Semi-empirical UHF-MO Studies of the Spin Distribution and the Bonding Character of Iron-group Fluorides and Some Other Similar Transition Metal Halides

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CNDO- and INDO-type UHF-MO calculations are carried out on MF_6^{n-} (M=V(II), Cr(III), Mn(II), Fe(III), Ni(II)), $NiCl_6^{4-}$, $MnCl_6^{4-}$, $MnCl_4^{2-}$, $MnBr_6^{4-}$, and $CuCl_4^{2-}$. The calculated spin fractions on the ligand orbitals agree well with the experimental values, with a few exceptions. Spin transfers to ligands are mainly attributed to the spin delocalization (SD) mechanism, except those to the 2s and $2p_\sigma$ orbitals of the F ligand in CrF_6^{3-} and VF_6^{4-}, in which spin transfer to those orbitals results from the spin polarization (SP) mechanism. Unpaired electrons are also transferred into the 4s and 4p orbitals of the central metal ion by the SP mechanism. The spin transfers to the ligand due to both the SD and SP mechanisms increase in the order of F<Cl<Br in MnX_6^{4-} and NiX_6^{4-}. The following characterisities of metal-halogen bonds are established; (1) the covalent interaction between the metal d-orbital and the fluorine atom increases in the order Ni(II)<Mn(II)$\sim$Fe(III)<Cr(III)$\sim$V(II) in MF_6^{n-}, and (2) in metal-halogen covalent interactions, the s-character of halogen decreases in the order F>Cl>Br, while the p-character increases in the same order.

^{19}F NMR studies of open-shell iron-group fluorides have revealed the existence of hyperfine interaction between the fluorine nuclei and the magnetic electrons.[1-7] Similar hyperfine interactions have also been observed in ESR studies of those complexes.[2,8-13] These hyperfine interactions have been explained in terms of the spin fractions on the F ligand.[2-15] It has been accepted that unpaired electrons have been brought into the s and p orbitals of the ligand by metal-fluorine covalency (the spin delocalization (SD) mechanism),[2-16] except in the cases of CrF_6^{3-} and VF_6^{4-}, in which the spin fractions on the 2s orbital of the F ligand are considered to result from the mixing of the excited states (the spin polarization (SP) mechanism).[4,10] However, the spin transfer due to the SP mechanism has not been ascertained theoretically.

Although some theoretical works have been carried out on the electronic structures of these complexes,[14-24] only a few UHF-MO calculations have been presented[19,20,23] which are suitable for studying the spin distribution. Only one INDO-type semi-empirical UHF-MO study of iron-group fluorides has been carried out, by Brown *et al.*[19] In that study, however, the fluorine's 2s orbital was neglected in the basis set, although this orbital is expected to contribute significantly to the metal-fluorine bond. There exists a possibility that this neglect leads to an incorrect conclusion as to the spin distribution.

In this work, semi-empirical UHF-MO calculations, which explicitly included all the valence orbitals, were carried out for iron-group fluorides and some other similar halides, such as $NiCl_6^{4-}$, $MnCl_6^{4-}$, $MnCl_4^{2-}$, $MnBr_6^{4-}$, and $CuCl_4^{2-}$. None of the latter compounds except $CuCl_4^{2-}$ and $MnCl_4^{2-}$ have ever been studied by means of the method, as for as we know. The MO method is a powerful means for studying the electronic structure of transition metal complexes. Especially we need much theoretical support when we attempt to interpret the results of NMR, ESR, *etc.* Thus, the purposes of this work are; (1) to investigate the electronic structures of these complexes, and (2) to ascertain how useful the semi-empirical SCF-MO method is in interpreting the NMR and ESR results of these complexes.

