ELECTRONIC MECHANISMS OF METAL CHEMICAL SHIFTS FROM Ab Initio THEORY

Hiroshi Nakatsuji
Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University, Kyoto 606, Japan
and
Institute for Fundamental Chemistry,
Nishi-Hiraki-cho, Kyoto 606, Japan

ABSTRACT. A progress report on the study of the mechanisms of the metal chemical shifts carried out in this laboratory is given. The major mechanism is understood by the atomic electron configuration of the central metal: p- and d-mechanisms for $d^{10}s^{1-2}p^0$ metal complexs, d-excitation mechanism for d^n metal complexes, and p-excitation mechanism for s^2p^2 metal complexes. Though the paramagnetic term is the origin for most complexes, the chemical shifts of the Ga and In (s^2p^1) halides are primarily determined by the diamagnetic term, and therefore by the structural factors (geometry and nuclear charges) alone.

1. INTRODUCTION

This article is intended to be a progress report of the theoretical studies on the metal NMR chemical shifts of various metal complexes performed in my laboratory. Due to recent advances in multi-nuclear NMR technique, a lot of experimental observations of metal chemical shifts have been reported [1]. Since chemical shifts depend largely on the angular momenta of electrons around the observed nuclei, they reflect p and d electronic structures in the bondings of the metal complexes. The purpose of our series of studies is four-fold.

(1) to establish a reliable ab initio method for calculating metal chemical shifts.
(2) to clarify electronic origins and mechanisms of metal chemical shift by analyzing calculated results.
(3) to give a guiding concept to experimental chemists which is useful for understanding the trends in metal chemical shifts.
(4) to thus have a deeper understanding on the electronic structure of metal complexes.

We classify the metal complexes we have studied so far into four groups, according to the similarity in the mechanism of the chemical shifts. They are

(1) $d^{10}s^{1-2}p^0$ metals; Cu, Ag, Zn, Cd complexes [2]
(2) d^n metals; Ti, Nb, Mo, Mn complexes [3]
(3) s^2p^2 metals; Si, Ge, Sn compounds [4]
(4) s^2p^1 metals; Ga, In halides [5]

J. A. Tossell (ed.), Nuclear Magnetic Shieldings and Molecular Structure, 263–278.

We briefly review our studies on the electronic mechanisms of the metal chemical shifts in these groups of compounds [6].

2. METHOD AND ANALYSIS

The chemical shift of the compound M is defined as a difference in the nuclear magnetic shielding constant σ relative to the reference compound as

$$\Delta\sigma_M = \sigma(\text{reference}) - \sigma(M). \quad (1)$$

The nuclear magnetic shielding constant σ is expressed as a sum of the diamagnetic term σ^{dia} and the paramagnetic term σ^{para},

$$\sigma = \sigma^{dia} + \sigma^{para}. \quad (2)$$

σ^{dia} and σ^{para} are the first and second order terms, respectively, in the perturbation theory [7];

$$(\sigma^{dia})_{xy} = -\frac{\mu_0 e^2}{8\pi m^2} < 0 \mid \sum_{\nu} \frac{r_\nu r_{A\nu}\delta_{xy} - r_{x\nu} r_{Ay\nu}}{r_{A\nu^3}} \mid 0 > \quad (3)$$

$$(\sigma^{para})_{xy} = -\frac{\mu_0 e^2}{8\pi m^2} \sum_{n} \frac{1}{E_n - E_0} [< 0 \mid \sum_{\nu} l_{x\nu} \mid n >< n \mid \sum_{\nu} \frac{l_{Ay\nu}}{r^3_{A\nu}} \mid 0 > + \text{c.c.}] \quad (4)$$

where $\mid 0 >$ and $\mid n >$ denote the ground and excited states, respectively, and $l_{Ay\nu}$ is the y component of the angular momentum operator of the νth electron around the nucleus A. The summation is taken over all the excited states.

The nuclear magnetic shielding constant is calculated by the Hartree-Fock/ finite perturbation method [8]. It is connected to and can be rewritten in the sum-over-state perturbation formula given by eq.(4) [9].

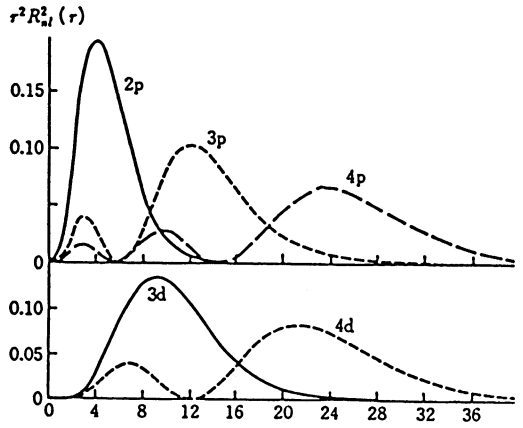


Figure 1. Radial distribution functions of the p- and d-orbitals of hydrogenic atom.

We analyze the magnetic shielding constant into AO contributions and MO contributions [2a]. They are defined by eqs.(10) and (11), respectively, of ref. 2a. The former is defined in the spirit of the Mulliken population analysis. It is important to note here that the shift in the paramagnetic term is dependent on the inner distributions of the valence electrons near the nucleus, since the NMR

operator in eq.(4) involves the term $1/r_A^3$. Figure 1 shows the radial distribution functions of the *n*p and *n*d orbitals of a hydrogenic atom. The 4p orbital, for example, has two small amplitudes in the 3p and 2p regions, which are important for the NMR operators. Namely, the valence electrons near the nucleus are observed through the NMR experiment.

In the following sections, we review our studies on the metal NMR chemical shifts. We do not discuss the geometries of the compounds, the basis sets, and some other computational details, which are explained in the original articles [2-5].

