# Mercury(II) Electrophiles as Electron Acceptors. Charge-Transfer Complexes with **Organometal and Aromatic Donors**

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Novel charge-transfer (CT) absorption bands are reported for electron donor-acceptor complexes of mercuric chloride and a series of tetraalkyltin compounds. The CT transition energies  $h\nu_{\rm CT}$  are correlated with ionization potentials  $I_{\rm D}$  of the alkylmetals. Steric interactions within these complexes are larger than those previously examined in the corresponding iodine and bromine complexes, which suggests that the mercury(II) acceptor is intimately associated with the organometal donor. The latter coincides with the observation of multiple charge-transfer absorption bands in hexamethylbenzene complexes of various mercury(II) derivatives, shown to arise from distortion of the linear X-Hg-X. Bent structures are proposed for both  $\sigma$  and  $\pi$  complexes of mercury(II) derivatives.

## Introduction

Mercury(II) complexes have been commonly employed as electrophiles in a variety of well-known organic and organometallic processes, such as addition to olefins,<sup>1</sup> aromatic substitution,<sup>2</sup> cleavage of alkylmetals,<sup>3</sup> etc. Despite such extensive use of mercury(II) derivatives, surprisingly little is known about the basic interactions involved in the activation barrier for these electrophilic processes.4

Although there are a few scattered reports in the extant literature of complex formation between mercuric halides and alkenes or arenes,<sup>5,6</sup> there has been no attempt to utilize such information for elucidating the mechanism of electrophilic mercurations. Earlier, we described how charge-transfer (CT) interactions in electron donor-acceptor (EDA) complexes can be incorporated as a mechanistic probe for electrophilic halogenations.<sup>7</sup> Since the application of this analysis depends on the knowledge gained from complex formation, our initial task is to determine whether mercury(II) derivatives do behave generally as electron acceptors. To this end, we examined the electron acceptor properties of a series of mercury(II) complexes with two basically different types of electron donors, namely, the organometallic tetraalkyltin compounds and the aromatic hexamethylbenzene, as representatives of  $\sigma$  and  $\pi$  donors, respectively.

Tetraalkyltin compounds belong to a general class of organometals in which the ionization occurs from highest occupied molecular orbital (HOMO) which has  $\sigma$ -bonding character; that is, they are  $\sigma$  donors.<sup>8</sup> Furthermore, the systematic variation of the alkyl ligands, by  $\alpha$ - and  $\beta$ methyl branching, allows the stereochemical properties as

 (a) Freeman, F. Chem. Rev., 1975, 75, 439. (b) Traylor, T. G. Acc. Chem. Res. 1969, 2, 152. (c) Fahey, R. C. Top. Stereochem. 1968, 3, 237.
 (2) Taylor, R. Compr. Chem. Kinet. 1972, 13, Chapter 1, p 186.
 (a) Abraham, M. H. Compr. Chem. Kinet. 1973, 12, Chapter 6, p
 (b) Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials"; McGraw-Hill: New York, 1968.
 (4) (a) Matteson, D. S. "Organometallic Reaction Mechanisms"; Aca-demic Press: New York, 1974. (b) Kochi, J. K. "Organometallic Mech-anisms and Catalysis"; Academic Press: New York, 1978; Chapter 18.
 (5) (a) Eliezer, I. J. Chem. Phys. 1965, 42, 3625. (b) Eliezer, I.; Avinur, P. Ibid. 1971, 55, 2300. (c) Eliezer, I.; Avinur, P. J. Chem. Soc., Faraday Trans 2 1974, 70, 1316. (d) See, however, Weiss, K. J. Chem. Phys. 1972, 56, 5746. 56, 5746.

(6) Vezzosi, I. M.; Peyronel, G.; Zanoli, A. Inorg. Chim. Acta. 1974, 8, 229

(7) Fukuzumi, S.; Kochi, J. K. J. Am. Chem. Soc. 1980, 102, 2141. (8) Fehlner, T. P.; Ulman, J.; Nugent, W. A.; Kochi, J. K. Inorg. Chem. 1976, 15, 2544 for leading references.

well as the ionization potentials of these alkylmetals to be finely tuned over a wide range.

Among numerous aromatic hydrocarbons, hexamethylbenzene (HMB) is ideally suited to be used as a  $\pi$ -electron donor with a variety of mercury(II) acceptors, since it has a low ionization potential (7.85 eV) but does not readily engage in further reactions.<sup>9,10</sup> (For example. the other partially alkylated arenes, such as mesitylene, undergo facile electrophilic substitution with mercury(II) trifluoroacetate.<sup>11</sup>)

### Results

Charge-Transfer Spectra of Mercury(II) Chloride with Tin Alkyls. The admixture of mercury(II) chloride with tetrabutyltin in acetonitrile solutions results in an immediate and substantial increase in the absorbance of the region in the electronic spectrum between 230 and 270 nm,<sup>12</sup> especially by comparison with the sum of the separate absorbances of  $HgCl_2$  and  $n-Bu_4Sn$  at the same concentrations. Indeed, the difference spectrum obtained under carefully calibrated conditions (see Experimental Section) clearly shows the presence of a new absorption band with a broad but distinct maximum centered at  $\lambda_{max}$ 242 nm, as illustrated in Figure 1. The validity of the difference spectrum was confirmed by the observation that the position of  $\lambda_{max}$  did not depend on tetrabutyltin, in the concentration range from  $5.0 \times 10^{-3}$  to  $3.0 \times 10^{-2}$  M.<sup>13</sup> No additional bands were discerned at longer wavelengths. (The difference spectrum could not be measured at shorter wavelengths owing to the severe overlap with the absorption bands of n-Bu<sub>4</sub>Sn and HgCl<sub>2</sub>.<sup>14</sup>) The broad absorp-

(14) When the overlap of absorption bands of n-Bu<sub>4</sub>Sn and HgCl<sub>2</sub> exceeds the detection limit of the valid difference spectrum described above,<sup>13</sup> the CT absorbance cannot be determined.

<sup>(1) (</sup>a) Freeman, F. Chem. Rev., 1975, 75, 439. (b) Traylor, T. G. Acc.

<sup>(9)</sup> Tamres, M.; Virzi, D. R.; Searles, S. J. Am. Chem. Soc. 1953, 75, 4358

<sup>(10)</sup> Undoubtedly owing to the absence of aromatic protons, the loss of which can lead to nuclear substitution.

<sup>(11)</sup> Brown, H. C.; McGary, C. W., Jr. J. Am. Chem. Soc. 1955, 77, 2310.

<sup>(12)</sup> For HgCl<sub>2</sub>,  $\lambda_{max} \sim 200$  nm ( $\epsilon \sim 4 \times 10^3$ ) in various solvents.<sup>23</sup> In CH<sub>3</sub>CN,  $\epsilon(240$  nm) =  $3 \times 10^2$  M<sup>-1</sup> cm<sup>-1</sup> in Figure 2 from ref 5d.

