A CNDO-type MO Method of the Third Transition Metal Complexes and the Electronic Structure of Methylmercury(II) Halides

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The parameters of a CNDO-type SCF-MO method are determined for some 5d transition metal complexes such as $IrCl_6^{3-}$, $AuCl_4^-$, and $HgCl_4^{2-}$ by comparing the calculated transition energies of these complexes with their experimental values. MO calculations with these established parameters are also carried out for $IrBr_6^{3-}$, $AuBr_4^-$, HgX_4^{2-}, HgX_2, and CH_3HgX (X=Cl, Br, and I). The transition energies and assignments obtained from MO calculations are in fair agreement with experimental ones, with a few exceptions. This MO method gives successful results for the electron density and the bond strength: (1) a linear relation is obtained between the calculated and observed net charges on the Hg atom of HgX_2 and CH_3HgX, and (2) similar linear relations are obtained between the bond index E_{M-X} values and the stretching force constant f_{M-X} and between the E_{Hg-C} value and the f_{Hg-C}. Some discussion is presented for the Hg–C bonding character of the CH_3HgX; the Hg–C bond is mainly contributed from the covalent interaction of the 6s and 6p orbitals of the Hg atom with the 2s and 2p orbitals of the C atom. The contributions of the Hg 5d orbitals and the electrostatic interaction are rather small.

There exist various organo-transition metal complexes which are interesting as model compounds of intermediates formed in reactions catalyzed by transition metal complexes.[1] These organometallic compounds have received many spectroscopic studies. There is, however, limited theoretical work on these complexes; such studies are especially few in the 5d organo-transition metal complexes.[2–5] Theoretical work is necessary to understand and discuss the electronic structures of organometallic complexes. Furthermore, theoretical studies can give us useful information on unstable and unisolable intermediates.[2–5,7] Thus, we should investigate a MO method powerful enough to achieve this purpose.

One of the authors presented a CNDO-type MO method which gave successful results in MO calculations of Pt-complexes.[5] By use of this method, he investigated the reaction mechanism and ligand effect in the ethylene insertion reaction into the Pt(II)–H bond.[5b] This MO method, therefore, can be expected to give us important information about organo-transition metal complexes. In the present study, we attemp to establish the parameters of Hg,Au,and Ir atoms by comparing the calculated transition energies of these metal complexes, such as $HgCl_4^{2-}$, $AuCl_4^-$, and $IrCl_6^{3-}$, with the observed ones. No MO calculation has been reported for HgX_4^{2-} and IrX_6^{3-} as far as we know; for $AuCl_4^-$, although an INDO-type MO calculation was carried out, neither d-d transition energies nor the bonding nature were discussed.[6]

Then, MO's of methylmercury(II) complexes are calculated by use of the established parameters. Although these complexes have been investigated in detail by means of various spectroscopic instruments, such as IR and Raman,[8–14] NMR,[15–18] and UV[19] spectroscopy, there has been reported only one theoretical work,[3] in which the extended Hückel MO calculations were carried out and the ligand effect on the ^{199}Hg–H coupling constant was interpreted theoretically. In the present study, the electronic spectra, the electron density, and the Hg–C bonding character are investigated.

Method, Parameters, and Geometries

Method and Parameters. The method used here is the CNDO-type approximate SCF-MO method which gave successful results in MO calculations of Pt complexes.[5] Details of this method are presented elsewhere.[20] Only the part of this method which concerns parametrization carried out in this work, is described here. The two-center Coulomb repulsion integrals are estimated by use of the modified Ohno's equation, which has been introduced in the previous paper:[5a]

$$\gamma_{rs} = 14.3986/(R_{rs}^2 + d^2)^{1/2} \qquad (1)$$

$$14.3986/d = 0.5(\gamma_{rr} + \gamma_{ss}) - a_r \qquad (2)$$

See Ref. 5 for the notation in the above equation. In the 3d and 4d transition metal series elements, values such as a_{4s}, a_{4p}, a_{5s}, and a_{5p} are determined from the atomic spectra. It has been found that there exist four linear relations between the atomic numbers and the a_{ns} values, and between the atomic numbers and a_{np} ones (n=4 and 5).[21] In the 5d transition metal elements, those values can not be obtained from the atomic spectra because there is not enough data to estimate those values. Thus, in the Pt atom, they have been determined as parameters so that the calculated transition energies agree with the observed ones.[5] In this work, the a_{6s} and a_{6p} values are also determined as parameters under consideration of the following conditions; the a_{6s} and a_{6p} values increase linearly with an increase in the atomic number, which is expected from the analogy to the 3d and 4d transition metal elements, and their two linear lines pass through the 1.5 and 2.5 eV[5a] at the Pt atom respectively. The values of the parameters are listed in Table 1.