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Method, Parametrization, and Geometries

Method. A semi-empirical UHF-MO method is used, in which either a CNDO- or INDO-type approximation is included. The approximations used here are the same as our previous ones for the CNDO-type MO method[25] and the same as Konishi's for the INDO-type one[26] respectively. Only the one-electron part of the Fock-matrix elements, H_{rt}, in the INDO-type MO method will be reiterated here:

$$H_{rr} = -I_r - (N_r-1)\gamma_{rr} - \sum_{t\neq r}^{A} N_r(\gamma_{rt}-0.5\kappa_{rt}) - \sum_{B\neq A}\sum_{s}^{B} N_s\gamma_{rs} \quad (1)$$

$$H_{rt} = -0.5KS_{rt}(I_r+I_t) \quad (2)$$

where r-AO is on the A atom and where $\sum^A$ means the summation on the A atom. H_{rr} in the CNDO-type MO method is obtained by the use of Eq. (1) by neglecting κ_{rt}. For the Wolfsberg-Helmholz parameter, K,[27] the values of 1.0 and 0.8 are used in the AO pair including the d-orbital and in that including only the s and p orbitals[25b] respectively.

Parametrization. The elements of the first transition series have $d^{n-2}s^2$ configurations in their ground states, except for the Cr atom, which contains the d^5s configuration, where n represents the number of valence electrons. Thus, for metal atoms, the following ionization processes may be considered as valence-state ionizations:

(1) 3d orbital ionization potential (IP); $3d^{n-2}4s^2 \rightarrow 3d^{n-3}4s^2$,

(2) 4s orbital IP; $3d^{n-2}4s^2 \rightarrow 3d^{n-2}4s$,

(3) 4p orbital IP; $3d^{n-2}4s4p \rightarrow 3d^{n-2}4s$.

These values are calculated by using the data of Di Sipio *et al.*[28] The values of the one-center Coulomb repulsion integrals are also taken from the same work.[28] For ligand atoms, the values of the VSIP and one-center Coulomb repulsion integrals are taken from Hinze's work.[29] The values of one-center exchange repulsion intergrals are adopted from Di Sipio's work[30] for metal atoms and from Kato's report[31] for ligand atoms.

In INDO-type MO calculations, the values of the one-center Coulomb repulsion integrals, γ_{ds} and γ_{dp}, are evaluated from Slater-Condon parameters.[30]

The double-ζ type orbitals of Richardson *et al.*[32] are used only for the d-orbitals,[33] while single Slater-type orbitals[34] are used for the s and p orbitals.

Bond Index. The contribution of the AB bond to the total energy, E_{AB}, is used as the bond index.[35,36] This quantity is represented as follows under both approximations, CNDO- and INDO-type used here;

$$E_{AB} = \sum_r^A \sum_t^B [2P_{rt}H_{rt} - \{(P_{rt}^{\alpha})^2 + (P_{rt}^{\beta})^2\}\gamma_{rt}] + \sum_r^A \sum_t^B (P_{rr} - N_r)(P_{tt} - N_t)\gamma_{rt} \quad (3)$$

where $P_{rt} = P_{rt}^{\alpha} + P_{rt}^{\beta}$. The first term on the right-hand side represents approximately the contribution of the covalent bonding interaction, and the second one, approximately that of the electrostatic one. In order to investigate the metal-halogen bonding nature, the first term is divided into individual AO-pair terms, such as $E_{AB(s)}$, $E_{AB(p)}$, and $E_{AB(d)}$;

$$E_{AB(s)} = \sum_r^A [2P_{rs}H_{rs} - \{(P_{rs}^{\alpha})^2 + (P_{rs}^{\beta})^2\}\gamma_{rs}] \quad (4)$$

$$E_{AB(p)} = \sum_r^A \sum_t^{B(p)} [2P_{rt}H_{rt} - \{(P_{rt}^{\alpha})^2 + (P_{rt}^{\beta})^2\}\gamma_{rt}] \quad (5)$$

where $\sum^{B(p)}$ means the summation on the p-orbitals of the B atom. $E_{AB(d)}$ is similarly defined. The quantity, $E_{AB(s)}$, represents the contribution of the B atom's s-orbital to the A-B bond; $E_{AB(p)}$, that of the B atom's p-orbital, and $E_{AB(d)}$, that of the B atom's d-orbital. The second term in Eq. (3) is not divided into individual AO-pair terms, since it approximately represents the electrostatic interaction, and so the division described above is meaningless.