<sup>(13) (</sup>a) It is important to point out the necessity of optimizing the concentrations of the reactants, as well as the sensitivity of the spectrometer, in order to obtain a valid difference spectrum when there is overlap of absorption bands. Otherwise the maximum concentrations of  $R_4Sn$  and  $HgCl_2$  would be limited to below those values which would make the difference spectrum inaccurate. (b) Thus the early report<sup>5b</sup> of mercury(II) complexes with arenes was questioned,<sup>6</sup> when the difference spectrum was found to be heavily dependent on the concentration of HgBr<sub>2</sub> in the pure arene.



Wavelength, nm

Figure 1. Charge-transfer spectra of mercury(II) chloride complexes with some tetraalkyltin compounds in acetonitrile at 25 °C. [Me4Sn]g  $\begin{array}{l} \text{HgCl}_{2} = 4.90 \times 10^{-3} \text{ M}; \ [\text{HgCl}_{2}]_{0} = 2.50 \times 10^{-3} \text{ M}; \ [\text{HgCl}_{3}]_{0} = 1.68 \times 10^{-2} \\ \text{M}; \ [\text{HgCl}_{2}]_{0} = 5.00 \times 10^{-3} \text{ M}; \ [n\text{-Bu}_{4}\text{Sn}]_{0} = 2.02 \times 10^{-2} \text{ M}; \ [\text{HgCl}_{2}]_{0} \\ = 5.00 \times 10^{-3} \text{ M}; \ [\textit{I}\text{-}\text{Pr}_{4}\text{Sn}]_{0} = 1.00 \times 10^{-2} \text{ M}; \ [\text{HgCl}_{2}]_{0} = 1.00 \times 10^{-2} \\ \text{M}. \ \text{The spectrum for Me}_{4}\text{Sn was measured at 3 °C (see Ex$ perimental Section).



Figure 2. (a) Variation in the intensity of the CT absorbance with the concentrations of tetraalkyltin compounds in acetonitrile solutions of HgCl<sub>2</sub> at 25 °C, monitored at 250 nm. (O) sec-Bu<sub>4</sub>Sn, [HgCl<sub>2</sub>]<sub>0</sub> = 5.00 × 10<sup>-3</sup> M; (**Φ**) Et<sub>4</sub>Sn, [HgCl<sub>2</sub>]<sub>0</sub> = 5.00 × 10<sup>-3</sup> M; (**Φ**) t<sub>4</sub>Sn, [HgCl<sub>2</sub>]<sub>0</sub> = 5.00 × 10<sup>-3</sup> M; (**Φ**) *n*-Bu<sub>4</sub>Sn, [HgCl<sub>2</sub>]<sub>0</sub> = 5.00 × 10<sup>-3</sup> M; (**Φ**) *n*-Bu<sub>4</sub>Sn, [HgCl<sub>2</sub>]<sub>0</sub> = 1.00 × 10<sup>-2</sup> M. (b) Variation in the concentration of HgCl<sub>2</sub> at different wavelengths. [HgCl<sub>2</sub>]<sub>0</sub> = (**Φ**) 1.00 × 10<sup>-3</sup> M, (**O**) 5.00 × 10<sup>-3</sup> M.

tion bands in Figure 1 are characteristic of intermolecular, electron donor-acceptor EDA complexes.<sup>15-17</sup>

The intensity of the charge transfer absorption band is linearly related to the concentrations of the tetraalkyltin compound and HgCl<sub>2</sub>, as shown in Figures 2, a and b, respectively. Furthermore, the linearity obtains irrespective of the wavelength at which the CT absorbance is measured. Since tetraalkyltin compounds and  $HgCl_2$  are both monomeric in acetonitrile solutions,<sup>18</sup> we conclude that the CT absorption bands are due to 1:1 complexes A of tetraalkyltin and mercury(II) chloride, as described in eq 1. The linear correlations in Figure 2 correspond to

$$n-\mathrm{Bu}_4\mathrm{Sn} + \mathrm{HgCl}_2 \xrightarrow{K_{\mathrm{DA}}} [n-\mathrm{Bu}_4\mathrm{SnHgCl}_2]$$
 (1)

formation constants of EDA complexes in which  $K_{DA}[D_0]$  $\ll$  1, according to the Benesi-Hildebrand equation, reexpressed by Person as:<sup>19,20</sup>

$$A = \frac{\epsilon K_{\mathrm{DA}}[\mathrm{A}_0][\mathrm{D}_0]}{1 + K_{\mathrm{DA}}[\mathrm{D}_0]}$$
(2)

 (17) Fukuzumi, S.; Kochi, J. K. J. Am. Chem. Soc. 1980, 102, 7290.
 (18) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed

; Interscience: New York, 1972; p 518. (19) Benesi, H. A.; Hildebrand, J. H. J. Am. Chem. Soc. **1949**, *71*, 2703.

TABLE I: Charge-Transfer Bands of Mercury Chloride **Complexes with Tetraalkyltin Compounds in** Acetonitrile at 25 °C

R₄Sn	I <sub>D</sub> , <sup>a</sup> eV	λ <sub>max</sub> , nm	<sup>hν</sup> cτ, eV	$\frac{\log \epsilon K_{\mathrm{DA}}}{\mathrm{M}^{-2} \mathrm{cm}^{-1}}$	$h\nu_{\mathrm{CT}}(\mathrm{I}_2),^b$ eV
1 Me <sub>4</sub> Sn	9.69	235	5.27	с	4.59
2 Et <sub>4</sub> Sn	8.90	<b>244</b>	5.08	3.3	4.27
3 <i>n</i> -Pr₄Sn	8.82	243	5.10	3.3	4.27
4 <i>n</i> -Bu₄Sn	8.76	242	5.12	3.5	4.30
5 n-BuSnMe,	9.10	240	5.17	3.3	4.49
6 n-Bu,SnMe,	8.80	247	5.02	с	4.35
7 i-Pr, SnMe,	8.56	249	4.98	<b>3.4</b>	4.27
8 t-Bu SnMe	8.22	255	4.86	с	4.10
9 <i>i</i> -Bu <sub>4</sub> Sn	8.68	243	5.10	2.9	4.22
10 <i>i</i> -Pr .Sn	8.46	241	5.14	3.0	4.20
11 s-Bu₄Sn	8.45	242	5.12	2.9	4.14

<sup>a</sup> From ref 24. <sup>b</sup> From ref 25. <sup>c</sup> Not determined.

TABLE II: Solvent Effects on the Charge-Transfer Bands of  $HgCl_2$  Complexes with  $R_4Sn$ 

		solv	solvent <sup>a</sup>	
R₄Sn	CH <sub>3</sub> CN	MeOH	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub> - hexane <sup>b</sup>
<i>n</i> -Bu₄Sn Me₄Sn	$242 \pm 1$ 235 ± 1	241 ± 1	$241 \pm 1$ 234 ± 2	242 ± 2
i-Bu <sub>4</sub> Sn i-Pr <sub>2</sub> SnMe <sub>2</sub>	$243 \pm 1$ 249 ± 1	$242 \pm 1$	$243 \pm 2$ $247 \pm 2$	242 ± 2
s-Bu₄Sn ´	$242 \pm 1$	$242 \pm 1$	$242 \pm 2$	$241 \pm 2$

<sup>a</sup> Numbers refer to  $\lambda_{max}$  in nm. <sup>b</sup> 1:2 v/v.