Values of other parameters, such as the Wolfsberg-Helmholz parameter, K, and the orbital exponents, are taken as well to be those in the case of the Pt complexes.[5a] These parameters give good results for the transition energies, the electron densities, *etc.*

Bond Index. The energy contribution of the AB bond to the total energy, E_{AB}, is used as the bond index.[5,7,22,23] The negative value means the bonding

TABLE 1. ORBITAL EXPONENTS, ζ_r, VALENCE STATE IONIZATION POTENTIALS, I_r, ONE-CENTER COULOMB REPULSION INTEGRALS, γ_{rr}, AND PARAMETERS OF MODIFIED OHNO'S EQ., a_{6s}, AND a_{6p}

Atom		Ir	Pt	Au	Hg
ζ_r[a]	5d	5.796 0.6351[b] 2.557 0.5556	6.013 0.6331[b] 2.696 0.5516	6.163 0.6442[b] 2.794 0.5356	6.436 0.6667[b] 3.032 0.5401
	6s6p	2.504	2.554	2.602	2.649
I_r	5d	6.65_{eV}[g]	8.24	11.85	15.66
	6s	8.16	9.00	9.22	10.44
	6p	5.80	4.20	6.49	5.00
γ_{rr}[d]	5d	11.54_{eV}	12.07	12.60	13.14[f]
	6s	7.11	7.24	7.37	7.49
	6p	5.92	6.05	6.18	6.31
a_{6s}		1.4_{eV}	1.5	1.7	1.8
a_{6p}		2.4	2.5	2.7	2.8

a) H. Basch and H. B. Gray, *Theor. Chim. Acta*, **4**, 367 (1966). b) For only the d-orbital, the double-ζ type orbitals are used. These values are their coefficients, which are re-normalized values, since the contributions of the 3d and 4d Slater type orbitals are neglected in this work. c) The calculated values from the atomic spectra (C. E. Moore, "Atomic Energy Levels," Natl. Bur. Std. Circ., No. 467 (1958). d) The estimated value.[7] e) In our previous paper,[5] these values are over-estimated. By the use of these correct values, the electronic spectra of $PtCl_4^{2-}$ are calculated successfully, and the differences between the correct and the previous calculation are very small; for example $^1B_{1g}=1.97$ eV in the present calculation and 1.99 eV in our previous report. f) R. D. Bach and H. F. Henneike, *J. Am. Chem. Soc.*, **92**, 5589 (1970). g) Ir's VSIP can not be calculated correctly from atomic spectra due to lack of experimental data. These values are estimated by assuming that the promotion energy from $^3F_4$ state of Ir(I) to the d^8 valence state is 1 eV. This assumption seems reasonable from considering that this energy is 0.87 eV for the isoelectronic Rh(I) atom.

interaction between the A and the B atoms, and the large absolute value shows the large interaction. The formula representing the E_{AB} under the used approximations has been given elsewhere.[5]

In order to investigate the detailed bonding character, the $E_{AB}^{(1)}$ and $E_{AB}^{(2)}$ which approximately represent the covalent interaction are divided into the $E_{AB(s)}^{(1)+(2)}$, $E_{AB(p)}^{(1)+(2)}$, and $E_{AB(d)}^{(1)+(2)}$ as has been described in the previous paper;[24] where the $E_{AB(s)}^{(1)+(2)}$, in which the suffix (1)+(2) denotes the sum of $E_{AB}^{(1)}+E_{AB}^{(2)}$, represents approximately the contribution of the s orbital of the B atom to the covalent interaction between the A and B atoms, and the $E_{AB(p)}^{(1)+(2)}$ and $E_{AB(d)}^{(1)+(2)}$ also represent similar meanings.

Geometries. The IrX_6^{3-}, AuX_4^-, HgX_4^{2-}, and HgX_2 belong to O_h, D_{4h}, T_d, and $D_{\infty h}$ symmetries, respectively. The following bond lengths are employed in MO calculations: Ir–Cl=2.47 Å,[25] Ir–Br=2.618 Å,[26] Au–Cl=2.42 Å,[25] Au–Br=2.57 Å,[25] Hg–Cl (in $HgCl_4^{2-}$)=2.50 Å,[27] Hg–Br (in $HgBr_4^{2-}$)=2.62 Å,[28] Hg–I (in HgI_4^{2-})=2.80 Å,[29] Hg–Cl(in $HgCl_2$)=2.252 Å,[30] Hg–Br (in $HgBr_2$)=2.41 Å,[31] and Hg–I(in HgI_2)=2.60 Å.[29] The CH_3HgX complex is known to have a linear structure. Its bond distance is taken as follows: for CH_3HgCl, Hg–C=2.052 Å, Hg–Cl=2.285 Å;[32] for CH_3HgBr, Hg–C=2.062 Å, Hg–Br=2.405 Å;[32] for CH_3HgI, Hg–C=2.070 Å, Hg–I=2.588 Å;[32] for $Hg(CH_3)_2$, Hg–C=2.083 Å;[33] for CH_3HgF, Hg–C=2.040 Å, and Hg–F=1.93 Å.[26] The methyl group is assumed to have the same structure in all the complexes because the kinds of the ligand can scarcely cause any structural change: ∠HCH=109.8° and C–H=1.096 Å.[33]

Results and Discussion

Parametrization and Electronic Spectra. $IrCl_6^{3-}$ and $IrBr_6^{3-}$: By considering the Pt's a_{6s}(=1.5 eV) and a_{6p}(=2.5 eV), the following values of the a_{6s} and a_{6p} were examined in MO calculations of $IrCl_6^{3-}$: a_{6s}=1.2, 1.4, and 1.6 eV, and a_{6p}=2.2, 2.4, and 2.6 eV. Results are given in Table 2.