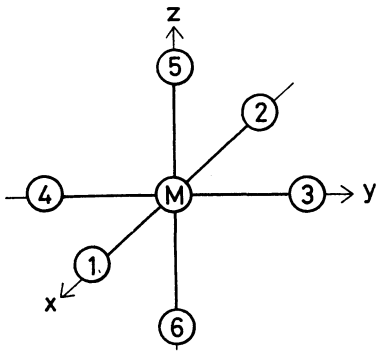

Fig. 1. The coordinate system of MX_6^{n-}.
In $CuCl_4^{2-}$ and $MnCl_4^{2-}$, x, y, and z axis are defined corresponding to their C_4 and C_2 axis respectively.
M–X bond lengths (Å unit): Ni–F=2.00, W. H. Bauer, *Acta Crystallogr.*, **11**, 588 (1958); Mn–F=2.095,[7] and 2.31,[11] see the footnote (f) of Table 3; Fe–F=1.994[11]; Cr–F=1.933;[4] V–F=1.994;[2] Ni–Cl=2.43;[40] Mn–Cl (Oh)=2.63;[13] Mn–Cl (Td)=2.32;[13]; Mn–Br=2.75 (the estimated value); Cu–Cl=2.26.[39]

Geometries. The structure of MX_6^{n-} is assumed for simplicitly to be a rigid octahedron, while its true structure is slightly distorted.[3,4,6] The coordinate system of MX_6^{n-} is shown in Fig. 1. The structures of $CuCl_4^{2-}$ and $MnCl_4^{2-}$ are considered to obey D_{4h}[37] and T_d[13] symmetries respectively.

Results and Discussion

Electron Densities. Table 1 gives the electron distributions calculated by the INDO-type MO method.

The INDO- and CNDO-type MO methods give similar electron densities on the 3d, 4s, and 4p orbitals of the central metal atom; for example, in the CNDO-

Table 1. Electron densities and atomic charges[a]

Compounds	Total density: Metal atom 3d	4s	4p	Halogen atom s	p_σ	p_π	Atomic charge: Metal	Halogen
NiF_6^{4-}	8.138	0.251	0.465	1.922	1.945	3.991	+1.146	−0.858
M–H–H–B[b]	8.023	0.071	0.060	1.985	5.986		+1.818	−0.970
$NiCl_6^{4-}$	8.151	0.449	0.764	1.923	1.864	3.985	+0.636	−0.773
FeF_6^{3-}	5.373	0.272	0.500	1.908	1.926	3.974	+1.855	−0.809
Obsd[c]							+1.33	
MnF_6^{4-}[d]	5.190	0.212	0.429	1.922	1.954	3.985	+1.169	−0.861
$MnCl_6^{4-}$	5.193	0.404	0.711	1.929	1.872	3.980	+0.692	−0.782
$MnBr_6^{4-}$	5.190	0.444	0.760	1.936	1.852	3.980	+0.607	−0.768
CrF_6^{3-}	3.701	0.226	0.479	1.878	1.919	3.968	+1.594	−0.766
Obsd[c]							+1.53	
VF_6^{4-}	3.449	0.192	0.447	1.885	1.956	3.977	+0.913	−0.819
$MnCl_4^{2-}$	5.247	0.394	0.780	1.864	1.933	3.848	+0.579	−0.645
$CuCl_4^{2-}$	9.197	0.471	0.599	1.904	1.807	3.973	+0.732	−0.683
D–V–W[e]	9.08	0.10[g]	0.15[g]	1.97[g]	1.92[g]	3.99[g]	+1.54	−0.88

a) The INDO-type MO method. The single annihilation scarcely affects on these results. b) Ref. 23. c) Ref. 38. d) Mn–F=2.095 Å. e) Ref. 39. g) These values are estimated by assuming that the core AO's are fully occupied.

type MO calculation of NiF_6^{4-}, the electron density on the 3d orbital is 8.201, that on the 4s one is 0.256, and that on the 4p one is 0.502. See also the results of the INDO-type MO calculation of NiF_6^{4-} in Table 1.

