	13.67		3.1	0.2	96.7
$5a_{1g}$	11.71	64.9		−0.1	35.2
$3e_{1u}$	11.23		3.2	0.1	96.7
$4e_{1g}$	11.13			0.1	99.9

[a] The orbitals of the σ-system of benzene interact to a minimal extent with those of Ga^+ and are therefore omitted for clarity. The Ga 3d orbitals are essentially nonbonding and are also omitted.

were relatively insensitive to changes in these ratios. The iterative SCF procedure was ended when the maximum relative change in potential was less than 10^{-4}.

Results and Discussion

The orbital energies and orbital compositions obtained from the calculations on $[(C_6H_6)K]^+$ and $[(C_6H_6)Ga]^+$ are given in Tables I and II. The relative orbital energies and the orbital compositions for $[(C_6H_6)K]^+$ are almost identical with those of free C_6H_6. The reason for this is that none of the orbitals of K^+ are close enough in energy to those of C_6H_6 to allow a significant bonding interaction. The two highest energy orbitals $3a_1$, $3e_1$ are the π-bonding orbitals of C_6H_6. While there is a very slight interaction between these orbitals and the 4s and 4p orbitals of the K^+ ion, it is clear that these orbitals remain almost 100% C 2p in character and that there is essentially no transfer of charge from the C_6H_6 molecule to the K^+ ion.

The situation is rather different for $[(C_6H_6)Ga]^+$ (Table II). In this case there is a strong interaction between the lower energy π-bonding orbital of C_6H_6 (a_1 symmetry) and the 4s orbital of Ga^+ to yield the two orbitals $4a_1$, $5a_1$, which are a strong admixture of C 2p and Ga 4s orbitals. However, as the 4s orbital in Ga^+ is already filled, this results in no overall charge transfer from C_6H_6 to Ga^+. However, because of the lower symmetry at the Ga^+ site caused by the approach of the C_6H_6 molecule from one side, mixing of the Ga 4s and 4p orbitals can occur in the molecular orbitals of a_1 symmetry. This takes place in the orbitals $4a_1$ and $5a_1$, resulting in transfer of about 0.05e to the Ga $4p_z$ orbital. The remaining charge transfer occurs in the orbital $4e_1$, which involves the interaction of the higher energy π-bonding orbital of C_6H_6 with the Ga $4p_x$, $4p_y$ orbitals. The amount of charge transfer into each of these orbitals is about 0.04e and so is about the same as that into the $4p_z$ orbital. Thus, the charge distribution in the Ga atom remains essentially spherically symmetrical, despite the lowering of symmetry that occurs upon complex formation. This contrasts with the situation that might have been expected on the basis of the qualitative discussion of the bonding published previously,[6] where only the interaction of the e_1 orbitals of C_6H_6 and Ga^+ was considered (see Introduction). The interaction of the Ga $4p_z$ orbital with the benzene a_1 orbital is clearly symmetry allowed, and the present results indicate that this is of comparable importance to the interaction involving the e_1 orbitals. Although the Ga 3d orbitals have energies that are comparable with the energies of some of the σ-bonding orbitals of C_6H_6, the orbital overlap is apparently so small that there is essentially no admixture of these orbitals. Thus, the orbitals $2a_1$, $1e_1$, and $1e_2$ are nearly 100% Ga 3d in character and can be considered as part of the Ga core.

The total charge transfer in $[(C_6H_6)Ga]^+$ is 0.13e. This compares with zero charge transfer in $[(C_6H_6)K]^+$. It could be claimed that this explains at least in part the much higher tendency of Ga^+ compounds relative to K^+ compounds to form complexes with aromatic compounds. In drawing this conclusion, it should be remembered that the lowest energy acceptor orbital in K^+ is the 4s orbital (a_1 symmetry in C_{6v}), so that charge transfer from the highest energy donor orbital of C_6H_6 (e_1 symmetry) into the K^+ 4s orbital is symmetry forbidden (see Introduction). However, there is also very little charge transfer from the lower energy C_6H_6 π-bonding orbital (a_1 symmetry), in contrast to the corresponding Ga^+ case. This suggests that the charge-transfer interaction between C_6H_6 and K^+ would always be much less than that with Ga^+, even in complexes of lower symmetry.