In $IrCl_6^{3-}$, various values of a_{6s} and a_{6p} give only a small effect on the transition energies. The first and the second small bands observed at 2.99 and 3.48 eV have been assigned to the $^1T_{1g}$ and $^1T_{2g}$.[35] In the present MO calculations, the $^1T_{1g}$ and $^1T_{2g}$ transitions are calculated to be *ca.* 2.9 and 3.5 eV, respectively. The large band observed at 6.01 eV may be assigned to the $^1T_{1u}$ transition calculated at 4.8 eV, since the $^1T_{1u}$ one is the only allowed one. This transition is the charge-transfer (CT) one from the halogen's p_π orbital

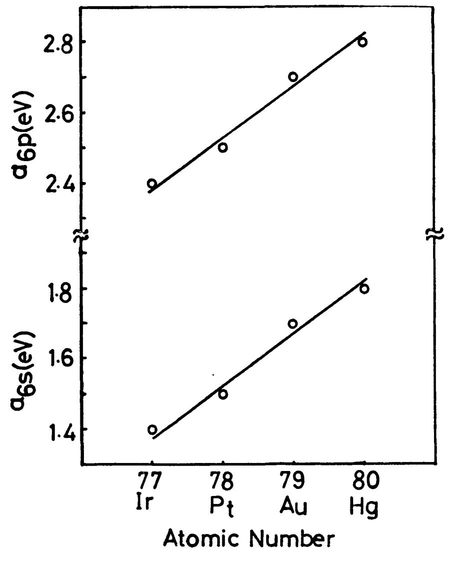

Fig. 1. The relations between the atomic number and the a_{6s} and a_{6p} values.

TABLE 2. TRANSITION ENERGIES[a)] OF $IrCl_6^{3-}$ AND $IrBr_6^{3-}$

$IrCl_6^{3-}$								$IrBr_6^{3-}$			
a_{6s}	1.2	1.4	1.6	1.4	1.4	Obsd[b)]		a_{6s}	1.4	Obsd[b)]	
a_{6p}	2.4	2.4	2.4	2.2	2.6			a_{6p}	2.4		
$^1T_{1g}$	2.92	2.86	2.81	2.96	2.78	$^1T_{1g}$	2.99	$^1T_{1g}$	1.74	$^1T_{1g}$	2.78
$^1T_{2g}$	2.98	2.90	2.86	3.01	2.84		(76)[c)]	$^1T_{2g}$	1.75		(230)
$^1T_{1g}$	3.39	3.40	3.40	3.38	3.41			$^1A_{2g}$	3.19		
$^1T_{2g}$	3.53	3.55	3.56	3.52	3.56	$^1T_{2g}$	3.48	^1E_g	3.30		
							(64)				
$^1A_{2g}$	3.88	3.93	3.88	4.06	3.87			$^1T_{1g}$	3.75		
^1E_g	4.13	4.08	4.03	4.15	4.01			$^1T_{2g}$	3.82	$^1T_{2g}$	3.20
											(200)
$^1T_{1g}$	4.69	4.63	4.57	4.72	4.53			$^1T_{1g}$	3.95		
$^1T_{1u}$	4.89	4.84	4.80	4.92	4.78	odd$\pi \rightarrow$d	6.01	$^1T_{1u}$	4.13	odd$\pi \rightarrow d_{e_g}$	4.56
	(2.18)[d)]	(2.22)	(2.24)	(2.15)	(2.29)		(28000)		(2.33)		(1200)
$^1T_{1u}$	4.93	4.87	4.81	4.96	4.78			$^1T_{1u}$	4.35	odd$\pi \rightarrow d_{e_g}$	5.10
	(0.23)	(0.23)	(0.23)	(0.23)	(0.23)				(0.22)		(2000)
$^1T_{1u}$	6.19	6.14	6.14	6.23	6.06			$^1T_{1u}$	5.39	odd$\sigma \rightarrow d_{e_g}$	5.94
	(1.57)	(1.59)	(1.62)	(1.57)	(1.62)				(1.93)		(6200)

a) eV unit. The transitions which satisfy both the following conditions are omitted for simplicity: (1) the transition is above the first CT one; (2) its transition moment is zero. These transitions do not relate to the present discussion. b) Ref. 35. c) Molar extinction coefficient (M^{-1} cm^{-1}). d) Transition moment (Å). Transition moments are zero in other transitions.

to the Ir's $5d_\sigma$ orbital. In all the calculations, these calculated transition energies roughly agree with the observed one, although the $^1T_{1u}$ transition energy is smaller than the observed one by *ca.* 1.2 eV.