WAVELENGTH, nm

Figure 3. Charge-transfer spectra of EDA complexes of mercury(II) halides with hexamethylbenzene: (a)  $4.5\times10^{-3}$  M HgCl<sub>2</sub> and 2.1  $\times10^{-2}$  M HMB; (b)  $2.5\times10^{-3}$  M HgBr<sub>2</sub> and  $8.2\times10^{-2}$  M HMB. The dashed curve represents the fit of Gaussian curves.

where A and  $\epsilon$  are the CT absorbance and the extinction coefficient, respectively,  $K_{DA}$  is the formation constant in eq 1, and  $[D_0]$  and  $[A_0]$  are the initial concentrations of the tetraalkyltin donors and the HgCl<sub>2</sub> acceptor, respectively, in an absorption cell of unit length. Thus the absence of significant curvature in Figure 2 indicates that the formation constants  $K_{DA}$  in eq 1 are small,<sup>21</sup> as may be expected from the limited orbital overlap between the tetraalkyltin  $\sigma$  donor and the mercury(II) acceptor.<sup>22,23</sup>

Figure 1 includes the charge-transfer spectra of HgCl<sub>2</sub> with various symmetrical tetraalkyltin compounds R<sub>4</sub>Sn, where R = Me, Et, and *i*-Pr. The CT spectral data for a series of unsymmetrical tetraalkyltin compounds RSnMe<sub>3</sub>

<sup>(15) (</sup>a) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wi-Transfer Complexes"; Academic Press: New York, 1969.

<sup>(16)</sup> The half-life of the CT absorbance of n-Bu<sub>4</sub>Sn under the conditions described in Figure 1 is 150 min, and it is inversely proportional to the concentration of n-Bu<sub>4</sub>Sn. The chemical reactions leading from these transient absorption bands are described in the following paper

<sup>(20)</sup> Person, W. B. J. Am. Chem. Soc. 1965, 87, 167.

<sup>(21)</sup> Use of higher concentrations was precluded owing to the following chemical reaction (vide infra) and the limitations described above to be the second of the first of  $K_{DA}$  can be estimated to be less than  $1.5 \, M^{-1}$ for Et<sub>4</sub>Sn based on the procedure described earlier.<sup>26</sup> (22) The LUMO of HgCl<sub>2</sub> is a mercury-centered  $2\pi_u^*$  orbital.<sup>23</sup> (23) (a) Griffiths, T. R.; Anderson, R. A. J. Chem. Soc., Faraday Trans. 2 1979, 75, 957. (b) Griffiths, T. R.; Anderson, R. A. Inorg. Chem.

<sup>1979, 18, 2506.</sup> 

TABLE III:	Charge-Transfer Ba	nds of Mercury(II) C	omplexes with Hexamet	hylbenzene in Methylene	Chloride at 25 °C
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	HgX <sub>2</sub>	$h_{v_{CT}}^{1,a}$ nm	$h\nu_{\rm CT}^{2,a}$ nm	$\Delta' h \nu_{\rm CT}, b  {\rm eV}$	$K_{\mathbf{DA}}, c \mathbf{M}^{-1}$	$\log \epsilon$ , $g M^{-1} cm^{-1}$
	a HgCl,	300	< 285	>0.22	$0.76 \pm 0.08$	3.1
	b HgBr,	312	286	0.36	$0.60 \pm 0.06$	3.1
	c Hg(CN)	302 sh	< 285	>0.25	$0.39 \pm 0.04$	2.9
	d Hg(O,ĆMe),	300 sh	289	0.19	$0.80 \pm 0.08$	2.6
	e Hg(O,CCHMe,),	302 sh	< 290	>0.15	$1.7 \pm 0.2$	2.6
	$f Hg(O, CCMe_{1}),$	302 sh	286	0.21	$2.2 \pm 0.2$	2.5
	$g Hg(O, CBu^n)$	<b>303 sh</b>	286	0.24	$1.7 \pm 0.2$	2.4
	h Hg(O,CCH,Cl),	305 sh	290	0.19	$2.1 \pm 0.2$	2.9
	j Hg(O,CCCHCl,)	303 sh	292	0.16	$0.76 \pm 0.08$	3.0
	k Hg(O,CCHF,)	310 sh	299	0.15	$3.8 \pm 0.4$	2.9
	$l Hg(O_2CCF_3)_2$	323  sh	305	0.22	$15.6 \pm 1.1$	3.4
I,		376 <sup>d, e</sup>	a a uf	0	$1.35^{e}$	$3.9^{e}$
TCNB		426'	334/	0.8		
				_		

<sup>*a*</sup> sh: shoulder. <sup>*b*</sup>  $\Delta' h \nu_{CT} = h \nu_{CT}^2 - h \nu_{CT}^1$  in eV. <sup>*c*</sup> Formation constant. <sup>*d*</sup> This study measured in methylene chloride. <sup>*e*</sup> From ref 30. <sup>*f*</sup> From ref 31. <sup>*g*</sup> Experimental error < ±0.1.

and  $R_2SnMe_2$  are listed in Table I, together with values of  $\epsilon K_{DA}$ . The CT transition energies  $h\nu_{CT}$  are also tabulated along with the gas-phase ionization potentials<sup>24</sup> of all of the tetraalkyltin complexes. For comparison, the values of  $h\nu_{CT}$  for the corresponding iodine complexes with the same tetraalkyltin compounds<sup>25</sup> are included in Table I. Although the presence of charge-transfer bands of the other mercury(II) halides HgBr<sub>2</sub> and HgI<sub>2</sub> was confirmed at longer wavelengths, their absorption maxima could not be determined with accuracy, owing to extensive overlap with their own bands.<sup>26</sup>

The charge-transfer spectra of tetraalkyltin-mercury(II) halide complexes were compared in several polar and less polar solvents such as methanol, methylene chloride, and hexane mixed with methylene chloride. It is noteworthy that the absorption maxima were essentially invariant in different solvents, within the experimental uncertainty given in Table II. A similar insensitivity of  $h\nu_{\rm CT}$  to solvent changes was previously noted in the iodine complexes of the same series of tetraalkyltin compounds.<sup>25</sup>

