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- (25) The CI results for both square and rhomboid structures were based on MO's obtained from SCF calculations for the ground state singlets (i.e., ¹B_{1g}).
- (26) In spite of the role of ψ_C and ψ_O in increasing the separation of ψ_A and ψ_B , it should be noted that this separation is still well within the "rule of thumb" upper limit of ~100 kcal/mol, below which stable nonsymmetric distortions are typically observed.
- (27) The mixing is even greater (~50-50%) when the 2-configuration wave function is obtained self-consistently (i.e., the MO's are calculated directly for the lowest ¹A_g state), as discussed in section IIIB.

Electronic Structure of Cyclopentadienylthallium(I)

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Abstract: An SCF calculation based on the recently developed theory of effective potentials has been carried out for gaseous cyclopentadienylthallium(I) in its experimental equilibrium conformation. In this compound, the thallium atom is found to be nearly neutral with an overall electron distribution of s^{1.75}p^{0.45}d^{0.71} as obtained from a Mulliken population analysis. The overlap population of 0.47 e between thallium and the cyclopentadienyl ring is about half of each C-C overlap in the ring. Bonding is principally due to the highest filled molecular orbital pair of E₁ symmetry based primarily on pd² of Tl and p of the C atoms interacting in π symmetry with respect to the C₅ axis of the molecule. A lesser contributor is the second highest a₁ orbital dominated by Tl sp interaction with the carbon p's that are again π with respect to the ring plane. The electronic basis for the half-sandwich structure of C₅H₅Tl is discussed.

The compound C₅H₅Tl, discovered by Fischer² in 1957, is a highly insoluble crystalline substance that sublimes to a monomeric vapor around 80 °C. The solid has found wide laboratory application as a donor of the cyclopentadienyl moiety. The chemical properties of solid C₅H₅Tl led Fischer to think that the compound was a half-sandwich rather than a structure exhibiting a Tl-C σ bond.

By X-ray diffraction,³ the solid form of cyclopentadienylthallium has been shown to have a chain structure consisting of alternating C₅H₅ rings and Tl atoms with the center of each ring being equidistant from the nearest thalliums and a 137° bend in the chain at each Tl atom. Raman spectroscopy⁴ did not show bands in the region where metal-ring frequencies are usually observed. Microwave spectra⁵ of the vapor of monomeric C₅H₅Tl demonstrated C_{5v} symmetry and provided a partial molecular geometry, while a full molecular structure⁶ was obtained by electron diffraction for the related compound C₅H₅In, which has the same symmetry. An interesting feature of the C₅H₅In structure is the fact that the C-H bonds are

pushed 4.5° out of the plane of the carbon ring by the indium atom.

The large core-electron structure of the thallium atom of pentadienylthallium has thus far precluded a full SCF calculation on this interesting molecule. However, the recent advances^{7,8} in effective potential theory and its application have made it feasible to study the electronic structure of the gaseous monomer of this compound by a nonempirical SCF method, and such calculations are reported below.

Computational Procedure

Our NOCOR theory of molecular effective potentials and pseudopotentials has been described previously.^{7,8} The resulting SCF equations are of the form

$$F\chi_{\nu}^i = \epsilon_{\nu}^i \chi_{\nu}^i \quad (1)$$

where χ_{ν}^i is the *i*th valence pseudo-wave function; ϵ_{ν}^i is the valence orbital energy; and *F*, the effective Fock operator, has the form