Then, the a_{6s} and a_{6p} values can be determined. The small a_{6s} and a_{6p} values give better results for the observed $^1T_{1g}$, $^1T_{2g}$, and $^1T_{1u}$ transitions, as shown in Table 2. The a_{6s} and a_{6p} values, however, are determined as 1.4 and 2.4 eV respectively, by considering the linear relation between the atomic number and the a_{6s} and a_{6p} values (See Fig. 1, the previous discussion in method and parameter, and Ref. 49. This determination seems reasonable, since the calculated transition energies do not much depend on the a_{6s} and a_{6p} values.

By using these values of a_{6s} and a_{6p}, transition energies of $IrBr_6^{3-}$ are calculated, as is shown in Table 2. Three large bands are observed at 4.5—6 eV: the first is assigned to the transition from the weak π-antibonding and weak σ-bonding $3t_{1u}$ MO, mainly composed of the halogen's p_π orbital, to the $2e_g$ MO, mainly composed of the Ir's $5d_\sigma$ orbital; the second is that from the $1t_{2u}$ MO composed of the halogen's non-bonding p_π orbital to the

TABLE 3. TRANSITION ENERGIES[a)] OF $AuCl_4^-$ AND $AuBr_4^-$

$AuCl_4^-$								$AuBr_4^-$			
a_{6s}	1.5	1.7	1.9	1.7	1.7	Obsd[b)]		a_{6s}	1.7	Obsd[b)]	
a_{6p}	2.7	2.7	2.7	2.5	2.9			a_{6p}	2.7		
$^1B_{2g}$	2.82	2.83	2.84	2.89	2.78			$^1B_{2g}$	2.23		2.23
^1E_g	2.83	2.83	2.84	2.88	2.79	$^1A_{2g}$	2.72	^1E_g	2.37		(300)[c)]
							(17.3)[c)]				
$^1A_{2g}$	2.84	2.84	2.85	2.87	2.81			$^1A_{2u}$	2.50		
$^1A_{2u}$	3.08	3.09	3.10	3.14	3.04			$^1A_{2g}$	2.52		
^1E_g	3.24	3.22	3.21	3.18	3.26	^1E_g	3.29	$^1B_{2u}$	2.80		
							(319)				
$^1B_{2u}$	3.44	3.45	3.46	3.51	3.40			^1E_g	3.09	^1E_g	2.70
											(1560)
$^1A_{2g}$	3.61	3.59	3.58	3.56	3.62			^1E_u	3.11	$^1E_u+^1A_{2u}$	3.15[e)]
$^1B_{1g}$	3.74	3.74	3.73	3.71	3.76				(1.64)		(4775)
^1E_u	3.80	3.80	3.81	3.81	3.79	$^1E_u+^1A_{2u}$	3.85[e)]	^1E_u	3.42	^1E_u	4.85
	(1.51)[d)]	(1.50)	(1.49)	(1.48)	(1.53)		(5750)		(0.95)		(48625)
^1E_u	3.96	3.98	4.00	4.05	3.91	^1E_u	5.47	^1E_u	6.54	^1E_u	6.24
	(0.76)	(0.76)	(0.77)	(0.77)	(0.75)		(47800)		(0.0)		(14000)
^1E_u	8.24	8.20	8.16	8.03	8.37	^1E_u	7.07	^1E_u	6.62	$^1A_{2u}$	6.61
	(0.35)	(0.35)	(0.35)	(0.36)	(0.34)		(—)		(1.04)		(17700)
								^1E_u	7.46	^1E_u	6.94
									(0.36)		(—)

a) d); See footnote a and d of Table 2, respectively. b) Refs. 36 and 37. c) Molar extinction coefficient (M^{-1} cm^{-1}). e) Ref. 39a.

$2e_g$ MO; and the last is that from the weak π- and σ-bonding $2t_{1u}$ MO, mainly composed of the halogen's $p\pi$ orbital, to the $2e_g$ MO. The calculated transition energies roughly agree with experimental ones,[35] but the calculated transition moments are unreasonable. For the first small band observed at 2.78 eV, the calculated transition energy is smaller than the observed one. For the small band observed at 3.20 eV, there is an ambiguity whether the $^1T_{2g}$ calculated at 1.75 eV or that at 3.82 eV should correspond to this band. Thus, although there is insufficiency in the $^1T_{1g}$ and $^1T_{2g}$ results, roughly good results are obtained for the CT bands.[51]

$AuCl_4^-$ and $AuBr_4^-$: The following values of the a_{6s} and a_{6p} were examined: a_{6s}=1.5, 1.7, and 1.9 eV, and a_{6p}=2.5, 2.7, and 2.9 eV. The calculated transition energies are compared with the observed ones in Table 3.