In NiF_6^{4-} and $CuCl_4^{2-}$, the electron densities on the 3d orbitals of the central metal atom agree well with those obtained by *ab initio* MO calculations,[23,38] while the electron densities on the 4s and 4p orbitals are remarkably larger than those obtained by the *ab initio* MO calculations. Generally speaking, the *ab initio* MO method gives reasonable electron densities. In transition metal complexes, however, the electron densities on 4s and 4p orbitals depend very much upon the orbital expandings.[39] Thus, the *ab initio* MO method, in which re-optimized AO exponents are not used, does not always give good results for the electron densities in transition metal complexes.

In FeF_6^{3-} and CrF_6^{3-}, the calculated net charges on the central metal ion agree fairly well with the experimental values, as is shown in Table 1. These agreements are better than those of the previous INDO-type method.[19]

In NiX_6^{4-} and MnX_6^{4-} (X=F, Cl, Br), the positive net charge on the central metal ion and the negative net charge on the ligand decrease in this order: F>Cl>Br. This result is reasonable considering the electronegativities of the halogens. While the electron densities on the p_π orbital of the halogen scarcely depend on the kind of halogen, those on the p_σ orbital decrease in this order: F>Cl>Br, and those on the s orbital increase slightly in this order: F<Cl<Br. Since the metal-halogen coordination bond is formed by the electron donation from the halogen anion to metal, and since the stronger interaction should bring about less electron density on the halogen, this result suggests that the contribution of the halogen's p_σ orbital to the metal-halogen bond increases in the order of F<Cl<Br, while that of the s orbital decreases. On this issue, a more detailed discussion will be presented in the following paragraph.

In $MnCl_4^{2-}$, the net charges on the Mn and Cl atoms are smaller than those of $MnCl_6^{4-}$. This suggests that more electrons are donated from ligands to the metal ion in $MnCl_4^{2-}$ than in $MnCl_6^{4-}$. A more precise inspection of the electron densities reveals that the strong electron donation in $MnCl_4^{2-}$ results from the formation of a strong π-bond between the Mn and Cl atoms; in $MnCl_4^{2-}$, the electron densities on the $3p_\pi$ orbitals of the Cl ligand are considerably smaller than those of $MnCl_6^{4-}$, while that on the $3p_\sigma$ orbital in $MnCl_4^{2-}$ is larger than that in $MnCl_6^{4-}$.

Metal-halogen Bonding Nature. In order to investigate the metal-halogen bonding nature, E_{MX} (M=metal atom, X=halogen atom) is divided into $E_{MX(s)}$, $E_{MX(p)}$, $E_{M(d)X}$, and $E_{M(s+p)X}$. The results are given in Table 2.

The absolute values of $E_{M(s+p)X}$ are remarkably large and do not depend very much on the kind of central metal, which suggests the 4s and 4p orbitals participate in the metal-halogen covalent bond to almost the same degree in all complexes. The absolute values of $E_{M(d)X}$ depend largely on the kinds of the metal atoms and increase in this order; Ni(II)<Mn(II)~Fe(III)<Cr(III)~V(II), which suggests that the contribution of the 3d orbitals to the metal-halogen bond increases in this order. This increasing order agrees with the decreasing tendency of the numbers of electrons held in the molecule; *i.e.*, as is shown in Fig. 2, the increasing numbers of electrons result in more electrons in the anti-bonding MO's, e_g^* and t_{2g}^*, and as a consequence