While the "half sandwich" structure of the model $[(C_6H_6)Ga]^+$ used in the above calculations corresponds approximately to the observed structure in a complex of $Ga[GaCl_4]$ with hexamethylbenzene,[9] the more frequently observed situation involves a full-sandwich structure in which the Ga^+ ion is coordinated to two aromatic molecules.[8,10–13] Calculations were therefore carried out on the species $[(C_6H_6)_2Ga]^+$. Two models were chosen, one in which the C_6 axes of the two benzene molecules are coincident (D_{6h} symmetry; Figure 1 c) and another in which the two C_6 axes intersect at an angle of 120° (C_{2v} symmetry; Figure 1d). The latter geometry corresponds to the situation that is exclusively found experimentally. The orbital energies and orbital compositions obtained for these two cases are given in Tables III and IV. The orbitals of the σ system of C_6H_6 interact to a minimal extent with those of Ga^+, so these have been omitted for clarity. The orbital energy level diagrams for the sandwich and half-sandwich complexes are shown in Figure 2.

The orbitals involved in the charge-transfer bonding in D_{6h} $[(C_6H_6)_2Ga]^+$ are $3a_{2u}$ and $3e_{1u}$. The former involves interaction of the lower energy π-bonding orbital of C_6H_6 with the Ga^+ $4p_z$ orbital, while the latter involves the interaction of the higher energy π-bonding orbital of C_6H_6 with the Ga^+ $4p_x$, $4p_y$ orbitals. As in the case of the half-sandwich complex, the amounts of charge transfer to each of the Ga 4p orbitals (about 0.06e) are almost equal, so that the electronic environment of the Ga^+ ion in the complex remains nearly spherically symmetrical. The lowering of the symmetry from D_{6h} to C_{2v} in the bent-sandwich complex allows admixture of the Ga 4s and 4p orbitals in the molecular orbitals of a_1 symmetry, resulting in a greater amount of charge transfer than in the D_{6h} case.

The total amounts of charge transfer for all of the model structures considered in this study are given in Table V. These results show that addition of a second C_6H_6 molecule to C_{6v} $[(C_6H_6)Ga]^+$ to give D_{6h} $[(C_6H_6)_2Ga]^+$ results in an

Table IV. Valence Orbital Energies and Orbital Compositions for C_{2v}[$(C_6H_6)_2Ga$]$^+$

orbital[a,b]			composition, %				
			Ga		C		H
D_{6h}	C_{2v}	$-E$, eV	4s	4p	2s	2p	1s
$4a_{1g}$	$9a_1$	14.28	35.7		0.3	63.8	
$3a_{2u}$	$9b_2$	13.43		2.7	0.2	96.9	0.2
$5a_{1g}$	$11a_1$	11.84	59.4	2.8		37.9	
$3e_{1u}$	$12a_1$	11.19	4.0	1.0	0.1	94.9	
	$7b_1$	11.09		3.5	0.2	96.4	
$4e_{1g}$	$10b_2$	10.93		0.6		99.4	
	$7a_2$	10.89			0.1	99.9	

[a] See footnote *a* in Table III. [b] The correlation of the orbitals of the C_{2v} complex with those of the D_{6h} complex (Table III) is shown.