3. $d^{10}s^{1-2}p^0$ METAL COMPOUNDS; Cu, Ag, Zn, Cd COMPLEXES

The metal complexes belonging to this group are characterized by the electronic configuration of the central metal, $d^{10}s^{1-2}p^0$. The results of the ab initio finite perturbation calculation reproduce well the experimental chemical shifts: as an example, Figure 2 shows the correlation between theoretical and experimental values for the Cd chemical shift [2b]. Table 1 shows the analysis for the Cd shift

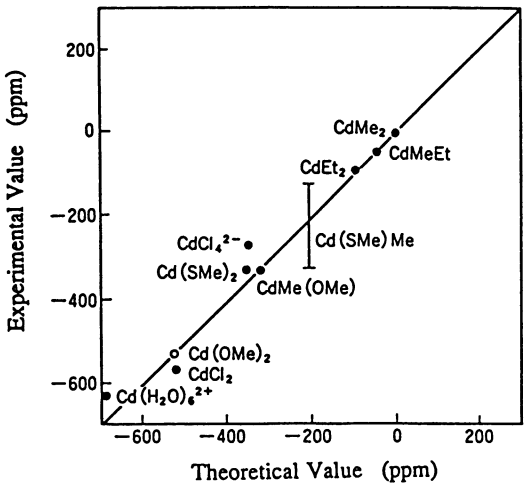


Figure 2. Comparison between experimental and theoretical values for the Cd chemical shifts of the cadmium complexes.

Table 1. Diamagnetic and paramagnetic contributions to the Cd magnetic shielding constant and their analysis into core and valence MO contributions (in ppm)

molecule	diamagnetic term σ^{dia}				paramagnetic term σ^{para}				magnetic shielding σ	
	core	valence	total	shift	core	valence	total	shift	total	shift
$CdMe_2$	4595	256	4851	0	-43	-1047	-1090	0	3761	0
CdMeEt	4602	272	4874	-23	-43	-1021	-1064	-26	3810	-48
$CdEt_2$	4607	289	4896	-45	-43	-995	-1038	-52	3857	-96
CdMe(OMe)	4602	276	4878	-27	-33	-755	-788	-302	4089	-328
$Cd(OMe)_2$	4609	296	4905	-54	-27	-590	-617	-473	4288	-527
CdMe(SMe)	4630	270	4900	-49	-36	-898	-934	-156	3965	-204
$Cd(SMe)_2$	4665	284	4949	-98	-31	-801	-832	-258	4117	-356
$CdCl_2$	4655	253	4908	-57	-25	-643	-668	-422	4240	-479
$CdCl_4^{2-}$	4731	314	5045	-194	-40	-875	-915	-175	4129	-368
$Cd(H_2O)_6^{2+}$	4626	378	5004	-153	-33	-442	-475	-615	4529	-768

into the diamagnetic and paramagnetic terms, which are further divided into core and valence MO contributions. The valence electron contribution to the paramagnetic term is the origin of the chemical shift. Table 2 further shows an analysis of the Cd paramagnetic term into Cd p and d AO contributions (s AO contribution is identically zero) and ligand contributions. We see that the p AO contribution is dominant, though the d AO contribution is not negligible. We conclude that for the Cd chemical shift, the valence p AO contribution is most important.

Table 2. Contributions to the paramagnetic term of the Cd nuclear magnetic shielding constant σ^{para} from the cadmium s, p and d AOs and the ligands (in ppm)

molecule	Cd					Ligand					
	s	p	shift	d	shift	Me	Et	OMe	SMe	Cl	H_2O
$CdMe_2$	0	-992	0	-68	0	-15	---	---	---	---	---
CdMeEt	0	-958	-34	-71	3	-15	-21	---	---	---	---
$CdEt_2$	0	-923	-69	-74	6	---	-21	---	---	---	---
CdMe(OMe)	0	-656	-336	-101	33	-14	---	-16	---	---	---
$Cd(OMe)_2$	0	-460	-532	-125	57	---	---	-16	---	---	---
CdMe(SMe)	0	-850	-142	-56	-12	-15	---	---	-14	---	---
$Cd(SMe)_2$	0	-766	-226	-38	-30	---	---	---	-14	---	---
$CdCl_2$	0	-291	-701	-124	56	---	---	---	---	-6	---
$CdCl_4^{2-}$	0	-604	-388	-52	-16	---	---	---	---	-7	---
$Cd(H_2O)_6^{2+}$	0	-723	-269	-166	98	---	---	---	---	---	-10

For Cu, Zn, Ag and Cd complexes, ab initio calculations are performed similarly and the mechanisms of the chemical shifts are investigated [2a]. Tossell reported ab initio calculations for Zn and Cd complexes [10].

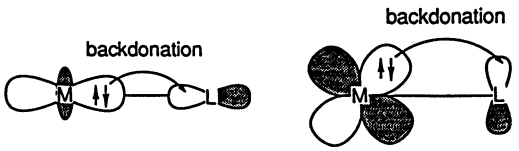
Table 3 shows a summary of the mechanisms of the metal chemical shifts for the Cu, Ag, Zn and Cd complexes [2a]. For the complexes of the $d^{10}s^{1-2}p^0$ metals, the paramagnetic term, which is an origin of the chemical shift, is due to the electrons in the outer valence p orbitals and the holes in the valence d orbitals of the metal atom. The mechanisms of these electrons and holes being produced are shown in Figure 3. These mechanisms of the chemical shifts are referred to as p-mechanism or p-electron mechanism and d-mechanism or d-hole mechanism. For the Cd and Zn complexes, the p-mechanism is more important than the d-mechanism, so that the chemical shift would go lower field as the electron donating ability of the ligand increases. For the Cu complexes, on the other hand, the metal chemical shift is due primarily to the d-mechanism so that it increases with increasing electron-withdrawing ability of the ligand. For the Ag complexes, the p and d mechanisms are competitive, and therefore, both of the donating and withdrawing properties of the ligand are important. Note that the effect of the electron donating (or with drawing) ligand on the chemical shift will be opposite, depending on whether the d- or p-mechanism is more important.