The calculated transitin energies do not much depend on the a_{6s} and a_{6p} values.[34] The transitions calculated at *ca.* 3.8, 4.0, and 8.2 eV seem to correspond to the observed bands at 3.85, 5.47,[36,37] and 7.07 eV,[36] respectively.[38] These assignments agree well with the experimental ones which have been proposed from the MCD study.[37] The calculated transition energies also agree well with the experimental ones,[36,37] but the second ^1E_u transition calculated at 4.0 eV is smaller than the experimental one by *ca.* 1.5 eV.

Table 4. Transition energies[a] of $HgCl_4^{2-}$

a_{6s}	1.6	1.8	2.0	1.8	1.8	Obsd[b]	
a_{6p}	2.8	2.8	2.8	2.6	3.0		
^1E	5.60	5.52	5.43	5.47	5.57		
$^1T_2$	5.62	5.54	5.45	5.49	5.58	$^1T_2$	5.28
	(0.99)[d]	(0.99)	(1.0)	(0.99)	(0.98)		(39200)[c]
$^1T_1$	5.63	5.56	5.48	5.51	5.61		
$^1T_2$	6.04	5.96	5.88	5.92	6.01		
	(0.42)	(0.42)	(0.41)	(0.42)	(0.41)		

a) eV unit. b) Ref. 40. c) Extinction coefficient (M^{-1} cm^{-1}). d) See footnote d of Table 2.

The two bands observed at 2.72 and 3.29 eV have been assigned to the $^1A_{2g}$ and ^1E_g transitions, respectively.[36] In our calculations, the $^1A_{2g}$ and ^1E_g transitions are calculated at *ca.* 2.8 and 3.2 eV, respectively, and the other four transitions, $^1B_{2g}$, ^1E_g, $^1A_{2u}$, and $^1B_{2u}$ are also calculated about 2.8—3.5 eV. Thus, detailed study should be carried out for the assignments of these transitions.

Then, the values of the parameters a_{6s} and a_{6p} can be determined. With regard to the $^1A_{2g}$ transition observed at 2.72 eV, the small a_{6s} and the large a_{6p} values give a better result, whichever of the three transitions, $^1B_{2g}$, ^1E_g, and $^1A_{2g}$ (calculated at about 2.8 eV), correspond to this transition at 2.72 eV. On the other hand, with regard to three ^1E_u transitions, the large a_{6s} and the small a_{6p} values give better results. Thus, the a_{6s} and a_{6p} values are determined as 1.7 and 2.7 eV, respectively.

Using these determined values of a_{6s} and a_{6p}, a similar MO calculation was carried out for $AuBr_4^-$. The

Table 5. Transition energies[a] of HgX_4^{2-}, HgX_2, and CH_3HgX

	$HgBr_4^{2-}$		HgI_4^{2-}	
	Calcd	Obsd[b]	Calcd	Obsd[b]
$^1T_1$	4.85		4.73	
^1E	4.85		4.78	
$^1T_2$	4.89	4.90	4.97	4.57
	(1.09)[c]	(41400)[d]	(1.23)[c]	(35400)[d]
$^1T_2$	5.25		5.04	
	(0.51)		(0.47)	

	$HgCl_2$		$HgBr_2$		HgI_2	
	Calcd	Obsd[e]	Calcd	Obsd[e]	Calcd	Obsd[e]
$^1E_{1g}$	5.19		4.26		4.13	
$^1E_{1u}$	5.54		4.49		4.32	
$^1A_{1u}$	7.52	6.20[f]	6.39	5.40[f]	6.25	4.63[f]
	(1.75)[c]	(2300)[d]	(2.04)	(1400)[d]	(2.23)	(3600)[d]
$^1A_{1g}$	7.70		7.30		7.37	
^1E_g	7.97		7.12		6.92	

	CH_3HgCl		CH_3HgBr		CH_3HgI	
	Calcd	Obsd[g]	Calcd	Obsd[g]	Calcd	Obsd[g]
^1E	5.76		5.03		4.82	
^1E	6.91		6.69		6.58	
$^1A_1$	7.36	6.02[f]	7.00	5.93[f]	6.92	5.39[f]
	(1.73)[b]	(1480)[d]	(1.87)[c]	(3470)[d]	(1.98)[c]	(3980)[d]
^1E	8.01		7.66		7.73	

a) eV unit. a_{6s}=1.8, a_{6p}=2.8 eV. b) Ref. 40. c) See footnote d of Table 2. d) Extinction coefficient (M^{-1} cm^{-1}). e) Ref. 42. f) Although the accurate assignment has never been presented, this transition has been proposed as a CT one. g) Ref. 41.

results are also shown in Table 3. Calculated transition energies agree well with the observed ones, except for the second ^1E_u transition observed at 4.90 eV.[36] Reasonable assignments are also obtained,[36,37] except with the $^1A_{2u}$ band observed at 6.61 eV.[39b]

$HgX_4{}^{2-}$ and HgX_2: Just as in the cases of the Ir and Au complexes, MO calculations of $HgCl_4{}^{2-}$ were carried out using various values of a_{6s} and a_{6p}: $a_{6s}=1.6$, 1.8, and 2.0 eV, and $a_{6p}=2.6$, 2.8, and 3.0 eV. Results are given in Table 4.

