

METAL CHEMICAL SHIFTS IN NMR SPECTROSCOPY - AB INITIO CALCULATIONS
AND PREDICTIVE MODELS

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ABSTRACT. The metal chemical shifts in NMR spectroscopy are studied theoretically. Electronic origins and mechanisms of the metal chemical shifts in the Cu, Ag, Zn, Cd, and Mn complexes are clarified based on ab initio molecular orbital calculations. The mechanisms accounting for the chemical shift are found to be very different for metals with a $d^{10}s^1p^0$ configuration (Cu, Ag, Zn, Cd) and those with a $d^5s^2p^0$ configuration (Mn), because of the filled and half-filled nature of the valence d subshell.

1. INTRODUCTION

The recent developments in organometallic and inorganic chemistry are largely based on knowledge of the electronic structures of bonding in metal complexes [1]. The chemistry is very different than organic chemistry because of the essential participation of d electrons. The symmetry, multiplicity and flexibility of d orbitals cause the chemistry to be quite varied in comparison with the chemistry of s and p electrons alone. A convenient way of looking at the role of the d electrons is to observe those properties which are sensitive to the angular momentum of electrons, since the d electrons have larger angular momentum than the p electrons and the s electrons have no angular momentum.

Nuclear magnetic resonance spectroscopy of metal species [2-4] gives valuable information about the role of the d electrons in the

chemical bonding of metal complexes, since the magnetic properties observed reflect the angular momentum of the electrons involved. The chemical shift of the metal nucleus is especially valuable, because it samples the angular momentum of electrons near the metal nucleus. It amplifies the role of the d electrons of the metal relative to that of the p electrons. The role of the s electron is effectively eliminated due to its having no angular momentum. Thus, the NMR spectroscopy of metal nuclei is important not only as a tool of analytical chemistry but also for the physical and chemical information concerning the rôle of the d (and also f) electrons in the chemistry of metal complexes.

We have recently carried out theoretical studies of the metal chemical shift in NMR spectroscopy [5-7]. The molecules studied are the Cu, Zn, Ag and Cd complexes [5-7], for which the metal atoms are characterized by the electronic configurations $d^{10}s^1p^0$ in their ground state, and the Mn complexes [6], for which the Mn metal is characterized by an open d-subshell d^5s^2 in its ground state. The purpose of the study is two-fold. One is to understand the origin of the metal chemical shift by performing reliable ab initio calculations and by analyzing the calculated results. We are especially interested in the role of the d electrons in the chemical bonds of the transition metal complexes. The other purpose is to clarify the mechanism of the metal chemical shift. The elucidation of this mechanism would be useful, since there seems to be no guiding concept, so far, which is useful for experimental chemists. This situation is completely different from that of the ^1H and ^{13}C chemical shifts. To the best of our knowledge, these are the first ab initio studies of the metal chemical shifts of transition metal complexes. We sketch here only the most important results of these studies in order to show an example of the close cooperation between quantum chemistry and experiment, which is the purpose of this book.

The metal complexes studied here are the following 27 molecules:

Cu complex: CuCl , CuCl_4^{3-} , $\text{Cu}(\text{CN})_4^{3-}$, $\text{Cu}(\text{NH}_3)_2^+$.

Zn complex: $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, ZnCl_2 , ZnCl_4^{2-} , $\text{Zn}(\text{CN})_4^{2-}$, $\text{Zn}(\text{NH}_3)_4^{2+}$.

Ag complex: $\text{Ag}(\text{H}_2\text{O})_6^+$, AgF_4^{3-} , AgCl_2^- , AgCl_4^{3-} , $\text{Ag}(\text{CN})_4^{3-}$,
 $\text{Ag}(\text{NH}_3)_2^+$.

Cd complex: $\text{Cd}(\text{H}_2\text{O})_6^{2+}$, CdCl_2 , CdCl_4^{2-} , $\text{Cd}(\text{CN})_4^{2-}$, $\text{Cd}(\text{CH}_3)_2$,
 CdMeEt , CdEt_2 , $\text{CdMe}(\text{OMe})$.