Referring to Table 1, we see that the paramagnetic term for the Cd chemical shift becomes more positive in the order of the ligands, Me < Et < SMe < OMe, which is the order of the electron withdrawing ability. Thus, the Cd chemical shift moves to higher field in this order of the ligands, in accordance with Table 3.

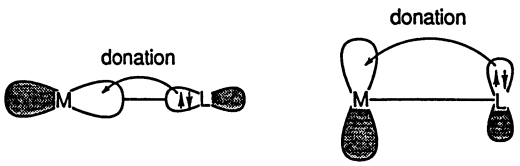
Now, why do these differences in the mechanism of the metal chemical shift occur ? The answer may be given from the atomic energy levels of the Cu^+, Ag^+, Zn^{2+}, and Cd^{2+} ions shown in Figure 4. It shows the energy levels of the d^{10}, d^9s^1, and d^9p^1 configurations [11]; the d^9s^1 level is taken as a standard since this configuration is important for the bonding with the ligands. The s-d separation of Cu is smaller than the s-p separation. The reverse is true for Zn and Cd, but for

Table 3. Major mechanism of the metal chemical shift for Cu, Zn, Ag, Cd complexes and the nature of ligand which gives lower field shift

Metal complex	Major mechanism	Lower field shifting ligand
Cu	d-mechanism	electron-acceptor
Cd, Zn	p-mechanism	electron-donor
Ag	p- and d-mechanisms	electron-donor electron-acceptor



d-mechanism : holes in d shell



p-mechanism : electrons in p orbital

Figure 3. Illustration of the d-hole and p-electrom mechanisms of the chemical shifts of the 1B and 2B metal complexes. They are due to the metal-ligand interactions which produce holes in the valence d shell and eletrons in the valence p orbital, respectively.

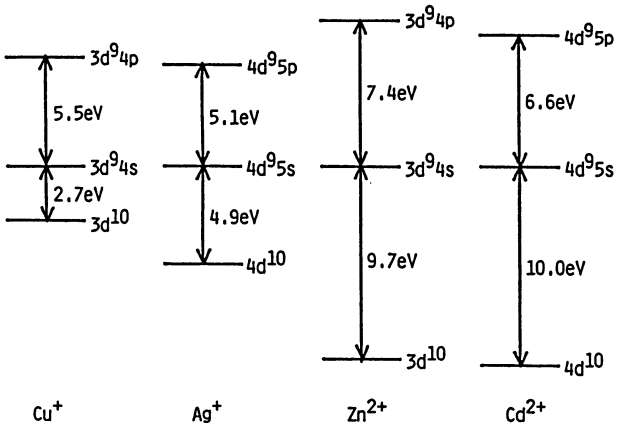


Figure 4. Atomic energy levels of the 1B (Cu, Ag) and 2B (Zn, Cd) metal ions. The energy levels of the d^9s^1 configurations are taken as a standard.

Ag the two separations are almost equal. Therefore, the d orbitals of Cu would more easily mix with the metal-ligand bonds than the p orbitals. On the contrary, the p orbitals of Zn and Cd would more easily mix with the metal-ligand bonds than the d orbitals. For Ag, the two tendencies should be almost equal. Thus, the major mechanisms of the metal chemical shifts of the Cu, Cd, Zn, and Ag complexes summarized in Table 3 are explained from the atomic energy levels of the central metal atoms: they are the intrinsic properties of the metals.

4. d^n METAL COMPOUNDS; Ti, Nb, Mo, Mn COMPLEXES

The transition metals, Ti, Nb, Mo, and Mn, are characterized by their open d subshells, d^2s^2, d^4s^1, d^5s^1, and d^5s^2, respectively: d-orbitals are active and split into both occupied and unoccupied MO's. The mechanism of the chemical shifts of these compounds is closely related to this open d-subshell nature of the central metal atoms and is commonly d-excitation or d-d* mechanism. We explain general features of the chemical shifts of these compounds, taking the Mo complexes, $MoO_{4-n}S_n^{2-}$ (n=0-4) and $MoSe_4^{2-}$, as an example [3b]. For Mo complexes, we also refer to the study of Combariza et al. [12].

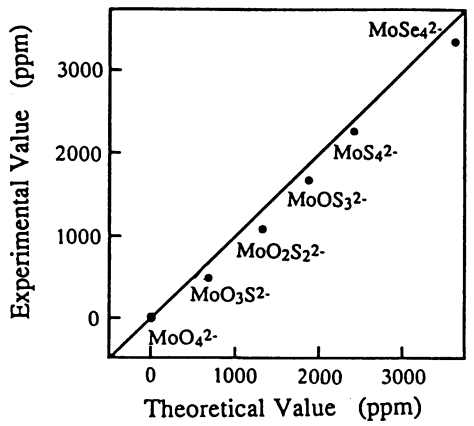


Figure 5. Comparison between theory and experiments for the Mo chemical shift.