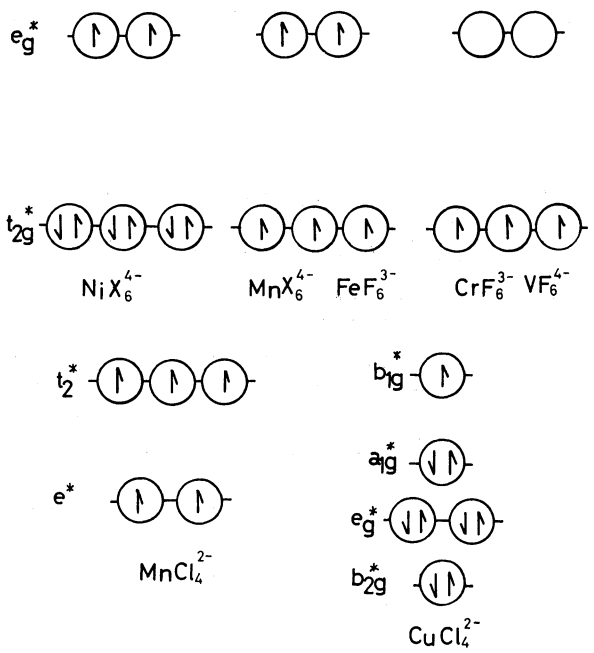

Fig. 2. Schematic MO's mainly contributed from d orbitals of the central metal ion.
These MO's have weak anti-bonding character.

TABLE 2. METAL-HALOGEN BONDING NATURES[a]

(A) Effect of metal atom on metal-halogen covalent bond

Metal atom	Ni(II)	Fe(III)	Mn(II)[b]	Cr(III)	V(II)
$E_{M(d)X}$ (eV)	−0.882	−1.903	−1.383	−4.909	−4.445
$E_{M(s+p)X}$ (eV)	−7.042	−7.451	−6.405	−7.622	−7.229

(B) Effect of halogen atom on metal-halogen covalent bond

Halogen atom	MnX_6^{4-}			NiX_6^{2-}	
	F[b]	Cl	Br	F	Cl
$E_{MX(s)}$ (eV)	−5.770	−3.349	−2.925	−5.844	−3.779
$E_{MX(p)}$ (eV)	−2.018	−3.793	−4.012	−2.079	−4.117

a) The INDO-type MO method. After a single annihilation. b) Mn–F=2.095 Å.

TABLE 3. SPIN FRACTIONS ON THE F⁻ LIGAND (%)

	Method	NiF_6^{4-}		MnF_6^{4-}		FeF_6^{3-}		CrF_6^{3-}		VF_6^{4-}	
		f_s	$f_{p_\sigma}-f_{p_\pi}$	f_s	$f_{p_\sigma}-f_{p_\pi}$	f_s	$f_{p_\sigma}-f_{p_\pi}$	f_s	$f_{p_\sigma}-f_{p_\pi}$	f_s	$f_{p_\sigma}-f_{p_\pi}$
Ours	CNDO	0.72	2.78	0.66	2.32	1.40	4.23	0.0	−1.79	0.0	−0.92
	INDO	0.49	1.80	0.38	1.05	0.94	3.76	−0.19	−1.79	−0.17	−0.88
				0.71	1.29[f]						
	INDO-aa	0.50	1.79	0.40	1.09	0.96	3.75	−0.11	−1.49	−0.10	−0.78
Clack[b]	CNDO-B	0.02	0.33	0.12	1.17	0.15	7.97	−0.003	−0.415	0.0	−0.2002
	CNDO-G	0.15	1.39	0.34	2.25	0.44	7.38	−0.01	−0.74	0.0	−0.30
Brown[c]	MCZDO	—	0.46	—	1.98	—	5.14	—	−4.74	—	—
Obsd	NMR	0.538	3.78[d]	0.52	0.18[g]	—	—	−0.021	−4.90[g]	—	—
	ESR	0.490	4.51[e]	0.47	0.80[e]	0.763	3.3[e]	−0.031	−4.76[e]	−0.072	−2.8[h]
				0.41	1.30[e]						

a) "aa" means the results after a single annihilation. b) Ref. 20). c) Ref. 19). d) Ref. 7). e) Ref. 11). f) Mn–F=2.095 Å. Since the ESR data (Mn–F=2.31 Å) is considerably different from NMR one (Mn–F=2.095 Å), two bond lengths of Mn–F are examined. g) Ref. 4). h) Ref. 2).

of this, the metal-halogen bond becomes weak.