Charge-Transfer Spectra of Various Mercury(II) Derivatives with Hexamethylbenzene. The characteristic broad charge-transfer spectrum shown in Figure 3a is obtained from hexamethylbenzene (HMB) and mercury(II) chloride in methylene chloride solution. The absorption maximum at 300 nm for the EDA complex of mercury(II) chloride and hexamethylbenzene **B** (see eq 3) is signifi-



cantly red shifted relative to  $\lambda_{max}$  for the alkyltin EDA complexes A in Table I. The absorption maximum of the CT band for the corresponding mercury(II) bromide complex is further red shifted to 312 nm. A close scrutiny of the absorption spectrum of HgBr<sub>2</sub>HMB obtained by the difference technique reveals the presence of a well-resolved second band centered at 286 nm, as shown in Figure 3b. (The dashed lines in the figure represent the Gaussian curves for the two absorption bands.) Unfortunately, the difference spectrum was of no avail in locating the highenergy band for the HgCl<sub>2</sub> complex, since it is obscured



**Figure 4.** Charge-transfer spectrum of the EDA complex of HMB and  $Hg(O_2CCF_3)_2$ : (a) 2.0 × 10<sup>-2</sup> M Hg(O\_2CCF\_3)\_2 and 2.5 × 10<sup>-3</sup> M HMB in CH<sub>2</sub>Cl<sub>2</sub>; (b) 2.0 × 10<sup>-3</sup> M Hg(O<sub>2</sub>CCF<sub>3</sub>)\_2 and 5.8 × 10<sup>-3</sup> M HMB.



**Figure 5.** Left: The Benesi–Hildebrand plot for (a)  $2.5 \times 10^{-3}$  M Hg(O<sub>2</sub>CCHMe<sub>2</sub>)<sub>2</sub>, (b)  $2.0 \times 10^{-3}$  M Hg(O<sub>2</sub>CCMe)<sub>2</sub>, and (c)  $2.0 \times 10^{-3}$  M HgBr<sub>2</sub>. Right: Continuous variation curves for [Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>] + [HMB] =  $1.5 \times 10^{-2}$  M at (•) 323 and (O) 350 nm. The solid curves are calculated from  $K_{DA} = 15.6$  M<sup>-1</sup>,  $\epsilon = 2.34 \times 10^{3}$  M<sup>-1</sup> cm<sup>-1</sup> at 323 nm and  $1.07 \times 10^{3}$  M<sup>-1</sup> cm<sup>-1</sup> at 350 nm.

by the intense  $\pi - \pi^*$  transition of hexamethylbenzene ( $\lambda_{max}$  273, log  $\epsilon$  2.35).<sup>27,28</sup>

The absorption maximum of the EDA complex of mercury(II) trifluoroacetate and HMB appears at 315 nm, with a shoulder at 323 nm. The resolution into two bands with  $\lambda_{max}$  305 and 323 is clearly shown in Figure 4 by the fit of two Gaussian curves at several concentrations of Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>HMB. Indeed the high solubility of Hg-(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub> coupled with the large extinction coefficient for the EDA complex in methylene chloride allowed an extensive search for additional absorption bands at both longer and shorter wavelengths using concentrations as dilute as  $10^{-3}$  M to obtain valid difference spectra. However, no other bands were found.

Charge-transfer absorption bands were also observed for the EDA complexes of hexamethylbenzene with the various mercury(II) derivatives listed in Table III. In each case, the absorption spectrum was similar to that of Hg- $(O_2CCF_3)_2HMB$  and showed two bands, the first as a

<sup>(24)</sup> Wong, C. L.; Mochida, K.; Gin, A.; Weiner, M. A.; Kochi, J. K.
J. Org. Chem. 1979, 44, 3979.
(25) Fukuzumi, S.; Kochi, J. K. J. Phys. Chem. 1980, 84, 608, 617.

<sup>(26)</sup> Fukuzumi, S.; Kocni, J. K. J. Phys. Chem. 1950, 34, 605, 617. (26) For example, the absorption maxima of both HgBr<sub>2</sub> ( $\lambda_{max}$  231 nm) and HgI<sub>2</sub> ( $\lambda_{max}$  270 nm) occur in the region of the CT bands with high extinction coefficients of 4.2 × 10<sup>3</sup> and 5.9 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively.<sup>23</sup>

<sup>(27)</sup> Nakamoto, K. J. Am. Chem. Soc. 1952, 74, 390.

<sup>(28)</sup> The same complication applies to the locally excited bands of the mercury(II) halides.



Figure 6. Correlation of the charge-transfer transition energy in  $\mathrm{HgCl}_2$ complexes with the ionization potential of the tetraalkyltin compounds: (•) R<sub>4</sub>Sn and (O) RSnMe<sub>3</sub> and R<sub>2</sub>SnMe<sub>2</sub> as identified in Table I.

shoulder. The difference in the frequency of the two bands,  $\Delta \nu_{\rm CT}$ , varied systematically according to the nature of the ligand. The spectral data for the EDA complexes of hexamethylbenzene with a series of mercury(II) derivatives are summarized in Table III.

The accurate measurement of the formation constants of the hexamethylbenzene complexes was facilitated by their stability, even in the presence of excess hexamethylbenzene. Under these conditions, the formation constant in eq 3 is given by the classic Benesi-Hildebrand expression:19

$$[\mathbf{A}_0]/A = 1/(K_{\mathrm{DA}}\epsilon[\mathbf{D}_0]) + 1/\epsilon \tag{4}$$

where the symbols are the same as those in eq 2. As shown in the left-hand part of Figure 5 the plots of 1/A against  $1/[D_0]$  are linear with clear positive intercepts from which  $\epsilon$  and  $K_{\rm DA}$  can be readily determined for all of the mercury(II) complexes with HMB. The formation of a 1:1 complex between  $Hg(O_2CCF_3)_2$  and HMB is further confirmed in the right-hand part of Figure 5, in which the continuous variation of the absorbances at both 323 and 350 nm was carried out at a constant level of  $[Hg(O_2CC F_{3}_{2}$ ] + [HMB] = 1.50 × 10<sup>-2</sup> M. The experimental data are indicated by the filled and open circles. The fit is unmistakable to the solid curves for the absorbances calculated by using  $K_{\text{DA}} = 15.6 \text{ M}^{-1}$  with  $\epsilon = 2.34 \times 10^3$  and  $1.07 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 323 and 350 nm, respectively.<sup>29</sup>

The formation constants and extinction coefficients obtained in this manner are included in Table III. For comparison, the spectral data for the electron donor-acceptor complexes C and D of hexamethylbenzene with the



well-known acceptors, iodine and tetracyanobenzene are also tabulated.<sup>30,31</sup> It is interesting to note that only one absorption band has been observed in C, whereas two bands have been reported in **D**.