Table 4. Diamagnetic and paramagnetic contributions to the Mo magnetic shielding constant and their analysis into core and valence MO contributions (in ppm)

molecule	diamagnetic term σ^{dia}				paramagnetic term σ^{para}				magnetic shielding σ		expt'l
	core	valence	total	shift	core	valence	total	shift	total	shift	shift
MoO_4^{2-}	3968	195	4163	0	-172	-5429	-5601	0	-1438	0	0
MoO_3S^{2-}	3958	190	4148	15	-34	-6236	-6269	668	-2121	683	497
$MoO_2S_2^{2-}$	3948	185	4132	31	122	-6933	-6810	1209	-2801	1367	1066
$MoOS_3^{2-}$	3938	180	4117	46	306	-7728	-7422	1821	-3305	1867	1654
MoS_4^{2-}	3928	175	4102	60	505	-8443	-7938	2337	-3835	2397	2258
$MoSe_4^{2-}$	3928	169	4097	66	668	-9820	-9152	3550	-5055	3616	3339

The correlation between theory and experiment for the Mo chemical shift is shown in Figure 5. The ab initio Hartree-Fock/finite perturbation method reproduces reasonably well the Mo chemical shifts of the compounds studied. An analysis

of the magnetic shielding constant into diamagnetic and paramagnetic contributions and further analysis into core and valence electron contributions are shown in Table 4. We see that the valence electron contribution to the paramagnetic term is the dominant origin of the chemical shift. In Table 5 we analyze the paramagnetic contribution into the molybdenum AO contribution and the ligand contribution and find that the change in the molybdenum d-AO contribution induced by the ligand substitution is the dominant origin of the chemical shift. Note that the Mo s-AO contribution is zero, since it does not have an angular momentum. Since Mo has an open d-subshell and since d-electrons have large angular momentum, the rotation of the d electrons around the Mo nucleus induced by the applied magnetic field gives an additional magnetic field at the nucleus. The ligand effect on this induced magnetic field is the origin of the chemical shift.

Table 5. AO contributions to the paramagnetic term of the Mo magnetic shielding constant (in ppm)

molecule	Mo				Ligand				σ^{para}
	s	p	d	total	O	S	Se	total	total
MoO_4^{2-}	0	-703	-4862	-5565	-8.9	---	---	-35	-5601
MoO_3S^{2-}	0	-679	-5566	-6264	-8.7	-1.1	---	-26	-6269
$MoO_2S_2^{2-}$	0	-661	-6127	-6793	-8.0	-0.8	---	-18	-6810
$MoOS_3^{2-}$	0	-671	-6746	-7413	-7.7	-0.5	---	-9	-7422
MoS_4^{2-}	0	-700	-7236	-7936	---	-0.4	---	-2	-7938
$MoSe_4^{2-}$	0	-656	-8489	-9145	---	---	-1.5	-6	-9151

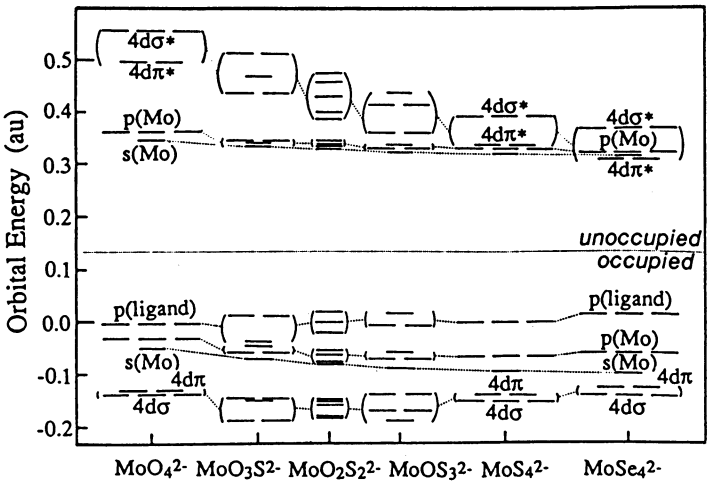


Figure 6. Molecular orbital energy diagram for the Mo complexes.

Now, how does the ordering of the chemical shifts among the $MoO_{4-n}S_n^{2-}$ (n=0 - 4) and $MoSe_4^{2-}$ arise ? The molecular orbital energy diagram shown in Figure 6 gives a solution to this question. Among the occupied and unoccupied valence MO's, the unoccupied $4d\pi^*$ and $4d\sigma^*$ MO's are much stabilized as the ligand is

substituted from O to S and to Se, namely from hard to soft ligands. We therefore expect that the excitations from the $4d\sigma$ and $4d\pi$ MO's to the $4d\sigma^*$ and $4d\pi^*$ MO's are the most important terms in the sum-over-state perturbation formula given by eq.(4). The softer the ligand is, the more stabilized are the $4d\sigma^*$ and $4d\pi^*$ MO's and the smaller is the excitation energy from the $4d\sigma$ and $4d\pi$ MO's to the $4d\sigma^*$ and $4d\pi^*$ MO's. This change in the excitation energy, appearing as a denominator of eq.(4), leads to an increase in the chemical shift. Our analysis [3a,3b], has shown that the stabilization of the $4d\sigma^*$ and $4d\pi^*$ MO's is due to the stabilization and the mixing of the outer p orbitals of the ligands. As the ligand becomes softer, its outer p orbitals are stabilized and the Mo chemical shift increases.

If the above analysis is correct, we expect from eq.(4) that the Mo chemical shift is inversely proportional to the d-d* excitation energy, ΔE as [3c]

$$\Delta\sigma = A(1/\Delta E_{\text{ref}} - 1/\Delta E)$$
$$= \alpha + \beta/\Delta E. \qquad (5)$$

Here we have assumed that only one state mainly contributes to the magnetic shielding constant and that the factor A is roughly constant among the complexes.