The $E_{MX(s)}$ and $E_{MX(p)}$ of MnX_6^{4-} and NiX_6^{4-} are also given in Table 2. The absolute value of $E_{MX(s)}$ decreases in this order; F>Cl>Br, while that of $E_{MX(p)}$ increases in this order; F<Cl<Br. These results suggest that the contribution of the halogen's s orbital to the metal-halogen bond decreases in this order; F>Cl>Br and that the contribution of the halogen's p orbital increases in this order; F<Cl<Br. This bonding nature is consistent with that discussed in the previous paragraph on the basis of electron density.

Spin Fraction on the Ligands. Results are given in Tables 3 and 4, compared with the experimental values[2,4,7,11] and the previously calculated ones.[19,20] In Table 3, "aa" represents the results after a single annihilation.

TABLE 4. SPIN FRACTIONS ON THE Cl⁻ LIGAND[a]

Compounds	f_s (%)		$f_{p_\sigma}-f_{p_\pi}$ (%)	
	Calcd	Obsd	Calcd	Obsd
$NiCl_6^{4-}$	0.33	0.58[b]	2.10	7.3[b]
$MnCl_6^{4-}$	0.37	0.4[c]	1.50	3.9[c]
$MnCl_4^{2-}$	0.25	—	−2.71[d]	—
$CuCl_4^{2-}$	0.27[d]	0.61	5.09	11.9[d]

a) The INDO-type MO method. After a single annihilation. b) Ref. 40). c) Ref. 13). d) This value is the one before annihilation, since our coordinate system cannot give spin fractions on p_σ and p_π orbitals after annihilation.

INDO-type MO calculations give smaller values of f_s and $f_{p_\sigma}-f_{p_\pi}$ than the CNDO-type MO calculations in all complexes.

As is shown in Fig. 2, NiF_6^{4-} has a $t_{2g}{}^{*6}e_g{}^{*2}$ configuration, and MnF_6^{4-} and FeF_6^{3-} have $t_{2g}{}^{*3}e_g{}^{*2}$ one. Metal-fluorine covalency results in positive spin fractions on the 2s and $2p_\sigma$ orbitals of the F ligand in NiF_6^{4-} and positive ones on the 2s, $2p_\sigma$, and $2p_\pi$ orbitals in MnF_6^{4-} and FeF_6^{3-}. In these complexes, both CNDO- and INDO-type MO methods can give reasonable results on spin fractions, as is shown in Table 3. Our results are in better agreement with the experiments than the previously calculated ones.[19,20] Single annihilations affect the values of f_s and $f_{p_\sigma}-f_{p_\pi}$ hardly at all.

In CrF_6^{3-} and VF_6^{4-}, which contain $t_{2g}{}^{*3}$ configurations, as is shown in Fig. 2, metal-fluorine covalency brings positive spin fractions into only two $2p_\pi$ orbitals of the F ligand. Negative spin fraction is also observed on the 2s orbital of the F ligand in these complexes; this is thought to be due to the spin polarization.[4,10] While the CNDO-type MO method fails to give this spin fraction, the INDO-type one can give it. The single annihilation, which gives almost complete eigenvalues of $\mathbf{S}^2$ (See Table 5), brings about remarkably large changes in the values of f_s and $f_{p_\sigma}-f_{p_\pi}$. Although, in these complexes, the values of f_s and $f_{p_\sigma}-f_{p_\pi}$ do not fit in with the experimental values except for the f_s value of VF_6^{4-}, these calculated values are better than the results obtained by the previous CNDO/II calculation[20] and seem reasonable considering the relatively large uncertainty in the experimental values.

The results for chloro complexes are given in Table 4; they were calculated by the INDO-type MO method. The calculated values of f_s agree fairly well with the experimental values except for the case of $CuCl_4^{2-}$. The $f_{p_\sigma}-f_{p_\pi}$ value in chloro complexes are larger than those in fluoro complexes, which is reproduced by our calculations. These calculated values, however, are considerably smaller than the experimental values, as is shown in Table 4.

Spin-transfer Mechanism. Spin fractions are divided into two components according to the method of Nakatsuji *et al.*;[42] the components due to the SD mechanism and the others due to the SP mechanism. The results are given in Table 5, together with the expected values of $\mathbf{S}^2$ before and after a single annihilation.