#### Discussion

The successful observation of charge-transfer transitions for the novel electron donor-acceptor (EDA) complexes of mercury(II) with organometals in this study bears directly on the previous examination of halogen complexes.<sup>25</sup> This interrelationship is particularly germane for the quantitative comparison of the steric effects of mercury(II) and halogen as electron acceptors, since they are interacting

with a common series of electron donors. In order to develop a quantitative basis for the evaluation of steric effects in these EDA complexes, we rely on Mulliken Theory to establish the nature of the CT transition energy,  $h\nu_{\rm CT}$ .<sup>7</sup> According to Mulliken and others, <sup>15,32</sup>  $h\nu_{\rm CT}$  corresponds to the electronic excitation from the ground state  $\Psi_{\rm N}$  of the complex to the excited singlet state  $\Psi_{\rm E}$ , as described in eq 5 and 6, respectively, where  $\Psi(DA)$  and  $\Psi_{\rm N} =$ 

$$a\Psi(\mathbf{D}\mathbf{A}) + \sum_{i} b_{i}\Psi_{i}(\mathbf{D}^{+}\mathbf{A}^{-}) + \sum_{j} c_{j}\Psi_{j}(\mathbf{D}^{*}\mathbf{A}) + \sum_{k} d_{k}\Psi_{k}(\mathbf{D}\mathbf{A}^{*})$$
(5)
$$\Psi_{\mathrm{E}} = a^{*}\Psi(\mathbf{D}\mathbf{A}) + \sum_{i} b_{i}^{*}\Psi_{i}(\mathbf{D}^{+}\mathbf{A}^{-}) + \sum_{j} c_{j}^{*}\Psi_{j}(\mathbf{D}^{*}\mathbf{A}) + \sum_{j} d_{k}^{*}\Psi_{k}(\mathbf{D}\mathbf{A}^{*})$$
(6)

 $\Psi_i(D^+A^-)$  represent the wave functions for the no-bond structure and the *i*th zero-order electron-transfer singlet state, respectively.  $\Psi_i(D^*A)$  and  $\Psi_k(DA^*)$  are the wave functions of the zero-order singlet states corresponding to the *i*th and *k*th local excitation within the electron donor and acceptor, respectively. For the weak EDA complexes, of the type between mercury(II) and tetraalkyltin in which the overlap integrals between the donor and acceptor orbitals are small, the transition energy can be expressed to first-order approximation as <sup>33</sup>

$$h\nu_{\rm CT}{}^i = I_{\rm D}{}^l - E_{\rm A}{}^m + \omega \tag{7}$$

where  $h\nu_{CT}^{i}$  corresponds to the transition energy from  $\Psi(DA)$  to  $\Psi_{i}(D^{+}A^{-})$ .  $I_{D}^{l}$  is the *l*th ionization potential of the donor,  $E_A^m$  is the *m*th electron affinity of the acceptor, and  $\omega$  is the interaction energy between the donor and acceptor moieties in the  $\Psi_i(D^+A^-)$  state. The chargetransfer absorption bands in Table I correspond to the first or lowest CT band in eq 7, since there are no additional discrete bands at lower energies other than those ascribed to  $\lambda_{max}$ . Accordingly, for our purposes here, the observed CT absorption band corresponds to eq 8, where  $\nu_{\rm CT}$  is  $\propto$ 

$$h\nu_{\rm CT} = I_{\rm D} - E_{\rm A} + \omega \tag{8}$$

 $1/\lambda_{\text{max}}$ ,  $I_{\text{D}}$  is the first vertical ionization potential of R<sub>4</sub>Sn, and  $E_A$  is the first vertical electron affinity of the acceptor, i.e., mercury(II) or halogen. The relationship in eq 8 predicts a linear correlation between  $h\nu_{\rm CT}$  and  $I_{\rm D}$  with a unit slope, provided the interaction energy  $\omega$  remains invariant in a series of EDA complexes involving a family of structural related donors.<sup>25</sup> Such a correlation is tantamount to a constant steric effect, since  $\omega$  reflects the mean separation between the donor and the acceptor moieties in the EDA complex.<sup>25</sup>

Steric Effects in EDA Complexes of Mercury(II) with Alkyltin. The CT transition energies in Table I are plotted against the ionization potentials of various alkyltin compounds in Figure 6. Although there is a roughly parallel relationship between  $h\nu_{\rm CT}$  and  $I_{\rm D}$ , the slope (of any imaginable correlation) is far from unity. In a previous study of related EDA complexes,<sup>25</sup> we showed how such a de-viation of this slope from unity can be related to the variation of  $\omega$  in eq 8.<sup>34</sup> Indeed, the presence of steric effects can be elaborated by comparing them with those

<sup>(29)</sup> The equation to calculate the absorbances is  $2A/\epsilon = [A_0] + [D_0] + K_{DA}^{-1} - \{([A_0] + [D_0] + K_{DA}^{-1})^2 - 4[A_0][D_0]\}^{1/2}$ . (30) (a) Andrews, L. J.; Keefer, R. M. J. Am. Chem. Soc. 1952, 74, 4500. (b) Murrell, J. N. Q. Rev. Chem. Soc. 1961, 15, 191. (31) Iwata, S.; Tanaka, J.; Nagakura, S. J. Am. Chem. Soc. 1966, 88, 804

<sup>894.</sup> 

<sup>(32)</sup> Nagakura, S. Excited States 1975, 2, 321 and references cited therein.

<sup>(33)</sup> For weak complexes of the type described here, when the non-diagonal terms in the secular equation derived from eq 5 and 6 is ne-glected,  $\Psi_E$  is given as  $\Psi_i(D^+A^-)$ ,  $\Psi_j(D^*A)$ , or  $\Psi_k(DA^*)$ , and the transition energy from  $\Psi(DA)$  to  $\Psi_i(D^+A^-)$  is given by eq 7.

<sup>(34)</sup> Any significant deviation from eq 7 owing to the interaction be-tween  $\Psi(DA)$ ,  $\Psi_i(D^+A^-)$ ,  $\Psi_j(D^*A)$ , and  $\Psi_k(DA^*)$  in eq 5 and 6 is unlikely for weak complexes.<sup>33</sup> For a detailed discussion see ref 25.



**Figure 7.** Comparison of the relative interaction energies  $\Delta E$  for the tetraalkyltin complexes of HgCl<sub>2</sub> with  $\Delta E$  for I<sub>2</sub> (left) and  $\Delta E$  for Br<sub>2</sub> (right). Numbers refer to compounds in Table I. See text for the significance of the pair lines in each figure.



**Figure 8.** Comparison of the steric effects in ( $\bullet$ ) HgCl<sub>2</sub> and ( $\odot$ ) I<sub>2</sub> complexes of various tetraalkyltin compounds identified by numbers in Table I. See text.

in the corresponding iodine and bromine EDA complexes examined earlier.<sup>25</sup> In order to carry out such a comparison of acceptors, we relate all of the interaction energies  $\omega$  of various alkyltins relative to  $\omega_0$  of the reference Me<sub>4</sub>Sn. It follows from eq 8 that the difference,  $\Delta E = \omega - \omega_0$  is given by eq 9, where  $\Delta I_D$  is the ionization potential of an alkyltin

$$\Delta E = -\Delta I_{\rm D} + \Delta h \nu_{\rm CT} \tag{9}$$

minus that of Me<sub>4</sub>Sn, and  $\Delta h \nu_{\rm CT}$  is the difference in the CT transition energies with a common acceptor.<sup>25</sup> The comparison of  $\Delta E$  for HgCl<sub>2</sub> with  $\Delta E$  for I<sub>2</sub> and for Br<sub>2</sub> are shown in Figure 7, a and b, respectively. In each case, two linear correlations appear-one for the series of unsymmetrical tetraalkyltin compounds RSnMe<sub>3</sub> and R<sub>2</sub>SnMe<sub>2</sub> with almost a unit slope, and the other for the symmetrical  $R_4Sn$  with a significantly larger slope. These slopes, interpreted in terms of a steric effect, suggest that the quasi-spherical R<sub>4</sub>Sn indicated by the filled circles in Figure 7 are more susceptible to steric interactions with  $HgCl_2$  than with either  $I_2$  or  $Br_2$ . By comparison, the quasi-oblate analogues RSnMe3 and R2SnMe2, indicated by the open circles, are less sterically hindered and thus less susceptible to changes in steric interactions with different acceptors.