Mn complex: $\text{Mn}(\text{CO})_5\text{H}$, $\text{Mn}(\text{CO})_5\text{CN}$, $\text{Mn}(\text{CO})_5\text{CH}_3$, $\text{Mn}(\text{CO})_5\text{Cl}$.

The experimental data for the chemical shifts are due to Cardin et al. [8], Ackerman et al. [9], Kennedy et al. [10], and Mennitt et al. [11] for the Cd complexes; Maciel et al. [12] for the Zn complexes, Endo et al. for the Ag and Cu complexes [13]; and, Calderazzo et al. [14] for the Mn complexes.

2. THEORETICAL BACKGROUND

The hamiltonian of a molecule in a magnetic field may be written as [15-17]

$$H = H_0 + \sum_x B_x H_x^{(1,0)} + \sum_A \sum_x \mu_{Ax} H_{Ax}^{(0,1)} + \\ + (1/2) \sum_A \sum_x \sum_y B_x H_{Axy}^{(1,1)} \mu_{Ay} + \dots \quad (1)$$

where H_0 is the hamiltonian free from the magnetic field, and B_x and μ_{Ax} are the magnetic field and the nuclear magnetic moment of nucleus A in the x direction. The perturbation hamiltonians $H_x^{(1,0)}$, $H_{Ax}^{(0,1)}$, and $H_{Axy}^{(1,1)}$ are given by

$$H_x^{(1,0)} = - (1\hbar e/2mc) \sum_j \ell_{jx}, \quad (2a)$$

$$H_{Ax}^{(0,1)} = - (1\hbar e/2mc) \sum_j \ell_{jx}/r_{Aj}^3, \quad (2b)$$

$$H_{Axy}^{(1,1)} = (e^2/4mc^2) \sum_j (r_j r_{Aj} \delta_{xy} - r_{jx} r_{Ajy}) / r_{Aj}^3 \quad (2c)$$

l_{jx} is an angular momentum operator for electron j in the x direction. The nuclear magnetic shielding constant is defined by

$$\sigma_{xy}(A) = \left[\frac{\partial^2 E(\beta, \mu)}{\partial \beta_x \partial \mu_{Ay}} \right]_{B=\mu_A=0}, \quad (3)$$

which is written with the use of the Hellmann-Feynman theorem as

$$\begin{aligned} \sigma_{xy}(A) &= \langle \psi(0) | H_{Axy}^{(1,1)} | \psi(0) \rangle \\ &+ \frac{\partial}{\partial B_x} [\langle \psi(B_x) | H_{Ay}^{(0,1)} | \psi(B_x) \rangle]_{B=0}. \end{aligned} \quad (4)$$

$\psi(0)$ and $\psi(B_x)$ are the wavefunctions in the absence and the existence, respectively, of the magnetic field. The first term of Eqn. (4) is the diamagnetic term σ^{dia} and the second term is the paramagnetic term σ^{para} . If we expand the perturbed wavefunction $\psi(B_x)$ in the set of unperturbed wavefunction $\{|n\rangle\}$, we obtain the familiar equation

$$\sigma_{xy}^{para}(A) = \sum_n \frac{\langle 0 | H_x^{(1,0)} | n \rangle \langle n | H_{Ay}^{(0,1)} | 0 \rangle}{E_0 - E_n} + C.C. \quad (5)$$

We note that both of the operators $H_x^{(1,0)}$ and $H_{Ay}^{(0,1)}$ include the angular momentum operator l .