The expectation values of $\mathbf{S}^2$ before annihilation are almost the same to the eigenvalues of $\mathbf{S}^2$ in all complexes, although there is a little difference between the two values in CrF_6^{3-} and VF_6^{4-}. This shows that we can investigate the electronic structures of these complexes with a single Slater determinant. In all the complexes, unpaired electrons are localized in the d orbitals of the central metal ion; this shows that it is reasonable to use the crystal field theory in the qualitative discussion of the electronic structures of these complexes.

TABLE 5. SPIN APPEARING MECHANISM[a)]

Complex		Metal ion (%)				Ligand ion (%)			S^{2} [b)]	
		$3d_{t_{2g}}$	$3d_{e_g}$	4s	4p	s	p_σ	p_π	ba	aa
NiF_6^{4-}	SD	0.0	93.12	0.0	0.0	0.51	1.78	0.0	2.000	2.000
	SP	0.0	0.0	0.11	0.0	−0.01	0.01	0.0		
$NiCl_6^{4-}$	SD	0.0	92.45	0.0	0.0	0.35	2.16	0.0	2.000	2.000
	SP	0.0	0.0	0.28	0.09	−0.02	−0.05	−0.01		
FeF_6^{3-}	SD	96.98	85.86	0.0	0.0	1.00	3.71	0.75	8.750	8.750
	SP	0.0	0.0	0.14	0.02	−0.04	0.03	−0.01		
MnF_6^{4-} [c)]	SD	99.34	94.53	0.01	0.0	0.46	1.37	0.16	8.750	8.750
	SP	0.0	0.0	0.61	0.18	−0.06	−0.12	0.0		
$MnCl_6^{4-}$	SD	98.77	92.16	0.03	0.0	0.47	2.15	0.30	8.751	8.750
	SP	0.01	0.01	1.42	0.52	−0.10	−0.37	−0.03		
$MnBr_6^{4-}$	SD	98.81	92.24	0.04	0.01	0.39	2.20	0.29	8.752	8.750
	SP	0.02	0.02	1.77	0.66	−0.09	−0.50	−0.02		
CrF_6^{3-}	SD	95.76	−0.04	0.0	0.0	0.0	0.01	1.04	3.753	3.750
	SP	0.03	1.34	0.30	0.14	−0.11	−0.46	0.0		
VF_6^{4-}	SD	97.42	0.01	0.0	0.0	0.0	0.0	0.64	3.751	3.750
	SP	0.0	0.49	0.21	0.11	−0.10	−0.15	0.0		
$MnCl_4^{2-}$ [d)]	SD	91.43	96.59	0.02	2.54	0.52	1.90[e)]		8.752	8.750
	SP	0.12	0.02	1.26	0.74	−0.27	−0.23[e)]			
		$d_{x^2-y^2}$	d_{z^2}	4s	4p	3s	$3p_\sigma$	$3p_\pi$		
$CuCl_4^{2-}$ [f)]	SD	79.00%	0.0%	0.0%	0.0%	0.27%	4.98%	0.0%	0.750	0.750
	SP	0.0	0.04	−0.21	−0.11	0.0	0.10	−0.10		

a) The INDO-type MO method. These data are spin fraction per an orbital after annihilation. b) "aa" and "ba" mean after and before a single annihilation, respectively. c) Mn–F=2.31 Å. d) In $MnCl_4^{2-}$, t_{2g} and e_g should be replaced by t_2 and e, respectively. e) These values are spin fraction on a p-orbital. In our coordinate system, spin fractions on p-orbital after annihilation can not be divided into those on p_σ and p_π orbitals. f) In $CuCl_4^{2-}$, the other 3d-orbitals and $4p_\pi$-orbital do not have spin fractions.