One large band is observed at 5.28 eV, which is assigned to the $^1T_2$ transition, since the $^1T_2$ transition is the only allowed one in the T_d symmetry.[40] Also in our calculation, the $^1T_2$ transition is calculated at 5.6 eV; the calculated value fairly agrees with the experimental one. As the a_{6s} value becomes large and the a_{6p} one becomes small, the calculated transition energy of the $^1T_2$ becomes small. Since this calculated value is slightly larger than the observed one,[40] the large value of the a_{6s} and the small one of the a_{6p} are preferable. The a_{6s} and a_{6p} values, however, are determined as 1.8 and 2.8 eV respectively, by considering the expected linear relation between the atomic number and the a_{6s} and a_{6p} values, and also by considering the a_{6s} and a_{6p} values of the Ir, Pt, and Au atoms. This determination seems reasonable, since the calculated transition energy does not depend so greatly on the a_{6s} and a_{6p} values, and since fairly good agreement with the experimental results is obtained in all the calculations.

By use of these values of a_{6s} and a_{6p}, MO calculations were carried out for $HgX_4{}^{2-}$ (X=Br and I), and HgX_2 and CH_3HgX (X=Cl, Br, and I). Calculated transition energies are given in Table 5. Those of $HgX_4{}^{2-}$ agree fairly well with the experimental ones,[40] where the large band is considered as the $^1T_2$ transition as is that of $HgCl_4{}^{2-}$. It has been proposed previously that these bands are the CT transitions.[40] The present calculation shows that these transitions are the $^1T_2$ CT ones from the $4t_2$ MO, mainly composed of halogen's p_π orbital, to the $3a_1$ MO, mainly composed of the Hg's 6s orbital.

In HgX_2, the moderately large bands observed at 4.5—6 eV are considered as the $^1A_{2u}$ transitions, since only this transition is allowed. Also, in the CH_3HgX, the moderately large bands are observed at 5.4—6 eV, and these are considered as similar to the $^1A_1$ transitions. These $^1A_{2u}$ and $^1A_1$ transitions calculated at 6—7 eV, are larger than the observed ones by *ca.* 1.5 eV.[41,42] The $^1A_{2u}$ transition of HgX_2 is the one electron transfer from the $2a_{1u}$ MO to the $4a_{1g}$ MO. Since the former MO is mainly composed of the halogen's p_σ orbital and the latter one mainly of the Hg's 6s orbital, this transition is the CT one, which agrees with the experimental proposal.[42] The $^1A_1$ transition of CH_3HgX is the one electron transfer from the $4a_1$ MO to the $5a_1$ MO; the former is largely contributed to from the p orbitals of the C and X atoms and the latter largely from the Hg's 6s orbital. Thus, this transition is also the CT one.

As described above, the results of the electronic spectra are reasonable, with a few exceptions. The values of the parameters established above are listed in Table 1. The a_{6s} and a_{6p} values are plotted against the atomic number in Fig. 1, where a nearly linear relation is obtained.

TABLE 6. ELECTRON DISTRIBUTION OF IrX^{3-}, $AuX_4{}^-$, $HgX_4{}^{2-}$, AND HgX_2

Cmpound	5d	6s	6p
$IrCl_6{}^{3-}$	6.776	0.527	0.927
$IrBr_6{}^{3-}$	6.812	0.560	0.963
$AuCl_4{}^-$	9.197	0.594	0.807
$AuBr_4{}^-$	9.327	0.612	0.807
$HgCl_4{}^{2-}$	9.989	0.704	0.722
$HgBr_4{}^{2-}$	9.989	0.783	0.755
$HgI_4{}^{2-}$	9.989	0.821	0.771
$HgCl_2$	9.933	0.915	0.456
$HgBr_2$	9.944	1.019	0.447
HgI_2	9.955	1.059	0.455

Electron Density. Electron densities are shown in Table 6. It is reasonable for all the complexes that the electron density of the central metal atom increases with a decrease in the electronegativity of the halogen.

Our calculations show that the net charge of the Au atom is +0.401 *e* in $AuCl_4{}^-$ and +0.254 *e* in $AuBr_4{}^-$, although these values have been reported to be negative from the Mössbauer spectroscopy:[43] −0.24 *e* in $KAuCl_4$ and −0.21 *e* in $KAuBr_4$. The authors wonder why the Mössbauer study reported that the net charge of the Au atom was −0.24 *e* in $KAuCl_4$ and +0.41 *e* in AuCl, although the formal net charge of the Au atom is +3 in the former complex and +1 in the latter one. Thus, these reported values should be re-investigated in more detail.