We calculated the magnetic shielding constant using the coupled perturbed Hartree-Fock theory or the finite perturbation theory of Cohen, Roothaan, and Pople et al. [18,19]. This theory has been shown to be the best expression of the second-order perturbation theory based upon the Hartree-Fock wavefunction [20]. We calculated the perturbed, complex wavefunction $\psi(B_x)$ in the Hartree-Fock approximation using a finite magnetic field. Then, the nuclear shielding constant was calculated with Eqn. (4). The origin of the gauge was

chosen at the position of the metal nucleus. We limit ourselves here only to the isotropic term,

$$\sigma_A = (1/3) \{ \sigma_{xx}(A) + \sigma_{yy}(A) + \sigma_{zz}(A) \} \quad (6)$$

The chemical shift is a relative value which is calculated by subtracting the nuclear magnetic shielding constant σ_0 from that of a standard molecule, i.e.

$$\Delta\sigma = \sigma - \sigma_0. \quad (7)$$

The basis set we used for calculations are the MIDI-1 basis of Tatewaki, Huzinaga, and Sakai [21] plus two outer p-type Gaussians for metal atoms [5,6]. This basis is of a double-zeta quality for valence electrons. For the ligands of the Mn complexes, we used the MINI-1 set [21] which is poorer than the MIDI-1 set. The geometries of the complexes are summarized in previous papers [57]. For the metal-ligand length, we assumed a sum of the tetrahedral covalent radii [22].

3. CORRELATION BETWEEN THEORETICAL AND EXPERIMENTAL VALUES

Table 1 shows the theoretical values of the magnetic shielding constants and the chemical shifts of the metal nuclei of the complexes studied here. The diamagnetic and paramagnetic contributions and their decomposition into core and valence MO contributions are also given. Figures 1 - 5 show the correlations between the theoretical values and experimental results for the Cd, Ag, Zn, Cu, and Mn complexes, respectively. The open circle on the line indicates that only the theoretical value exists. For the Ag complexes, we compared the theoretical results for AgF_4^{3-} and AgCl_4^{3-} with the experimental values of AgBr_4^{3-} and AgI_4^{3-} .

The largest number of examples are seen in Figure 1 for the cadmium complexes. In addition to the results of Table 1, it includes the results for CdMeEt , CdEt_2 , and CdMe(OMe) [7]. The correlation between theory and experiment is good except for Cd(CN)_4^{2-} . For the experiment in aqueous solution [8], the geometry of the complex is unknown and the effect of the solvent should be large.

Table 1. Diamagnetic and paramagnetic contributions, σ_M^{dia} and σ_M^{para} , to the metal magnetic shielding constant σ_M and their analyses into core and valence MO contributions (in ppm.).

Molecule	σ_M^{dia}			σ_M^{para}			σ_M		
	Core Valence	Total	Shift	Core Valence	Total	Shift	Core Valence	Total	Shift
CuCl_4^{3-}	2292	375	2667	0	-63	-818	-881	0	1786
$\text{Cu}(\text{CN})_4^{3-}$	2190	387	2577	-90	-103	-1588	-1691	-810	886
$\text{Cu}(\text{NH}_3)_2^+$	2150	314	2464	-203	-73	-2582	-2655	-1774	-191
CuCl	2171	279	2450	-217	-79	-4617	-4696	-3815	-2246
$\text{Zn}(\text{H}_2\text{O})_6^{2+}$	2266	486	2752	0	-44	-272	-316	0	2436
ZnCl_4^{2-}	2376	406	2782	30	-55	-447	-502	-186	2280
ZnCl_2	2294	342	2636	-116	-42	-414	-456	-140	2179
$\text{Zn}(\text{CN})_4^{2-}$	2272	420	2692	-60	-74	-654	-728	-412	1964
$\text{Zn}(\text{NH}_3)_4^{2+}$	2250	418	2668	-84	-75	-711	-786	-470	1882
$\text{Ag}(\text{H}_2\text{O})_6^+$	4514	361	4875	0	-41	-431	-472	0	4403
$\text{Ag}(\text{NH}_3)_2^+$	4484	239	4722	-153	-33	-628	-661	-189	4062
AgCl_2^-	4549	241	4790	-85	-46	-1001	-1047	-575	3742
AgF_3^-	4504	328	4832	-43	-75	-1083	-1158	-686	3673
AgCl_3^-	4631	307	4938	63	-76	-1296	-1372	-900	3566
$\text{Ag}(\text{CN})_4^{3-}$	4521	308	4829	-46	-96	-1416	-1512	-1040	3318

Table 1 (cont.)