The steric effect of alkyltin donors in EDA complexes arises from the encumbrance of the alkyl ligands, leading to changes in the intermolecular separation.<sup>25</sup> If for the moment, the interaction energy is considered to be made up mainly of electrostatic terms,  $\omega = -e^2/r_{\rm DA}$ , where  $r_{\rm DA}$ is the mean separation in the EDA complex.<sup>35</sup> Values of  $r_{\rm DA}$  calculated from eq 8 on the basis of this assumption are plotted in Figure 8 for both mercury(II) and iodine complexes.<sup>36</sup> Indeed the mean separation of HgCl<sub>2</sub> complexes are consistently larger than that of the corresponding iodine complex, and it increases more sharply



**Figure 9.** Correlation of the formation constants of hexamethylbenzene complexes of various mercury(II) derivatives, identified by letters in Table III, with the first CT transition energy.

as the bulk of the alkyl ligand is enhanced (compare tetraalkyltin compounds 9-11).

The presence of significant steric effects of alkyltin donors in the EDA complexes with  $HgCl_2$  can result in the distortion of the tetrahedral configuration such as<sup>37</sup>

$$s_1 + HgCl_2 \Rightarrow Sn HgCl_2$$

since 5-coordinate trigonal bypyramidal structures are known for tin. These structures are properly classified as inner-sphere complexes. As such, we now inquire as to the structural effects inflicted on the mercury(II) acceptor as a result of complex formation. However, before we proceed with this question, the origin of the interesting and rather unusual multiple CT bands in the series of hexamethylbenzene complexes **B** with various mercury(II) derivatives (see Figures 3 and 4 or Table III) is examined in the following section.

Multiple Charge-Transfer Bands in Hexamethylbenzene Complexes of Mercury(II) Derivatives. The strong electron-donor properties of hexamethylbenzene are underscored by the rather stable EDA complexes formed with a wide range of mercury(II) derivatives, with formation constants  $K_{DA}$  as low as 0.39 M<sup>-1</sup> for Hg(CN)<sub>2</sub> and as high as 15.6 M<sup>-1</sup> for Hg(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>. As illustrated in Figure 9, there is an inverse trend between  $K_{DA}$  and the first CT transition energies, as expected from Mulliken theory.<sup>38</sup>

transition energies, as expected from Mulliken theory.<sup>38</sup> The presence of two CT bands in Figure 4 can be ascribed with two transitions  $h\nu_{\rm CT}{}^1$  and  $h\nu_{\rm CT}{}^2$  corresponding to the excited state  $\Psi_1(D^+A^-)$  and  $\Psi_2(D^+A^-)$  in eq 6, since there is no reason, a priori, to believe that only the HOMO of the donor and the LUMO of the acceptor can be involved in CT excitations.<sup>39</sup> Indeed, multiple CT absorption bands have been observed for EDA complexes containing strong electron acceptors such as iodine, chloranil, bromanil, and tetracyanoethylene.<sup>39</sup> In these examples, the existence of two close-lying occupied orbitals of the donor have been identified with the difference in the CT transition energy, according to eq 10, where  $I_{\rm D}{}^2$  and  $I_{\rm D}{}^1$  are

$$\Delta' h \nu_{\rm CT} = I_{\rm D}^2 - I_{\rm D}^1 \tag{10}$$

<sup>(35)</sup> As shown in Table II, the solvent effects here are negligible. (36) In Figure 8,  $r_{DA}$  is plotted against  $I_D$ , which decreases smoothly with the bulkiness of alkyl substituents owing to the increase in the donor ability.

<sup>(37)</sup> Fukuzumi, S.; Wong, C. L.; Kochi, J. K. J. Am. Chem. Soc. 1980, 102, 2928.

<sup>102, 2928.</sup> (38) (a) The relationship between  $K_{\text{DA}}$  and  $h\nu_{\text{CT}}$  is given by  $RT \ln K_{\text{DA}}$ =  $(\beta^2/h\nu_{\text{CT}}) + T\Delta S$ , where  $\beta$  is the interaction integral as described by Mulliken in ref 15a, and  $\beta$  increases as  $h\nu_{\text{CT}}$  decreases.<sup>25</sup> (b) The deviation from the line is observed for HgBr<sub>2</sub> and Hg(CN)<sub>2</sub> which may arise from the differences in  $\beta^{25}$  in the other homologous series. The solid line in Figure 9 represents a least-squares analysis, excluding the points for HgBr<sub>2</sub> and Hg(CN)<sub>2</sub> with  $\rho = 0.94$ .

HgBr<sub>2</sub> and Hg(CN)<sub>2</sub> with  $\rho = 0.94$ . (39) (a) DeMaine, P. A. D. J. Chem. Phys. 1957, 26, 1189. (b) Kuboyama, A. Nippon Kagaku Zasshi 1962, 83, 376. (c) Lepley, A. R.; Thomson, C. C., Jr. J. Am. Chem. Soc. 1967, 89, 5523. (d) Briegleb, G.; Czekalla, J.; Reuss, G. Z. Phys. Chem. (Frankfurt am Main) 1961, 30, 316. (e) Kuroda, H.; Ikemoto, I.; Akamatsu, H. Bull. Chem. Soc. Jpn. 1966, 39, 1842.

the second and first ionization potentials of the donor. The reverse situation is much more unusual, and the series of EDA complexes of 1,2,4,5-tetracyanobenzene (TCNB) with a series of alkylarenes is a rare case in which the two CT bands arise from two close-lying *unoccupied* orbitals in the acceptor (TCNB).<sup>31</sup> In the EDA complex of hexamethylbenzene and TCNB, the difference in the two CT transition energies  $\Delta' h \nu_{\rm CT} = 0.8$  eV is found to be close to the calculated difference of 0.7 eV in the unoccupied orbital energies of TCNB;<sup>40</sup> that is, according to eq 7

$$\Delta' h \nu_{\rm CT} = \mathcal{E}^2 - \mathcal{E}^1 \tag{11}$$

where  $\mathcal{E}^1$  and  $\mathcal{E}^2$  are energies of the first and second vacant orbitals in TCNB.