We note that the excitation involved in eq.(5) is not necessarily an optically allowed transition but should be a magnetically allowed transition; the transition for which the numerator of eq.(4) is non-zero. For molecules with higher symmetry, like tetrahedral as MoX_4^{2-} (X=O, S, Se), the magnetically allowed excited states have T_1 symmetry, while the optically allowed excited states have T_2 symmetry. Thus, we can not expect an existence of the observed d - d* transition energies which are magnetically allowed. We therefore calculated the excitation energies of the Mo complexes using the symmetry adapted cluster-configuration interaction (SAC-CI) method [13]. The SAC-CI method has been shown to give excited states to a considerable accuracy within a reasonable amount of computational time [14].

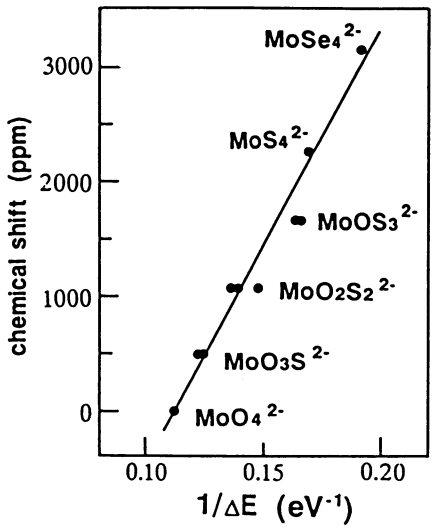


Figure 7. Relationship between the inverse of the lowest magnetically allowed d-d* excitation energy and the chemical shift. The chemical shifts are the experimental values and the excitation energies are the SAC-CI theoretical values.

Figure 7 shows a plot of the experimental Mo chemical shift against $1/\Delta E$ of the energy ΔE calculated for the $4d\sigma \rightarrow 4d\pi^*$ excitation, the lowest possible

magnetically allowed d-d* transition. The two and three points for the C_{3v} and C_{2v} molecules, respectively, occur because T_1 splits into $A_2 + B_1 + B_2$ and $A_2 + E$, respectively. We see a very beautiful linear relationship, which justifies the validity of the mechanism of the Mo chemical shift discussed above. We call this mechanism of the chemical shift as d-excitation mechanism or d-d* mechanism.

From our systematic studies for the Ti, Nb, Mo, and Mn chemical shifts [3], it became clear that the d-excitation mechanism is common to these metal complexes. The origin of the d-excitation mechanism is attributed to the open d-subshell nature of these transition metals, so that we expect that the d-excitation mechanism is common to most of the transition metal complexes.

5. s^2p^2 METAL COMPOUNDS; Si, Ge, Sn COMPLEXES

The chemical shifts of the Si, Ge, and Sn complexes show interesting common behaviors on substitutions of ligands [1]. The compounds which are written as $MR_{4-x}R'_x$ with R and R' both representing organic ligands like H, Me, Ph, etc. show a linear dependence of the metal (M) chemical shift on the number of the ligands x. On the other hand, the complexes of the type $MR_{4-x}Y_x$ with Y being electronegative ligand like halogen, alkoxy, amino, etc., show U-shaped dependence on x. We here want to elucidate the electronic mechanism of the metal chemical shifts and the origins of the linear and U-shaped dependences, taking the Sn compounds, $SnMe_{4-x}H_x$ and $SnMe_{4-x}Cl_x$, as an example. The chemical shifts of some Si and Ge compounds are studied by Ditchfield et al. [15] and Fleischer et al. [16], respectively.

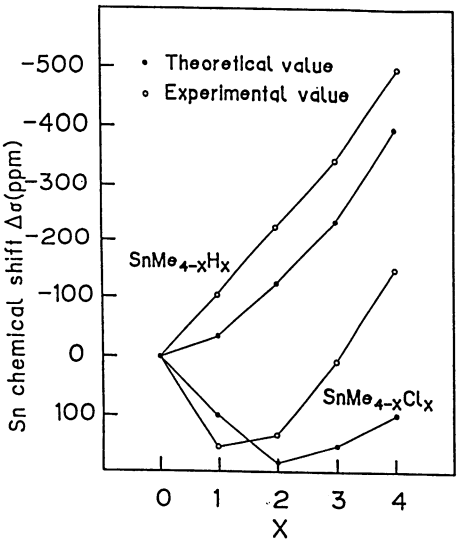


Figure 8. Comparison between theoretical and experimental values for the Sn chemical shifts of $SnMe_{4-x}H_x$ and $SnMe_{4-x}Cl_x$.

We show in Figure 8 the x dependence of the Sn chemical shift. The theoretical values roughly reproduce the linear and U-shaped dependences of the Sn chemical shifts in $SnMe_{4-x}H_x$ and $SnMe_{4-x}Cl_x$, respectively. The MO and AO analyses of the diamagnetic and paramagnetic terms shown in Table 6 reveal that the Sn chemical

shift reflects mainly the change in the Sn valence 5p orbital induced by the ligand substitution. The Sn d AO contribution and the diamagnetic ligand contribution are of secondary importance and are compensating to each other.

Table 6. Diamagnetic and paramagnetic contributions to the Sn magnetic shielding constant and their analysis into Sn p- and d-AO contributions and ligand contributions (in ppm)

molecule	diamagnetic term σ^{dia}					paramagnetic term σ^{para}						
	Sn	Ligand				Sn^a			Ligand			
	total	Me	Cl	H	total	p	d	total	Me	Cl	H	total
SnH_4	5073	---	---	6	24	-1432	-253	-1686	---	---	-2	-8
$SnMeH_3$	5072	38	---	6	56	-1581	-282	-1864	-16	---	-2	-23
$SnMe_2H_2$	5071	38	---	6	88	-1684	-308	-1992	-16	---	-2	-36
$SnMe_3H$	5070	38	---	6	120	-1768	-330	-2098	-16	---	-2	-50
$SnMe_4$	5069	38	---	---	152	-1795	-356	-2152	-16	---	---	-64
$SnMe_3Cl$	5069	38	69	---	183	-1927	-365	-2292	-16	-13	---	-61
$SnMe_2Cl_2$	5070	38	69	---	214	-2028	-378	-2407	-16	-13	---	-58
$SnMeCl_3$	5070	38	70	---	248	-2019	-392	-2411	-16	-13	---	-55
$SnCl_4$	5070	---	70	---	280	-1973	-421	-2394	---	-13	---	-52

a) s AO contribution is zero since it has no angular momentum.