Table V. Electron Transfer and M–C Overlap Populations for C_6H_6 Complexes

complex	electron transfer, e to M^+	from each C_6H_6	M–C overlap population, e
C_{6v} [$(C_6H_6)K$]$^+$	0.0	0.0	–0.0080
C_{6v} [$(C_6H_6)Ga$]$^+$	0.131	0.131	0.0124
D_{6h} [$(C_6H_6)_2Ga$]$^+$	0.175	0.088	0.0012
C_{2v} [$(C_6H_6)_2Ga$]$^+$	0.182	0.091	0.0044
C_{2v} [$(C_6H_6)_2Ga(GaCl_4)$]	0.242	0.044	–0.0058

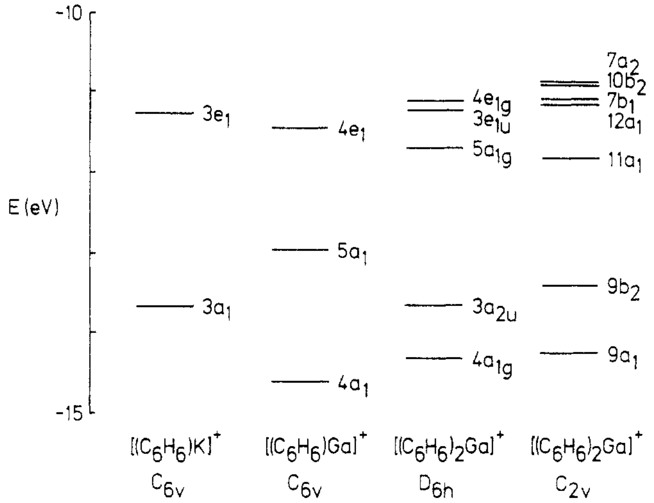

Figure 2. Valence orbital energy level diagrams for the sandwich and half-sandwich complexes (the orbitals of the σ system of C_6H_6 have been omitted for clarity).

increase of 0.044e in the amount of charge transfer to Ga^+, but this increase is much smaller than the amount 0.131e involved in the addition of the first C_6H_6 molecule to Ga^+. Thus, the addition of a second benzene molecule results in an overall weakening of the dative bond. The distortion of the [$(C_6H_6)_2Ga$]$^+$ complex from D_{6h} to C_{2v} results in the transfer of an additional 0.007e to Ga^+, and this represents a slight increase in the strength of the dative bond between the C_6H_6 molecules and Ga^+ consequent upon the formation of the "bent sandwich" structure. This agrees with the conclusion based on a qualitative discussion of the changes in the molecular orbital energies that occur with this distortion.[5] Also listed in Table V are the M–C overlap populations (the overlap populations per M–C atom pair). The trends in these quantities agree with the conclusions concerning the relative strengths of the dative bonds deduced from the amounts of charge transfer from C_6H_6. The differences in the charge-transfer and overlap populations for the D_{6h} and C_{2v} [$(C_6H_6)_2Ga$]$^+$ species are very small, however, and it is not clear whether this represents a sufficiently large energy difference to guarantee a "bent sandwich" structure for this species in the presence of other interactions (e.g. intermolecular forces in a solid-state structure). The total energies yielded by the DV Xα method are not sufficiently reliable to give a more quantitative answer to this question.

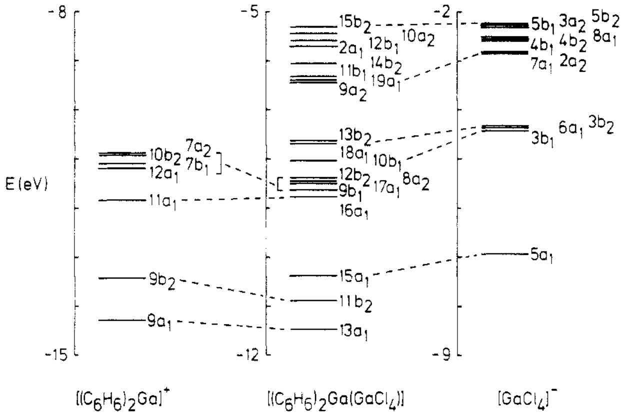

Figure 3. Molecular orbital correlation diagram for C_{2v} [$(C_6H_6)_2Ga$]$^+$, [$(C_6H_6)_2Ga(GaCl_4)$], and [$GaCl_4$]$^-$.