For the mercury(II) complexes of hexamethylbenzene, the difference in the two transition energies  $\Delta'h\nu_{\rm CT}$  listed in Table III varies slightly with the ligand—ranging from ~0.2 eV for Hg(O<sub>2</sub>CR)<sub>2</sub> to 0.36 eV for HgBr<sub>2</sub>. The multiple CT bands do not arise from the hexamethylbenzene donor, since only one absorption band is observed in the iodine-hexamethylbenzene complex. (This conclusion accords with  $D_{6h}$  symmetry of hexamethylbenzene leading to a pair of degenerate HOMOs, i.e.  $\Delta I_D = 0$ .) Thus the origin of the two CT bands must be attributed to closelying unoccupied orbitals in the mercury(II) acceptors which are separated by

$$\Delta' h \nu_{\rm CT} = \Delta \mathcal{E} \tag{12}$$

where  $\Delta \mathcal{E}$  is the difference between the energies of the second and first vacant orbitals in the mercury(II) derivatives. It is noteworthy that  $\Delta' h \nu_{\rm CT}$  for the HMB complexes of mercury(II) derivatives in the range of 0.1–0.3 eV is significantly smaller than that observed in the HMB complex of TCNB. (See Table III).

We shall now focus on the origin of such a small difference in the vacant orbital energies in the mercury(II) derivatives and discuss how it relates to the structure of the EDA complexes.

Origin of the Splitting of the CT Bands in Mercury(II) Complexes. Mercury(II) halides exist in the gas phase as discrete linear molecules,<sup>41</sup> and there are strong indications that they are also linear, or nearly linear, in solution<sup>23,42</sup> as well as in the molten state.<sup>43,44</sup> The lowest unoccupied orbitals of linear mercury(II) derivatives  $HgX_2$  with  $D_{\infty h}$ symmetry consist of a pair of degenerate  $2\pi_u^*$  orbitals. However, when the linear HgX<sub>2</sub> is bent, the  $2\pi_u^*$  orbitals are split into  $2b_1^{\prime\prime}$  and  $3a_1^{\prime}$  with  $C_{2\nu}$  symmetry. This change, as well as the change in the HOMO  $(1\pi_g)$  in the linear molecule is illustrated in the Walsh diagram for AB<sub>2</sub> molecules in Figure 10.45 The important feature here is the sharp decrease of one of the  $2\pi_u^*$  orbitals to  $3a_{1'}$  in the bent structure. Since the  $3a_1'$  orbital is largely localized on an s orbital on mercury, whereas the  $2\pi_u^*$  orbital has an antibonding character for  $Hg \Leftrightarrow X$  in the linear structure,<sup>23</sup> the splitting labeled as  $\Delta \mathcal{E}$  in Figure 10 in-

(45) Walsh, A. D. J. Chem. Soc. 1953, 2266.



Figure 10. Walsh diagram for the bending of HgX<sub>2</sub>. Only the changes in the LUMO and HOMO of HgX<sub>2</sub> in the linear structure are included. See text.

creases with distortions from linear to bent structures. Thus we interpret the varying magnitudes of  $\Delta' h \nu_{\rm CT}$  in Table III to deviations from linearity in complexes **B**, e.g.<sup>46</sup>



Although the spectral overlap obscured the multiple CT bands in the alkyltin complexes A, the susceptibility of the interaction energy  $\omega$  to steric effects, as shown in Figure 7, suggests that the mercury(II) moiety is also bent in these rather tight inner-sphere complexes, illustrated above.

#### **Summary and Conclusion**

Charge-transfer absorption spectra have been observed for the first time between mercury(II) derivatives and  $\sigma$ donors, represented in this study by a series of alkyltin compounds. Variations in the steric effects of these donors can be evaluated from the charge-transfer transition energies and shown to be more important than steric effects in the corresponding iodine and bromine complexes<sup>25</sup> with the same tetraalkyltin compounds. Importantly, the observation of multiple charge-transfer bands with various mercury(II) derivatives and hexamethylbenzene provides direct evidence of bent structures for the X-Hg-X moiety in the complex.

In a more general light, the electron *acceptor* properties shown here by the binary mercury(II) derivatives  $HgX_2$ , with X = halo, cyano, and carboxylato, is in marked contrast to the electron *donor* properties shown earlier<sup>47</sup> by the homoleptic mercury(II) alkyls  $HgR_2$ , where R = methyl, ethyl, isopropyl, and *tert*-butyl. Such a pronounced dichotomy in the behavior of mercury(II) complexes underscores the powerful influence of ligand structures in determining the electron donor-acceptor character of metal complexes, in general.

#### **Experimental Section**

Materials. Mercuric chloride, bromide, and cyanide were obtained commercially and purified by recrystallization from methanol and dried in vacuo. The mercury carboxylates,  $Hg(O_2CMe)_2$ ,  $Hg(O_2CCHMe_2)_2$ ,  $Hg(O_2CCMe_3)_2$ ,  $Hg(O_2CCH_2Cl)_2$ ,  $Hg(O_2CCH_2CL)_$ 

<sup>(40)</sup> The relation between  $E_A^m$  in eq 7 and the energy of  $m^{\text{th}}$  lowest vacant orbital of acceptor,  $\mathscr{E}^m$ , is given by  $E_A^m = -\mathscr{E}^m$ . (41) (a) Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford

<sup>(41) (</sup>a) Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford University Press: New York, 1962; p 357 references cited therein. (b) See, also, Steudel, R. "Chemistry of the Non-Metals", English edition by Nachod, F. C. and Zuckerman, J. J.; Walter de Gruyter and Co.: Berlin, 1977: p 119.

 <sup>1977;</sup> p 119.
 (42) Rolfe, J. A.; Sheppard, D. E.; Woodward, L. A. Trans. Faraday Soc. 1954, 50, 1275.

<sup>(43)</sup> Janz, G. J.; Baddiel, C.; Kozlowski, T. R. J. Chem. Phys. 1964, 40, 2055.

<sup>(44)</sup> Bent structures have also been proposed by: (a) Zangen, M.; Marcus, Y. Isr. J. Chem. 1964, 2, 91. (b) Kolling, O. W. Inorg. Chem. 1962, 1, 561. (c) Zangen, M. J. Phys. Chem. 1965, 69, 1835.

<sup>(46)</sup> The change of  $\Delta' h_{\nu_{CT}}$  in Table III can be compared with a recent X-ray and Raman study of mercury halide in dimethyl sulfoxide by Sandström, M. [Acta Chem. Scand. Ser. A 1978, 32, 627.]; HgI<sub>2</sub> (159°), HgBr<sub>2</sub> (163°), HgCl<sub>2</sub> (a slight deviation from linearity was indicated by the appearance of a weak  $\nu_3$  band in the Raman spectrum of HgCl<sub>2</sub>). (47) (a) Gardner, H. C.; Kochi, J. K. J. Am. Chem. Soc. 1976, 98, 2460. (b) Chen, J. Y.; Gardner, H. C.; Kochi, J. K. Ibid. 1976, 98, 6150.