The 5p AO contribution to Sn σ^{para} is determined by the two factors: the excitation energy in the denominator of eq.(4) and the integral terms in the numerator. The larger factor is the excitation energy from the Sn-L σ bonding MO to the antibonding MO. We call this mechanism as p-excitation or p-p* mechanism. Table 7 shows the experimentally observed excitation energies for SnH_4, $SnMe_4$, and $SnCl_4$ [17]. For $SnCl_4$, the lowest transition is the excitation of the Cl lone pair electron to the Sn-L antibonding MO, and the second peak observed at 7.80 eV is $\sigma \rightarrow \sigma^*$. We note that the Rydberg state mixes to some extent with the σ^* state. These excitations have T_2 symmetry, so that they are optically allowed but magnetically forbidden. However, we can expect a rough parallelism between them. We have confirmed that the experimental chemical shifts show a rough linear relationship with $1/\Delta E$ where ΔE is the $\sigma - \sigma^*$ excitation energy [4a]. We thus understand the ordering of the observed chemical shifts, SnH_4 <$SnCl_4$ <$SnMe_4$, though the ordering between $SnCl_4$ and $SnMe_4$ was not reproduced in our calculation.

Table 7. Observed excitation energy of the Sn compounds.

Compound	Nature	Excitation Energy (eV)
SnH_4	$3t_2 \rightarrow 3a_1$; $\sigma \rightarrow \sigma^*$	8.86
$SnMe_4$	$3t_2 \rightarrow 3a_1$; $\sigma \rightarrow \sigma^*$	6.63
$SnCl_4$	$3t_2 \rightarrow 3a_1$; $n(L) \rightarrow \sigma^*$	6.23
	$2t_2 \rightarrow 3a_1$; $\sigma \rightarrow \sigma^*$	7.80

The Sn AO contributions and the ligand contributions in the diamagnetic and paramagnetic terms are plotted in Figure 9 against x for the $SnMe_{4-x}Cl_x$ and $SnMe_{4-x}H_x$ series. It is clearly seen that the origin of the U-shaped dependence in the former compounds is the p-AO contribution to σ^{para}. The linear relationship for the $SnMe_{4-x}H_x$ series is understood from the large change in the excitation energy and the similarity between the H and Me ligands. On the other hand, the U-shaped relationship in the $SnMe_{4-x}Cl_x$ series is considered to be due to the change in both denominator and numerator of eq.(4). In the excitation energy term, two

transitions showing opposite behaviors seem to exist: the mixing of these two transitions in the compounds with x = 1,2,3 is interesting. In the numerator, the anisotropy of the Sn p-AO density would be induced for less symmetric compounds by a large inductive effect of the Cl ligand and works to enlarge the paramagnetic term. For more details, we refer to Ref. 4a.

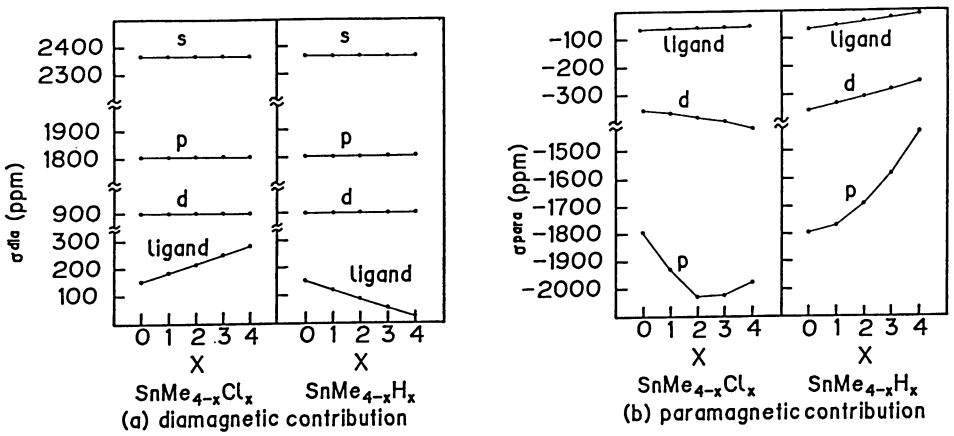


Figure 9. The change as a function of x in the (a) diamagnetic and (b) paramagnetic terms divided into the Sn s, p and d contributions and ligand contributions in $SnMe_{4-x}H_x$ and $SnMe_{4-x}Cl_x$.

6. s^2p^1 METAL COMPOUNDS; Ga, In HALIDES

All of the metal chemical shifts so far studied have been dominated by the paramagnetic term. The chemical shifts of gallium and indium halides are unique in that they are predominantly determined by the diamagnetic term [5]. Since the diamagnetic term depends only on the structural factors, like bond distance and ligand nuclear charge, as the Flygare-Goodisman equation [18] implies, the chemical shifts of these compounds can be calculated without the knowledge of the electronic structure. They show normal halogen dependence [1], in contrast to the reverse halogen dependence for the compounds dealt with in the previous sections. We briefly explain these facts in this section.