Molecule	σ^{dia}			σ^{para}			σ
	Core Valence	Total Shift	Total Shift	Core Valence	Total Shift	Total Shift	
$\text{Cd}(\text{H}_2\text{O})_6^{2+}$	4626	378	5004	0	0	4529	0
CdCl_2	4655	253	4908	-96	-668	4240	-286
CdCl_4^{2-}	4731	314	5045	41	-915	4129	-400
$\text{Cd}(\text{CH}_3)_2$	4595	256	4851	-153	-1090	3761	-768
$\text{Cd}(\text{CN})_4^{2-}$	4640	343	4983	-21	-1604	3378	-1151
$\text{Mn}(\text{CO})_5\text{H}$	1889	318	2207	0	-13068	-10861	0
$\text{Mn}(\text{CO})_5\text{CN}$	1905	345	2249	42	-13182	-10933	-72
$\text{Mn}(\text{CO})_5\text{CH}_3$	1898	339	2237	30	-14457	-12220	-1359
$\text{Mn}(\text{CO})_5\text{Cl}$	1929	339	2267	60	-16240	-13973	-3112

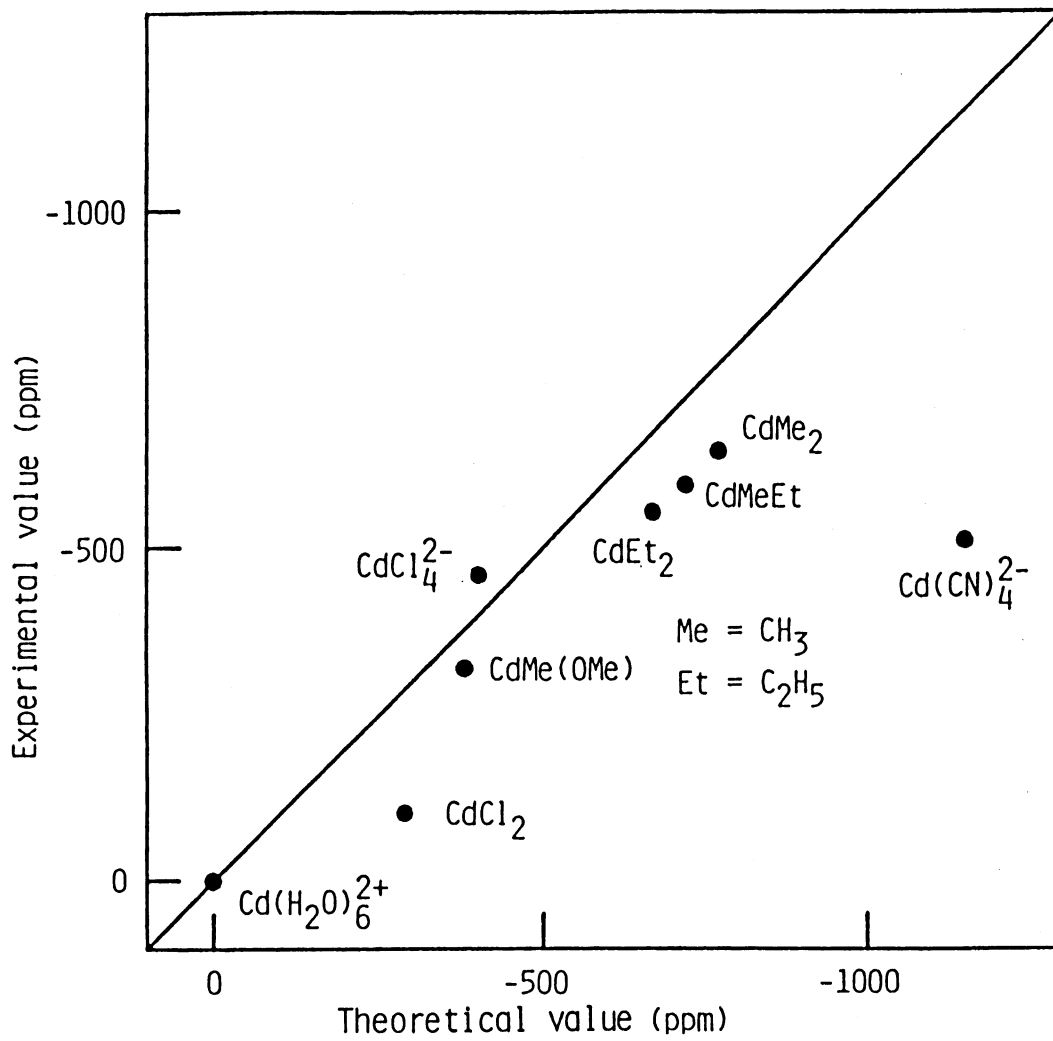


Figure 1. Comparison between theoretical and experimental values for the ^{113}Cd chemical shifts of the cadmium complexes.