In order to investigate the role of the counterion in the bonding in complexes of the above type, calculations were carried out on the species [$(C_6H_6)_2Ga(GaCl_4)$] (C_{2v} symmetry, Figure 1e). This does not correspond exactly to the structure of the solid complex of C_6H_6 with Ga[$GaCl_4$], which contains dimeric units [$(C_6H_6)_2Ga(GaCl_4)$]$_2$ in which the two Ga^I centers are bridged by two [$GaCl_4$]$^-$ ions.[4,5] However, the model structure is very similar to one observed for a mixed bis(arene)gallium(I) complex containing coordinated hexaethylbenzene and toluene molecules.[12] This structure involves bidentate coordination of the [$GaCl_4$]$^-$ ion to the Ga^I atom and is similar to one previously proposed in a vibrational spectroscopic study of the structure of the species present in solutions of Ga[$GaCl_4$] in benzene.[21] The Ga–Cl bond lengths were taken from the structure of the mixed hexaethylbenzene/toluene complex[12] but were averaged to yield ideal C_{2v} symmetry.

The valence orbital energies and orbital compositions for [$(C_6H_6)_2Ga(GaCl_4)$] are given in Table VI, and the molecular orbital correlation diagram for C_{2v} [$(C_6H_6)_2Ga$]$^+$, [$(C_6H_6)_2Ga(GaCl_4)$], and [$GaCl_4$]$^-$ is shown in Figure 3. In the [$GaCl_4$]$^-$ calculation, the structure of the ion was unchanged from that in [$(C_6H_6)_2Ga(GaCl_4)$]; i.e., it has a slight C_{2v} distortion from ideal tetrahedral symmetry. In undistorted T_d [$GaCl_4$]$^-$, the σ-bonding orbitals involving the Cl 3p orbitals and the Ga 4s and 4p orbitals would have symmetries a_1 and t_2, respectively. The orbital $5a_1$ for C_{2v} [$GaCl_4$]$^-$ (Figure 3) is the one that involves the Ga 4s orbital, and this correlates with the orbital $15a_1$ in [$(C_6H_6)_2Ga(GaCl_4)$]. It is evident from Table VI that this orbital remains localized on the $GaCl_4$ entity in this com-

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(21) Kinsella, E.; Chadwick, J.; Coward, J. *J. Chem. Soc. A* **1968**, 969.

Table VI. Valence Orbital Energies and Orbital Compositions for C_{2v} $(C_6H_6)_2Ga(GaCl_4)$

		composition, %											
		Ga^I		C		H	Ga^{III}			Cl_b		Cl_t	
orbital[a]	$-E$, eV	4s	4p	2s	2p	1s	3d	4s	4p	3s	3p	3s	3p
$13a_1$	11.46	17.4	0.3	0.2	80.9	0.6		0.1			0.4		
$11b_2$	10.88		1.7	0.1	97.9	0.3							
$15a_1$	10.37	0.1			0.4			34.7	0.5	8.0	31.9	8.0	16.4
$16a_1$	8.78	18.8	2.6		69.8				0.5	0.4	7.7		0.1
$9b_1$	8.63		2.1		96.5			0.2			1.1		0.1
$17a_1$	8.49	40.6	0.2		43.4				1.2	0.5	13.3	0.1	0.7
$8a_2$	8.47				99.9								
$12b_2$	8.37		0.3		99.4						0.2		
$10b_1$	8.03		0.4		1.5		0.2		17.2	2.6	69.3		8.7
$18a_1$	7.69	10.3	0.1		1.7		0.1	1.0	16.3	0.9	28.3	3.1	38.2
$13b_2$	7.62		0.1		0.3				18.2		33.8	4.1	43.6
$9a_2$	6.42				0.1		0.1				91.6		8.2
$19a_1$	6.41	12.2	3.0		1.7		0.2	0.1	0.4		69.0	0.2	13.3
$11b_1$	6.33		1.3		0.2		0.2			0.5	97.3		0.6
$14b_2$	6.05		0.2		0.1		0.3		1.2		59.7	0.7	37.8
$20a_1$	5.70	0.2	0.1				0.3	0.1	0.1		9.0	0.1	90.2
$12b_1$	5.58		0.4		0.1		0.2		0.7		13.4		85.4
$10a_2$	5.42										8.3		91.7
$15b_2$	5.30						0.1				2.2		97.7