We compare in Figure 10 the experimental and theoretical values of the Ga chemical shifts for the compounds $GaCl_{4-x}Br_x^-$ (x=0 - 4). The agreement is excellent. Table 8 shows a breakdown of the magnetic shielding constant into the paramagnetic and diamagnetic terms. The diamagnetic term is three times larger than the paramagnetic one. Table 9 shows the atomic contributions to σ^{dia}. The individual atomic contributions are quite constant, so that σ^{dia} of the complex is written in a Pascal-rule like formula as

$$\sigma^{dia}(\text{complex}) = \sigma^{dia}(\text{M atom}) + \sum_{L} n_L \sigma^{dia}(L) \qquad (6)$$

where σ^{dia}(M atom), σ^{dia}(L) and n_L are the free atom and ligand contributions and the number of the ligands, respectively. On the other hand, Flygare and Goodisman

showed that σ^{dia} is written to a good approximation as

$$\sigma^{dia}(\text{complex}) = \sigma^{dia}(\text{M atom}) + \frac{e^2}{3mc^2}\sum_{L} Z_L/R_L \qquad (7)$$

where R_L and Z_L are metal-ligand distance and ligand nuclear charge, respectively.

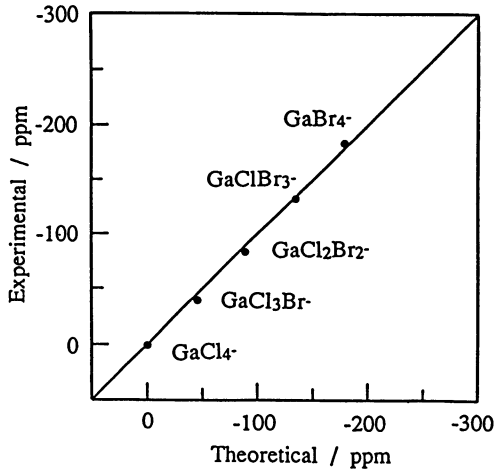


Figure 10. Correlation between experimental and theoretical values of the Ga chemical shifts in $GaCl_{4-n}Br_n^-$ (n = 0 - 4).

Table 8. Diamagnetic and paramagnetic contributions to the Ga magnetic shielding constant (in ppm)

molecule	diamagnetic term		paramagnetic term		magnetic shielding		expti
	σ^{dia}	shift	σ^{para}	shift	σ	shift	shift
$GaCl_4^-$	2932.1	0.0	-888.7	0.0	2043.4	0.0	0.0
$GaCl_3Br^-$	3000.1	-68.0	-911.7	23.0	2088.4	-45.0	-39.8
$GaCl_2Br_2^-$	3068.4	-136.4	-936.0	47.4	2132.4	-89.0	-83.8
$GaClBr_3^-$	3136.1	-204.0	-958.5	69.9	2177.5	-134.1	-132.8
$GaBr_4^-$	3204.1	-272.0	-982.3	93.6	2221.8	-178.4	-183.8

Table 9. Metal and ligand contributions to the diamagnetic term σ^{dia}(in ppm)

molecule	Metal	Ligand		σ^{dia}
	Ga	Cl	Br	
$GaCl_4^-$	2630.6	75.4		2932.1
$GaCl_3Br^-$	2630.8	75.4	143.2	3000.1
$GaCl_2Br_2^-$	2631.1	75.5	143.2	3068.4
$GaClBr_3^-$	2631.3	75.3	143.1	3136.1
$GaBr_4^-$	2631.6		143.1	3204.1

We compare in Table 10 the values calculated by eq.(7) with those of the ab initio calculations. σ^{dia}(M atom) in eq.(7) is the free atom value and taken from Malli and Froese [19]. The agreement of the two methods is excellent, so that the

diamagnetic term is determined solely by the structural factors, R_L and Z_L alone. For chemical shifts, σ^{dia}(M atom) cancels out. Thus, if we neglect the paramagnetic contribution σ^{para}, which is roughly one third of σ^{dia} with opposite sign, we can say that the Ga chemical shifts of the complexes $GaCl_{4-x}Br_x$ are determined by the structural factors, R_L and Z_L alone.

Table 10. Estimate of the diamagnetic term of the Ga magnetic shielding constant from Flygare-Goodisman equation compared with the ab initio results (in ppm)

molecule	Flygare-Goodisman eq.			ab initio result		
	Ga	ligands	σ^{dia}	Ga	ligands	σ^{dia}
$GaCl_4^-$	2638.6	296.0	2934.6	2630.6	301.6	2932.1
$GaCl_3Br^-$	2638.6	364.1	3002.7	2630.8	369.4	3000.1
$GaCl_2Br_2^-$	2638.6	432.2	3070.8	2631.1	437.4	3068.4
$GaClBr_3^-$	2638.6	500.3	3138.9	2631.3	504.6	3136.1
$GaBr_4^-$	2638.6	568.4	3207.0	2631.6	572.4	3204.1

It is interesting to examine this possibility for a wider class of compounds. Since σ^{dia} is very easily calculated when molecular geometry of a complex is known, we plot in Figure 11 the experimental values of the Ga chemical shifts of various halide complexes againt $\Delta\sigma^{dia}$, which is calculated from the second term of eq.(7). We see the points fall above and below the 45 degree line. These compounds are further classified into $GaCl_{4-x}Br_x^-$, $GaCl_{4-x}I_x^-$, $GaBr_{4-x}I_x^-$, and some mixed ones. We find an approximate linearity among each class of compounds, and the slope is steeper as the ligands become heavier. It is interesting to investigate the origin of this slope: is it explained without including the spin-orbit effect of the ligand ?