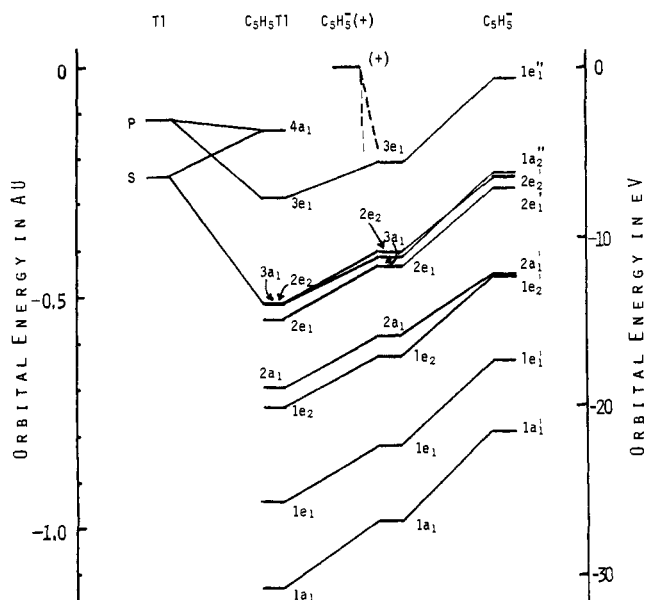


Figure 1. Valence orbital energies of a neutral thallium atom, cyclopentadienylthallium, a cyclopentadienide anion neutralized by a positive point charge at the position of the Tl in C_5H_5Tl , and a bare cyclopentadienide anion.

$$F = \hat{F} + V^{PP} + W \quad (2)$$

In equation 2, the Fock operator, \hat{F} , depends only on the coordinates of the valence electrons, V^{PP} is the molecularly optimized Phillips-Kleinman pseudopotential operator,⁸ and W is the local potential describing the core-valence Coulomb and exchange interactions. This theory (in its several minor modifications) has been tested and proven valid in a number of example calculations⁷⁻¹⁴ which were compared with all-electron SCF results, usually done in exactly the same basis set. For the study described below, we have chosen the exponential representation of W , which has been shown to be appropriate for this type of calculation.^{7,9-13,15} Use of a relativistic core¹⁸ was not deemed necessary for the purposes of this study.

The basis set consisted of an atom-optimized minimal set of Slater functions¹⁶ for each atom except H, for which a Slater function with an exponent of 1.2 was employed. Each of these functions was expanded into a set of four Gaussians. The core orbitals were chosen to be those of the neutral atoms in their ground states, i.e., 3P for carbon and 2P for thallium. The valence orbitals were defined to be the 2s and 2p functions of C and the 6s and 6p functions of Tl. Although the validity of this orbital partitioning into core and valence regions has not yet been demonstrated for Tl compounds, it has recently been employed successfully in studying compounds of Hg¹⁷ and Pb.¹⁸

The screening exponents determining the local potential are then 4.4209 au^{-1} for C and 2.7084 au^{-1} for Tl. In addition to these valence orbitals, a set of 6d polarization functions centered on the Tl was added to the molecular basis set. The exponent of these 6d functions was chosen to be 3.05 according to the procedure described by Absar and Van Wazer.¹⁹

The molecular geometry used in the calculations was based on a , the experimental Tl-ring bond length of 2.41 \AA determined from the microwave spectrum⁵ of the monomeric vapor, and b , a structure of D_{5h} symmetry of the cyclopentadienyl group with a C-C distance of 1.45 \AA and a C-H distance of 1.12 \AA . In the cyclopentadienyl ring, the hydrogen atoms were constrained to be coplanar with the carbon atoms so that the C_5H_5 ring structure could be readily compared with that of the cyclopentadienide ion.

Precisely parallel valence-electron calculations were carried out on C_5H_5Tl and as a comparison on the free cyclopentadienide ion with and without a counter charge.

Results

Recently an all-electron SCF calculation on the bare cyclopentadienide ion has been reported²⁰ which employed a basis set nearly identical to ours but assumed a somewhat different geometry (a C-C bond distance of 1.43 \AA and a C-H distance of 1.09 \AA). Comparison of the orbital energies obtained from these two calculations shows them to agree precisely as to the relative ordering of the valence orbitals, although the energies we obtain are consistently higher by approximately 0.07 au due to the larger bond distances we have employed.