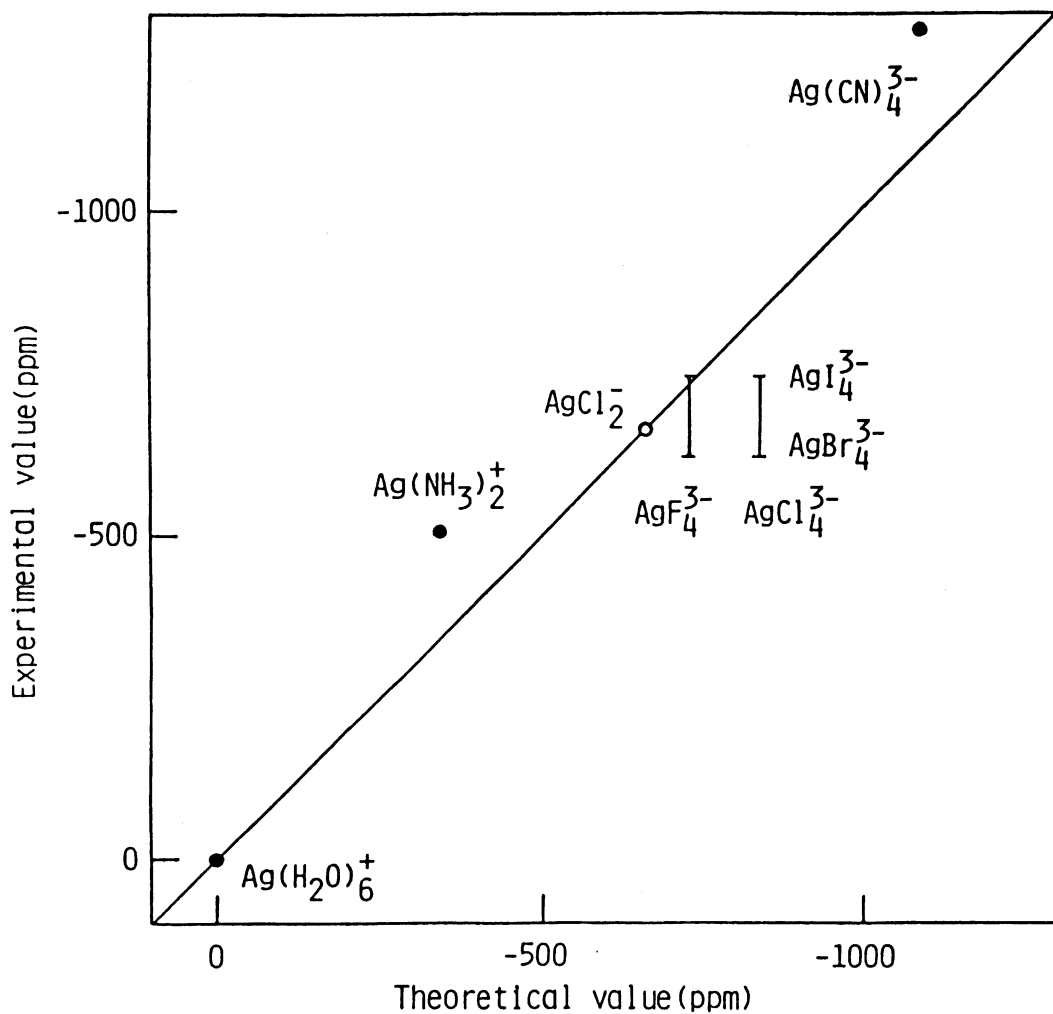


Figure 2. Comparison between theoretical and experimental values for the ^{109}Ag chemical shifts of the silver complexes. For the halides see the text.