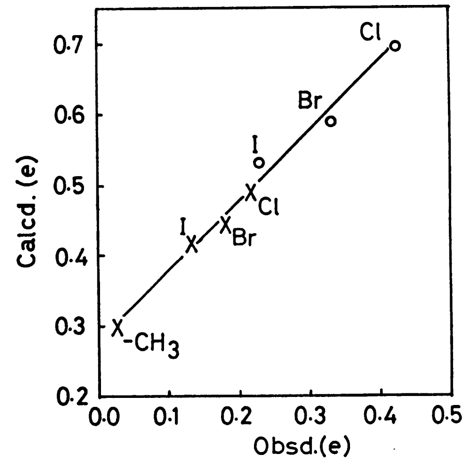

Fig. 2. The relation between the observed[a)] and the calculated net charges of the Hg atom in HgX_2 and CH_3HgX. ○; HgX_2, ×; CH_3HgX. a) Ref. 44.

In $HgX_4{}^{2-}$ and HgX_2, all the d orbitals seem to be of the non-bonding type, since they have about 10 electrons. The Hg–X bond is mainly contributed to from the 6s and 6p orbitals of the Hg atom. Our calculated net charges of the Hg atom are compared with the estimated ones from the ESCA study,[44] as is shown in Fig. 2. Although these two values do not agree with each other, a linear relation is obtained between these two values, and it should be further noted that its slope is about 1.0. This result reveals that our method is at least qualitatively successful.

The ^{35}Cl NQR studies of $HgCl_2$ and CH_3HgCl give the unbalance in the p-electron population on the Cl atom, U_p, which is defined in Ref. 44. From MO calculations, the U_p values can be estimated: 0.526 for $HgCl_2$ and 0.474 for CH_3HgCl. These are in moderately good agreement with the experimental values: 0.402 for $HgCl_2$ and 0.383 for CH_3HgCl.[45] Since the quantity of U_p depends upon the electron populations of the p_σ and p_π orbitals of the Cl atom, it is suggested that the calculated electron distribution agrees with the experimental one.

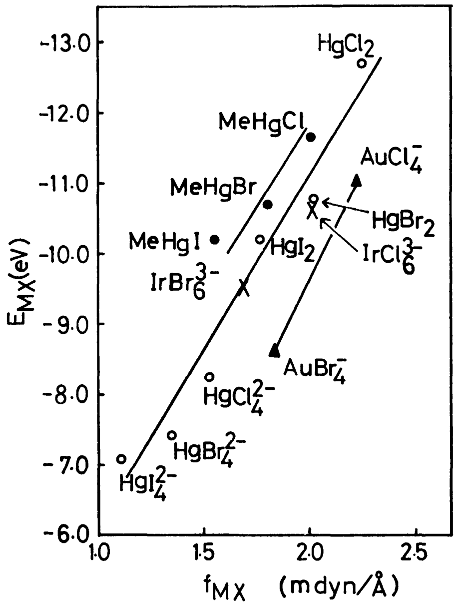

Fig. 3. The relation between the force constant f_{M-X}[a] and the E_{M-X} values.
a) HgX_2 and HgX_4^{2-}, Ref. 29; IrX_6^{3-}, Ref. 46; CH_3HgX, Ref. 8; AuX_4^-; Ref. 47.

Bond Strength. The E_{M-X} values are compared with the M–X force constants in Fig. 3, since the force constant and E_{M-X} approximately represent the bond strength. Three different linear relations are obtained: the first one concerning the HgX_2, HgX_4^{2-}, and IrX_6^{3-}, the second concerning the CH_3HgX, and the last concerning the AuX_4^-. Generally speaking, the value of the force constant depends upon their calculation method. The force constants of HgX_2 and HgX_4^{2-} were calculated with the simple method,[29] those of IrX_6^{3-} were done with the generalized force field,[46] those of CH_3HgX were done with a simple valence force field,[8] and those of AuX_4^- were done with an Urey-Bradley force field.[47] Thus, it seems reasonable that in all the calculations, a linear relation can not be obtained. It should be noted that linear relations do exist between the E_{M-X} values and the M–X force constants which are calculated by use of the same force field, and the three lines have almost the same slopes.

Similar relations are also obtained between the E_{Hg-C} values and the Hg–C force constants,[8] and between the E_{Hg-C} values and the Hg–C dissociation energies of CH_3HgX,[48] as are shown in Figs. 4 and 5. Thus, our method gives successful results for the bond strength.

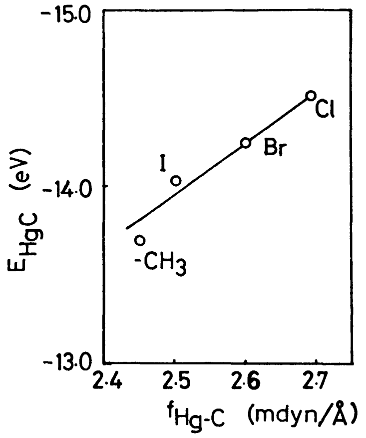

Fig. 4. The relation between the Hg–C force constant f_{Hg-C}[a] and the E_{Hg-C} value.
a) Ref. 8.