In monomeric cyclopentadienylthallium, the 14 filled valence molecular orbitals exhibit orbital energies ranging from -1.12 to -0.14 au and appear in repetitive ordering of A_1 , E_1 , and E_2 symmetry except for the outermost orbital. The orbital energies are shown in Figure 1 in which they are correlated with the orbital energies of the cyclopentadienide bare anion and of this anion having a single positive charge positioned at the site of the thallium nucleus in C_5H_5Tl . It is generally found that the valence molecular orbitals of bare molecule anions exhibit orbital energies that are consistently higher by an approximately fixed amount than those obtained when the ion is accompanied by variously arranged countercharges to give a net charge of zero. Indeed the less-energetic filled molecular orbitals calculated for bare molecule anions (particularly multiply charged ones) often exhibit positive energies. A common approach to avoid this problem by better emulation of the natural ionic environment is to surround ball-shaped ions with a spherical potential surface of equal and opposite charge (a Watson sphere).²¹ Rather than treating the cyclopentadienide anion similarly by placing an appropriate oblate ellipsoid of countercharge around it, we thought this study would be better served by merely putting a point positive charge at the position of the thallium nucleus in the C_5H_5Tl structure.

Note in Figure 1 that the thallium is shown energetically to contribute significantly only to the four least stable of the filled molecular orbitals of C_5H_5Tl ($4a_1$, the $3e_1$ pair, and $3a_1$) and that all of the C_5H_5Tl molecular orbitals (except $4a_1$) are closely related to the corresponding orbitals of the cyclopentadienide ion, the orbitals of which are stabilized by a considerable amount in the thallium complex. Slightly more than half of this stabilization may be achieved by the thallium formal ionic charge alone, as shown by placing the unit positive charge at the position of the thallium nucleus. The stabilization thereby achieved is quite uniform for all of the orbitals, being $0.182 \pm 0.009 \text{ au}$, a value which should be compared with the average stabilization of 0.109 ± 0.018 for going from the charge-neutralized cyclopentadienide to the thallium complex.

The calculated electronic structure of C_5H_5Tl is described in terms of a Mulliken population analysis in Table I. According to this interpretation of the wave function, the thallium bears a charge of $+0.101$; each carbon, -0.246 ; and each hydrogen, $+0.227$. In the charge-neutralized cyclopentadienide ion, the electron bookkeeping must show a net electronic charge of -1 , and in our calculation this is achieved by a -0.344 charge for each carbon atom and $+0.144$ for each hydrogen. The atomic charges calculated for the C_5H_5Tl monomer show that the major charge transfer in this structure occurs within the cyclopentadienyl ring, with little transfer between the thallium (considered as a neutral atom) and the ring. However, the overlap population between the thallium and the cyclopentadienyl ring is quite high, being calculated as 0.480 . This situation may be described formally in terms of a transfer of

Table I. Mulliken Population Analysis of the Valence Orbitals of Cyclopentadienylthallium

molecular orbitals ^a	gross populations			overlap populations		
	Tl	C	H	Tl-ring	C-C	C-H
1a ₁	-0.047	0.395	0.014	-0.102	0.169	0.014
1e ₁	0.001	0.722	0.078	-0.002	0.268	0.089
1e ₂	0.002	0.608	0.192	0.002	0.044	0.239
2a ₁	0.003	0.281	0.118	0.003	0.043	0.119
2e ₁	0.007	0.549	0.249	0.011	0.131	0.206
2e ₂	0.001	0.678	0.122	0.001	0.142	0.125
3a ₁	0.236	0.353	0	0.282	0.101	0
3e ₁	0.743	0.651	0	0.476	0.086	0
4a ₁	1.953	0.009	0.000	-0.197	0.009	0.001
Total	2.899	4.246	0.773	0.474	0.993	0.793

^a For the orbitals of E symmetry, the electronic populations correspond to the particular degenerate orbital pair.

essentially a whole electron from the C₅H₅⁻ anion to the Tl⁺ cation, with about a quarter of this transferred charge being involved in back bonding between the C₅H₅ ring and the essentially neutral thallium atom.