Spin transfer to the ligands is mainly contributed to by the SD mechanism in NiX_6^{4-}, MnX_6^{4-}, and FeF_6^{3-}. It should be noted, however, that the SP mechanism brings a little negative spin fractions on the P_π orbitals of the ligand in MnX_6^{4-}. In these complexes, spin transfer to the halogen s orbital through the SD mechanism roughly decreases in this order; F≳Cl>Br, while that to the halogen p orbital through the same mechanism increases in the same order; F<Cl<Br. It is interesting that the former decreasing order agrees with decreasing order of the halogen's s orbital contribution to the metal-halogen bond, and that the latter increasing one agrees with the increasing order of the halogen's p-orbital contribution (See Table 2-B). The spin fraction due to the SP mechanism increases in this order; F<Cl<Br. It is also interesting that this order agrees with the reverse order of the spectrochemical series. These interesting features should be investigated in more detail.

In CrF_6^{3-} and VF_6^{4-}, the SD mechanism brings about positive spin fractions on the two $2p_\pi$ orbitals of the F ligand, while the SP mechanism induces negative spin fractions on the 2s and $2p_\sigma$ orbitals of the F ligand. These results support the previous proposal of spin transfer in these complexes.[3,10] In $MnCl_4^{2-}$ and $CuCl_4^{2-}$, the spin fractions on the ligand are mainly due to the SD mechanism, while in $MnCl_4^{2-}$ the SP mechanism contributes considerably to f_s and f_p. In $MnCl_4^{2-}$, spin transfer to the Cl ligand is larger than that in the $MnCl_6^{4-}$.

The SP mechanism also induces spin fractions on the 4s and 4p orbitals of the central metal ion in all the complexes. Furthermore, in CrF_6^{3-} and VF_6^{4-} its mechanism also induces positive spin fractions on the $3d_{e_g}$ orbitals.

Comparison between the CNDO- and INDO-type Methods. The CNDO-type MO method can not give the spin fraction due to the SP mechanism, while the INDO-type one can; in CrF_6^{3-} and VF_6^{4-}, the CNDO-type MO method can not give the spin fraction on the 2s and $2p_\sigma$ orbitals of the F ligand which is induced by the SP mechanism, as has been described in the previous paragraph and shown in Table 5. Thus, the CNDO-type method is inferior to the INDO-type method in treating the spin fraction induced by the SP mechanism. It is worthwhile to compare these two methods in the MO calculation of such complexes as NiF_6^{4-}, where the SD mechanism mainly brings about the spin fraction on the ligand (See Table 5) and where the CNDO-type MO method gives good results for the spin distribution. Table 6 gives the MO energies and MO coefficients of NiF_6^{4-}. The CNDO-type MO method gives quite the same MO energies and the same MO coefficients between α-spin and β-spin MO's, while the INDO-type method gives considerably different values. Thus, the CNDO-type method does not show the polarization effects on the MO energy and MO coefficients sufficiently well and is not satisfactory even in NiF_6^{4-}.

In conclusion, the INDO-type MO method used here can give good results on spin fractions. It is expected that this can be used in studies of the electronic structures of open-shell transition metal complexes and

Table 6. Comparison between the CNDO-type and INDO-type MO methods
$2t_{2g}$* MO of NiF_6^{4-}

Method		ε (eV)[a]	Eigenvector[b]
CNDO	α-spin	7.848	$0.783\,d_{xz} - 0.311[(1z)-(2z)+(5x)-(6x)]$
	β-spin	7.848	$0.783\,d_{xz} - 0.311[(1z)-(2z)+(5x)-(6x)]$
INDO	α-spin	7.621	$0.201\,d_{xz} - 0.201[(1z)-(2z)+(5x)-(6x)]$
	β-sinp	8.818	$0.952\,d_{xz} - 0.153[(1z)-(2z)+(5x)-(6x)]$

a) These positive MO energies would be due to the neglect of effects of cation and/or crystal lattice[19]. The extra potential, such as crystal lattice, do not give so great effect on spin fraction.[19] b) $(1z)$ *etc.* means the p_z orbital of the ligand 1 (See Fig. 1.).

can be of great help in interpreting the results of NMR, ESR, *etc.*

These calculations were carried out using the Facom 230-75 Computer of the Data Processing Center in Kyoto University.

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