TABLE IV:Mean Separation in Tetraalkyltin Complexeswith HgCl2 and I2 Assuming an ElectrostaticInteraction Energy

r <sub>DA</sub> , Å		, Å		r <sub>DA</sub> , Å	
$R_4Sn$	HgCl <sub>2</sub> <sup>a</sup>	I <sub>2</sub> <sup>b</sup>	$R_4Sn$	HgCl <sub>2</sub> <sup>a</sup>	I <sub>2</sub> <sup>b</sup>
Me₄Sn	4.62	4.11	<i>i</i> -Pr <sub>2</sub> SnMe <sub>2</sub>	6.32	5.35
Et₄Sn	5.71	4.75	t-Bu,SnMe,	6.99	5.71
<i>n</i> -Pr₄Sn	5.95	4.88	<i>i</i> -Bu₄Sn	6.32	5.03
$n-\mathbf{Bu}_{A}\mathbf{Sn}$	6.15	5.03	<i>i</i> -Pr₄Sn	7.13	5.41
n-BuSnMe,	5.47	4.78	sec-Bu₄Sn	7.09	5.31
<i>n</i> -Bu,SnMe,	5.81	5.05			

<sup>a</sup> Calculated from eq 8 and  $\omega = -e^2/r_{DA}$ ;  $r_{DA} = e^2(I_D - E_A - h\nu_{CT})^{-1}$ . The value of  $E_A$  for HgCl<sub>2</sub> is estimated as 1.30 eV from  $\Delta h\nu_{CT}$  between the HgCl<sub>2</sub> and I<sub>2</sub> complexes with hexamethylbenzene in Table III using  $E_A(I_2) = 1.60$  eV from ref 25. <sup>b</sup> From ref 25.

from the reaction of mercuric oxide and the corresponding carboxylic acid. As an illustrative example, mercury dichloroacetate was prepared by treating 10.8 g (0.05 mol) of mercuric oxide in 12.1 mL (0.147 mol) of dichloroacetic acid. After the initial vigorous evolution of heat had subsided, an additional 10 mL of dichloroacetic acid was added and the mixture heated. The hot suspension was filtered and chilled in an ice bath. The white crystals were filtered off and dried. Mercury monochloroacetate was prepared from mercuric oxide, and a solution of monochloroacetic acid dissolved in tetrahydrofuran. Since the reaction is slow at room temperature, the tetrahydrofuran solution was refluxed until all of the mercuric oxide had dissolved and was worked up in the usual manner. Hexamethylbenzene from Aldrich Chemical Co. was recrystallized from absolute ethanol. The preparation of the tetraalkyltin compounds used in this study was described earlier.2

The solvents, obtained commercially as analytical reagents, were repurified according to standard methods.<sup>48</sup> Dioxane was refluxed with HCl and water for 12 h, accompanied by a slow passage of nitrogen to remove acetaldehyde. After treatment with solid KOH to remove any aqueous phase, the decanted dioxane was refluxed with sodium for 12 h and then directly distilled. Acetonitrile was stirred with calcium hydride overnight, filtered, treated with potassium permanganate, and then redistilled from  $P_2O_5$  under a nitrogen atmosphere.

Spectral Measurements of CT Absorption Bands. Mercuric chloride has an absorption at  $\lambda_{max}$  206 nm with  $\epsilon_{max} = 4000$  in methanol,<sup>23</sup> but the tail of the absorption is significant above 240 nm in the concentration range of HgCl<sub>2</sub> studied ( $2.5 \times 10^{-3}$ – $1.0 \times 10^{-2}$  M). The tetraalkyltin compounds also have tail absorptions in the region of interest. In order to educe the charge-transfer spectra, we obtained the difference spectra under calibrated conditions on a Cary 14 spectrophotometer with the compartment

thermostated at either 25 or 3 °C (vide infra). In a typical procedure, the spectrum of the solution of the tetraalkyltin and mercuric chloride was first measured against a reference solution containing tetraalkyltin at the same concentration by using a matched pair of 10-mm quartz cuvettes. The maximum concentrations of the tetraalkyltin and mercuric chloride were limited to below that which would cause the slit width of the spectrometer to open to its maximum (3.0 mm). Next, the solution of the same concentration of mercuric chloride was run against the same solvent. The second spectrum was subtracted from that obtained in the first run to afford the spectrum of the EDA complex. All transfers were effected with glass pipets to obviate contamination from trace metal impurities. In most cases, the use of  $5.0 \times 10^{-3}$  M HgCl<sub>2</sub> and  $\sim 10^{-2}$  M  $R_4$ Sn afforded the optimum conditions to observe clear absorption maxima of the EDA complexes. Rather low concentrations of R<sub>4</sub>Sn were necessitated (especially for tetraalkyltin compounds with bulkier alkyl substituents such as i-Pr<sub>4</sub>Sn and sec-Bu<sub>4</sub>Sn) because of the experimental limitation described above (see Figure 1).

For Me<sub>4</sub>Sn, *n*-BuSnMe<sub>3</sub>, *n*-Bu<sub>2</sub>SnMe<sub>2</sub>, and *i*-Pr<sub>2</sub>SnMe<sub>2</sub>, the measurements were carried out at 3 °C to retard the cleavage reaction.<sup>16</sup> In these cases, the absorption spectra in acetonitrile decreased measurably within a few minutes, which necessitated the rapid measurement of the spectrum. The values of  $\lambda_{max}$ , obtained by the rapid measurement of the spectrum, were redetermined as pointby-point measurements at fixed wavelengths, and the absorbance was extrapolated to time zero (see Me<sub>4</sub>Sn in Figure 1 as a typical example).

For the measurements of CT spectra of various mercury derivatives with hexamethylbenzene, essentially the same procedures as those employed for tetraalkyltin complexes were carried out. Thus, a known amount of hexamethylbenzene (0.01-0.1 g) was added to the sample cuvette containing a methylene chloride solution of the mercury derivative, as well as to the reference cuvette. When the measurements involving low concentrations of hexamethylbenzene were required ( $\sim 10^{-3}$  M), the sample and the reference solutions were prepared in a volumetric flask (25 or 50 cm<sup>3</sup>), and an aliquot of the solution was transferred to the sample and reference cuvettes, as required. In control experiments, it was shown that no chemical reaction occurred between hexamethylbenzene and all mercury derivatives used during the time required for the measurement of their CT spectra.

Mean Separation in HgCl<sub>2</sub> and I<sub>2</sub> Complexes of Various Tetraalkyltin Compounds. The mean separations  $r_{DA}$  in the electron donor-acceptor complexes were calculated from eq 8, assuming the interaction energy to be Coulombic, i.e.,  $\omega = -e^2/r_{DA}$ . The values of  $r_{DA}$  for various tetraalkyltin compounds with HgCl<sub>2</sub> and I<sub>2</sub> are listed in Table IV.

Acknowledgment. We thank the National Science Foundation for the financial support of this study.

<sup>(48)</sup> Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Elmsford, NY, 1966.