The data of Table I show that, except for some negative overlap in the most stable of the valence orbitals (orbital 1a₁), the main contributions to the thallium gross population as well as to the total overlap between the thallium and the cyclopentadienyl ring are to be found in the four less-stable molecular orbitals (3a₁, 3e₁, and 4a₁). Electron-density plots of these outer orbitals are shown in Figure 2, which corresponds to a slice through the C₅H₅Tl molecule passing through the C₅ axis, the thallium atom, and one of the carbon atoms of the ring. It is obvious from these diagrams that all four of these orbitals exhibit essentially no electron density in the plane of the C₅H₅ ring. Indeed, in the corresponding orbitals of the cyclopentadienide bare ion (see Figure 1), the ones related to 3a₁ and the 3e₁ pair represent pure ring π bonding, with zero electron density in the ring plane. However, in the cyclopentadienide anion neutralized by a point charge on one side of the plane, as well as in the monomeric C₅H₅Tl, there is a small amount of charge in the ring plane of these three orbitals due to polarization of the electronic cloud along the C₅ axis. Table I and Figure 2 show that in orbital 3a₁ there is little net charge (0.095 e) on the thallium and considerable shared charge which shows up in the electronic charge associated with the C₅H₅ ring.

A more detailed gross population analysis than is presented in Table I shows that, for the contribution of the thallium atomic orbitals to molecular orbital 3a₁, a charge of 0.138 is attributed to the thallium s orbitals, 0.068 to its p orbitals, and 0.031 to its d orbitals, with the p and d contributions being σ with respect to the C₅ axis of the molecule. It should be noted that an orbital such as 3a₁ which is π bonding with respect to the cyclopentadienyl ring is σ bonding with respect to interactions between the ring and the thallium atom (i.e., along the C₅ axis). On the other hand, the pair of 3e₁ molecular orbitals must be π bonding with respect to the C₅ axis since their combination shows no electron density in the center of the cyclopentadienyl ring. The thallium contribution to the gross population of the pair of 3e₁ orbitals consists of 0.202 p and 0.540 d charges, both exhibiting π symmetry with respect to the C₅ molecular axis. It is clear that the 3e pair of molecular orbitals represents π interaction between the Tl and the cyclopentadienyl ring. As shown by Table I and Figure 2, orbital 4a₁ consists of a thallium lone pair. The detailed gross population analysis shows that the thallium contribution to this orbital is made up of 1.632 s, 0.225 p, and 0.100 d electronic charges, all having σ symmetry with respect to the C₅ axis.

The bonding between the thallium atom and the cyclopentadienyl ring can be investigated with respect to the atomic contributions to the overlap between the thallium and the five

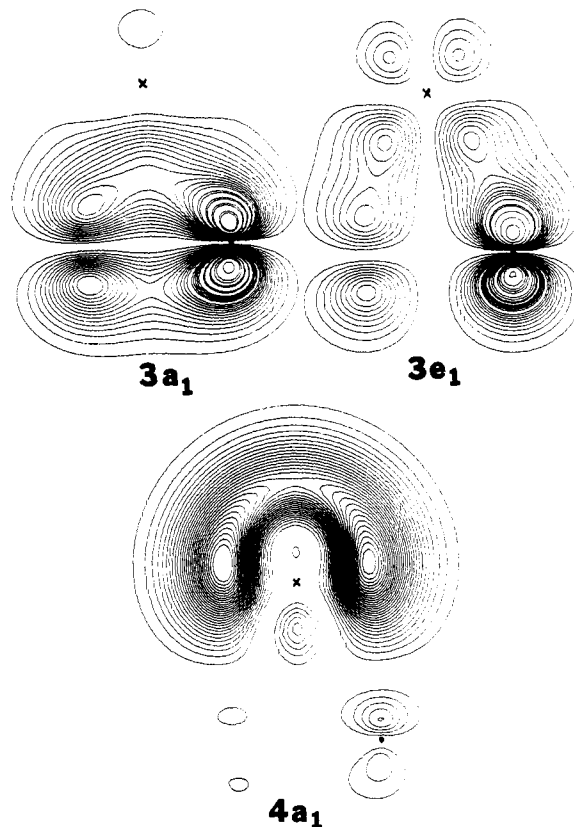


Figure 2. Electron-density contours for the three highest valence molecular orbitals of cyclopentadienylthallium. The plane of the figure contains the C₅ axis and bisects the Tl and one of the C atoms. The cross denotes the position of the Tl atom, and the dot the position of the C in each orbital.