[a] See footnote *a* in Table III. The Cl 3s orbitals are also essentially nonbonding and are omitted for clarity.

plex. The orbitals $3b_1$, $6a_1$, and $3b_2$ for C_{2v} $[GaCl_4]^-$ (Figure 3) correspond to the t_2 orbital, whose degeneracy has been lifted by the distortion from ideal T_d symmetry. It is evident, however, that this geometric distortion causes only a slight splitting of these orbitals. These orbitals correlate with the orbitals $10b_1$, $18a_1$, and $13b_2$ in $[(C_6H_6)_2Ga(GaCl_4)]$. The results in Table VI show that these orbitals are still largely localized on the $GaCl_4$ entity in this complex, although the orbital $18a_1$ shows a significant interaction with the 4s orbital on the Ga^I center. The highest energy group of occupied molecular orbitals in $[GaCl_4]^-$ are the eight nonbonding 3p orbitals on the Cl atoms. In the ideal T_d complex these would have symmetry $e + t_1 + t_2$. Again, it is clear from Figure 3 that the splitting of these levels by the purely geometric distortion from ideal T_d symmetry is small. However, these splittings become greater in the presence of the interaction with the Ga^I center in $[(C_6H_6)_2Ga(GaCl_4)]$.

The interaction of the Ga^I center with its surroundings occurs mainly through charge transfer into the vacant Ga 4p orbitals, as discussed above. Inspection of Table VI shows that many of the orbitals listed contribute to this charge transfer. The largest single contribution occurs in the orbital $19a_1$, which involves an interaction between the Cl 3p nonbonding electrons in $[GaCl_4]^-$ with the 4p orbital of the Ga^I atom. The results of the complete population analysis (Table V) show that the $[GaCl_4]^-$ ion is coordinated to the Ga^I center to an extent which is comparable to that of the C_6H_6 molecules. The total charge transfer to the Ga^I atom is 0.242e, and this consists of 0.154e from $[GaCl_4]^-$ and 0.088e from the two C_6H_6 molecules. The distribution of the transferred charge between the Ga^I 4p orbitals is not as symmetrical as it was in the complexes without the $[GaCl_4]^-$ counterion; in this case half of the transferred charge resides in the Ga $4p_z$ orbital (the p orbital that has its symmetry axis parallel to the C_2 axis). In this model complex, whose structure is closest to that observed experimentally, the amount of charge transfer from each C_6H_6 molecule is very small, at about 0.04e. This implies that the dative bond between C_6H_6 and Ga^I in these complexes is very weak indeed, and this is consistent with the experimental observation that the benzene can be easily removed from the solid complexes under vacuum at room temperature.[5] By way of comparison, the amount of charge transfer from C_6H_6 to Cl_2 in the $C_6H_6 \cdot Cl_2$ complex has been estimated to be about 0.03e by CNDO/2 molecular orbital calculations.[22] Analysis of the ^{13}C chemical shifts in the solid complex of hexamethylbenzene with tetracyanoethylene resulted in an estimate of <0.1e for the amount of charge transfer.[23] Thus, the various estimates for several complexes of benzene and substituted benzenes acting as π-donors agree on an amount of <0.1e for the degree of charge transfer. This can be compared with the rather larger value of about 0.3e, which has been determined for complexes of pyridine and substituted pyridines acting as n-donors.[24,25]

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Registry No. $[(C_6H_6)Ga]^+$, 126724-05-8; $[(C_6H_6)_2Ga]^+$, 126724-06-9; $[(C_6H_6)_2G(GaCl_4)]$, 126724-07-0.

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