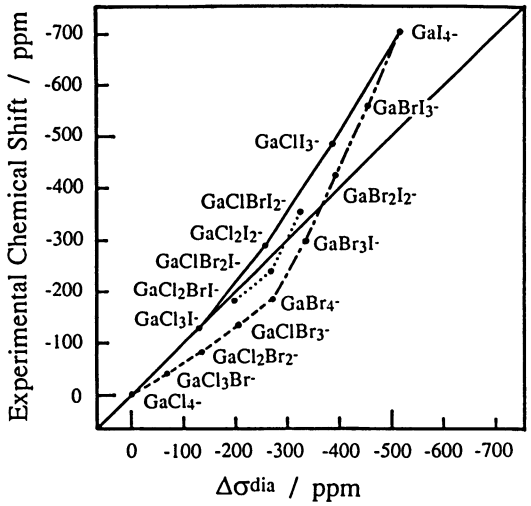


Figure 11. Correlation between experimental Ga chemical shift and diamagnetic shift value $\Delta\sigma^{dia}$ calculated by the Flygare-Goodisman equation.

Figure 12 is the plot of $\Delta\sigma^{dia}$ against the experimental chemical shifts for the indium complexes. The plots for light halides, $InCl_{4-x}Br_x^-$ lie nicely on the 45 degree line, but those for heavier halides deviate upwards. It is safe to conclude that the diamagnetic term is an important origin of the indium chemical shifts of

these complexes.

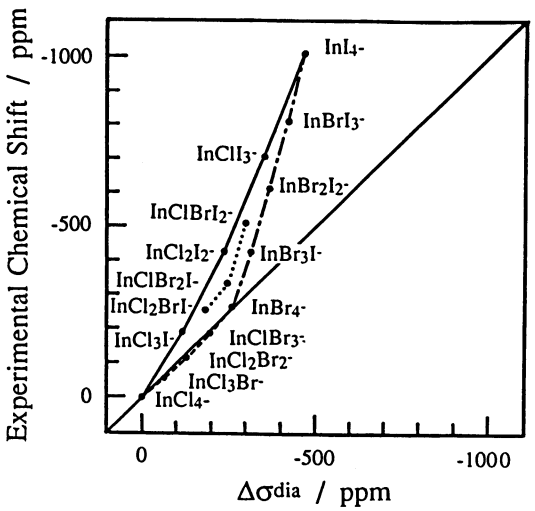


Figure 12. Correlation between experimental In chemical shift and diamagnetic shift value $\Delta\sigma^{dia}$ calculated by the Flygare-Goodisman equation.

One may expect that the aluminum chemical shift may also belong to this class of compounds. However, we have confirmed this is not the case. For aluminum chemical shifts, the paramagnetic term is important.

Now, why is σ^{para} small in this class of compounds ? The reason is that the single p electron of gallium or indium is tightly bound in the M-L bond, so that the excitation energy for this electron is large, leading to a small σ^{para} as eq.(4) implies.

7. CONCLUSION

In this progress report, we have emphasized that the mechanism of the metal chemical shifts of the complexes is closely related with the atomic electronic structure of the central metal atom. When the central metal atom has the valence electron configuration $d^k s^l p^m$ in its free atomic ground state, the open subshell nature of the d or p orbitals determines the major mechanism, since the angular momentum of the chemical shift operator is represented by that open subshell. The chemical shift is a measure of the ligand perturbation on this angular momentum. The s orbital and the full and empty orbitals do not give angular momentum.

In the $d^{10}s^{1-2}p^0$ complexes, the d subshell is full and the p subshell is empty. Therefore, the p electrons suplied by the ligand and the d holes produced by the electron withdrawing ligand give angular momenta and chemical shifts. These mechanisms of the chemical shifts are referred to as the p-electron mechanism (or p-mechanism) and the d-hole mechanism (or d-mechanism), respectively. The relative importance of the p- and d-mechanisms is primarily determined by the relative s-p and d-s spacings in the atomic spectrum of the metal atom: when the d-s spacing is smaller than the s-p spacing, the d-mechanism is more important and in the reverse situation, the p-mechanism is importnat. The Cu complex belongs to the former and the Zn and Cd complexes to the latter. In the Ag complexes, two spacings are close, so that the two mechanisms are competitive. Further, as

being self-evident, the effect of the electron donating (or withdrawing) ligand on the metal chemical shift is opposite, depending on whether the p- or d-mechanism is important.

For the d^* complexes (n=2 $\cdots$ 8), the chemical shift is dominated by the d-excitation mechanism: the angular momentum is produced by the transition of electrons from the occupied d orbital to the unoccupied d orbital. Therefore, the induced angular momentum would be proportional to $1/\Delta E$ with ΔE being the d-d^* excitation energy, as the perturbation theoretic formula eq.(4) implies. This is proved for the Mo complexes [3c]. Therefore, the chemical shift is measured by the magnitude of the ligand effect on the d-d^* excitation energy. Generally speaking, the softer the ligand is, the ΔE is smaller and the chemical shift is larger: this mechanism is explained in our articles [3].

For the p^* complexes (n=2 $\sim$ 4), the p-excitation mechanism is important. The origin is similar to the d-excitation mechanism. An interesting behavior of the chemical shifts of this class of compounds is the existence of the linear and U-shaped dependences on the number of the ligands. The linear dependence is normal. The U-shaped dependence is caused by two factors; one is the existence of two competitive excitations, p-p^* and n(L)-p^* excitations (n(L) is the lone pair on the ligand) and the other is the anisotropy of the metal p-electron distribution in the non-symmetric compounds.

Though most chemical shifts originate from the paramagnetic term, those of the Ga and In halides are dominated by the diamagnetic term. The halogen dependence [1] is also clearly different. For the former case, most show the reverse halogen dependence, but the Ga and In complexes show the normal halogen dependence. Since the p electron of the s^2p^1 Ga and In complexes are tightly bound in the M-L bond, the paramagnetic term is small. Therefore, the Ga and In chemical shifts are determined mostly by the geometrical factors, the M-L bond length and ligand nuclear charge. This is quite unique among the metal complexes.

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