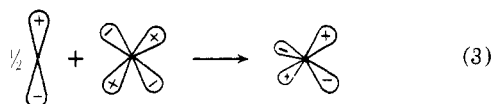
carbon atoms of the ring for each molecular orbital. Thus, for the 3e₁ orbital pair, the main contribution to the Tl-ring overlap (+0.282 e) is attributable to interaction between the thallium d orbitals that exhibit π symmetry with respect to the C₅ axis and the carbon p orbitals, with a somewhat smaller contribution (+0.221 e) from overlap between the p electrons on both centers (again, with π symmetry with respect to the C₅ axis). There is also a much smaller antibonding contribution to this molecular orbital from overlap of the p_π and d_π electrons of the thallium with the s electrons of the carbon atoms, which because of the cyclic structure of the C₅H₅ moiety may be considered as exhibiting a paired π-like symmetry with respect to its C₅ axis. A similar treatment for molecular orbital 3a₁ shows σ overlap between the thallium s orbital and the five carbon p orbitals (+0.173 e) and between the p orbitals of the thallium and carbon atoms (+0.115 e). For molecular orbital

$3a_1$ there is also a smaller antibonding contribution due to interaction between the Tl d and the p's of the C atoms.

Discussion

Cyclopentadienyl-metal complexes are usually segregated²² into three categories: (1) ionic species, $M^+C_5H_5^-$, (2) those in which the metal is centered on the C_5 axis of the ring (called π complexes), and (3) those in which the metal lies closer to one of the ring carbons than to the others, called σ complexes. Cyclopentadienylthallium(I) and its indium analogue lie in the class of π -type complexes, although the s^2 configuration of the Tl^+ ion and the s^2p configuration of the neutral Tl atom do not seem to be conducive to such bonding. According to our calculation this apparent problem is resolved by the promotion of almost a full electronic charge (0.69 e) to contracted outer d orbitals. Indeed for the gross population of the thallium atom in cyclopentadienylthallium(I), we have obtained the following accounting, in which the subscripts σ and π refer to the atomic-orbital symmetry with respect to the fivefold axis of rotation of the molecule: $s_\sigma^{1.75}p_\sigma^{0.26}p_\pi^{0.19}d_\sigma^{0.13}d_\pi^{0.58}$.

As shown by the data of Table I, the population for the overlap between the thallium and the C_5H_5 ring for the molecular orbitals ($1a_1$, $1e_2$, $2a_1$, $2e_2$, $3a_1$, and $4a_1$) that exhibit σ symmetry with respect to the fivefold axis adds up to only -0.01 , so that the bonding of the thallium to the ring is dominated by the e_1 orbitals. Of these, orbital $3e_1$ contributes nearly all of the overlap, and this molecular orbital is based on thallium pd^2 hybridization of the form $\frac{1}{2}(p_x + 2d_{xz}) + \frac{1}{2}(p_y + 2d_{yz})$, each part of which has the following general shape (for the z coordinate being the C_5 axis of the molecule):



It is this hybridization that allows the thallium(I) atom preferentially to direct its valence charge toward the cyclopenta-

dienyl ring and to form a stable π compound with only a single cyclopentadienyl moiety. This may account for the short Tl-ring bond length in the monomeric C_5H_5Tl (2.41 Å compared to 2.51 Å in monomeric C_5H_5In and 3.19 Å in its polymer) and also the tendency of Tl to form stable π compounds in comparison to elements, such as Au and Hg, that lack valence p electrons and thus are found to form σ complexes.

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