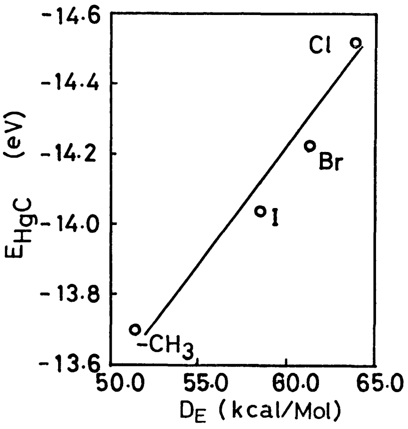

Fig. 5. The relation between the Hg–C dissociation energy, D_E,[a] and the E_{Hg-C} values.
a) Ref. 48.

Electronic Structure of CH_3HgX. In this section, the electron distribution and bonding nature of the Hg–C and Hg–X of CH_3HgX are investigated. Results are given in Table 7.

First, the electron distribution is investigated in detail. The electron density of the 5d orbitals of the Hg atom is *ca.* 10 *e*, suggesting that the 5d orbitals hardly contribute to the Hg–C and Hg–X bonds in these complexes as well. On this point, a more detailed discussion will be presented in a following paragraph. The electron densities of the 6s and 6p orbitals of the Hg atom increase in the order $F < Cl < Br < I < CH_3$. This order accords with the decreasing order of the halogen's electronegativity. The electron density of the Hg atom in $Hg(CH_3)_2$ is larger than that in CH_3HgI by *ca.* 0.1 *e*, and larger than that in the corresponding dihalide HgX_2 by *ca.* 0.1—0.2 *e*. These results suggest that the methyl anion tends to donate electrons more than the halogen anion by *ca.* 0.1 *e*.

Then the nature of the Hg–C and Hg–X bonds will be investigated. As is shown in Table 7, the absolute values of $E^{(1)+(2)}_{Hg(s)-C}$ and $E^{(1)+(2)}_{Hg(p)-C}$ are remarkably large, and those of $E^{(1)+(2)}_{Hg(d)-C}$ and $E^{(3)}_{Hg-C}$ are less than one-tenth of $E^{(1)+(2)}_{Hg(s)-C}+E^{(1)+(2)}_{Hg(p)-C}$. Similar results are obtained with

TABLE 7. ELECTRONIC STRUCTURES OF CH_3HgX

X		F	Cl	Br	I	CH_3
Electron density	5d	9.92	9.93	9.93	9.94	9.93
	6s	0.99	1.07	1.10	1.11	1.15
	6p	0.42	0.51	0.52	0.53	0.62
Net charge of the Hg atom						
	CH_3HgX	0.68	0.49	0.45	0.42	0.30
	HgX_2		0.70	0.59	0.53	
Hg–C	$E^{(1)+(2)}_{\mathrm{Hg(d)-C}}$	−1.17	−1.08	−1.04	−0.98	−0.95
	$E^{(1)+(2)}_{\mathrm{Hg(s)-C}}$	−7.53	−6.95	−6.71	−6.55	−5.85
	$E^{(1)+(2)}_{\mathrm{Hg(p)-C}}$	−5.00	−5.44	−5.53	−5.60	−6.14
	$E^{(3)}_{\mathrm{Hg-C}}$	−1.36	−1.03	−0.94	−0.91	−0.76
	$E_{\mathrm{Hg-C(total)}}$	−15.06	−14.52	−14.23	−14.04	−13.70
Hg–X	$E^{(1)+(2)}_{\mathrm{Hg(d)-X}}$	−0.68	−0.59	−0.55	−0.48	
	$E^{(1)+(2)}_{\mathrm{Hg(s)-X}}$	−3.55	−4.20	−4.10	−4.20	
	$E^{(1)+(2)}_{\mathrm{Hg(p)-X}}$	−6.32	−5.76	−5.19	−4.85	
	$E^{(3)}_{\mathrm{Hg-X}}$	−2.57	−1.10	−0.85	−0.69	
	$E_{\mathrm{Hg-X(total)}}$	−13.11	−11.65	−10.70	−10.22	

E_{AB}: eV unit.

regard to the Hg–X bond. These results reveal that the Hg–C and Hg–X bonds are mainly contributed to from the covalent interaction of the 6s and 6p orbitals of the Hg atom with the C and X atoms. The 5d orbital of the Hg atom hardly contributes to these bonds, which is in conformity with the results that the 5d orbital has about 10 electrons, as has been described above.

Our MO method can give successful results for the electronic spectra, the electronic distribution, and the bond strength of the 5d transition metal complexes. It has been ascertained that this MO method is also useful in studying the electronic structures and the bonding nature of organometallic complexes.

These calculations were carried out with the FACOM 230-75 Computer of the Data Processing Center of Kyushu University.

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