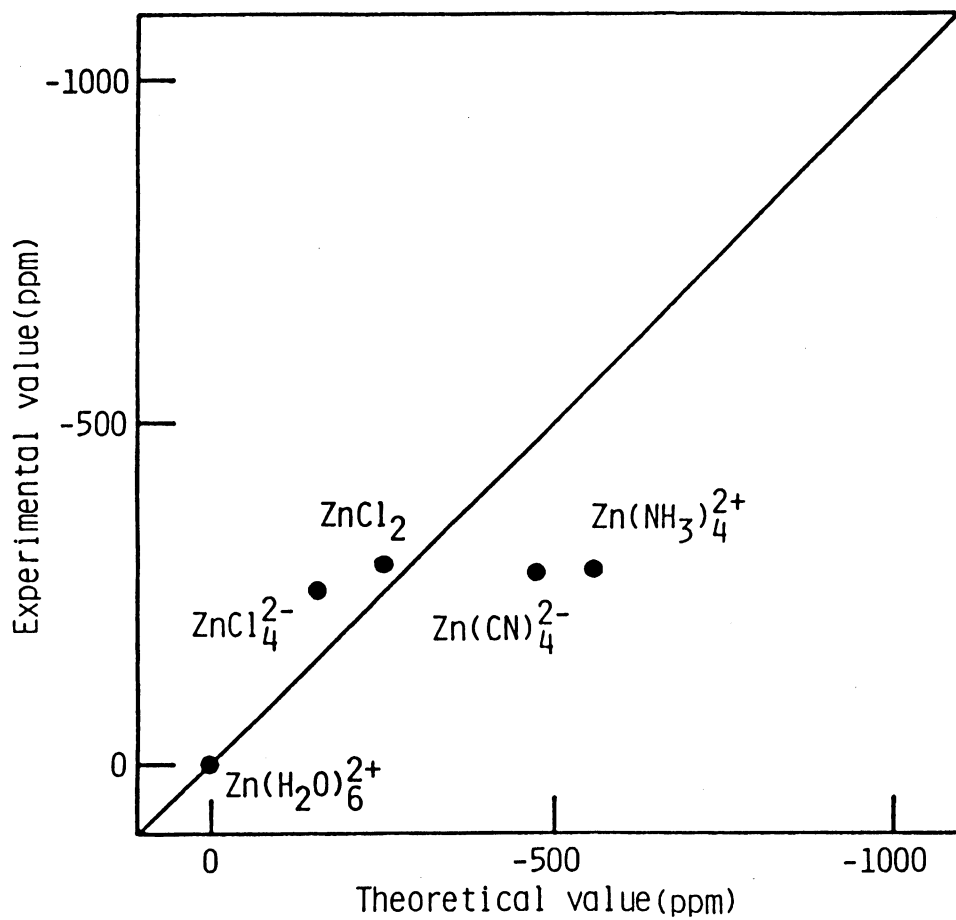


Figure 3. Comparison between theoretical and experimental values for the ^{67}Zn chemical shifts of the zinc complexes.

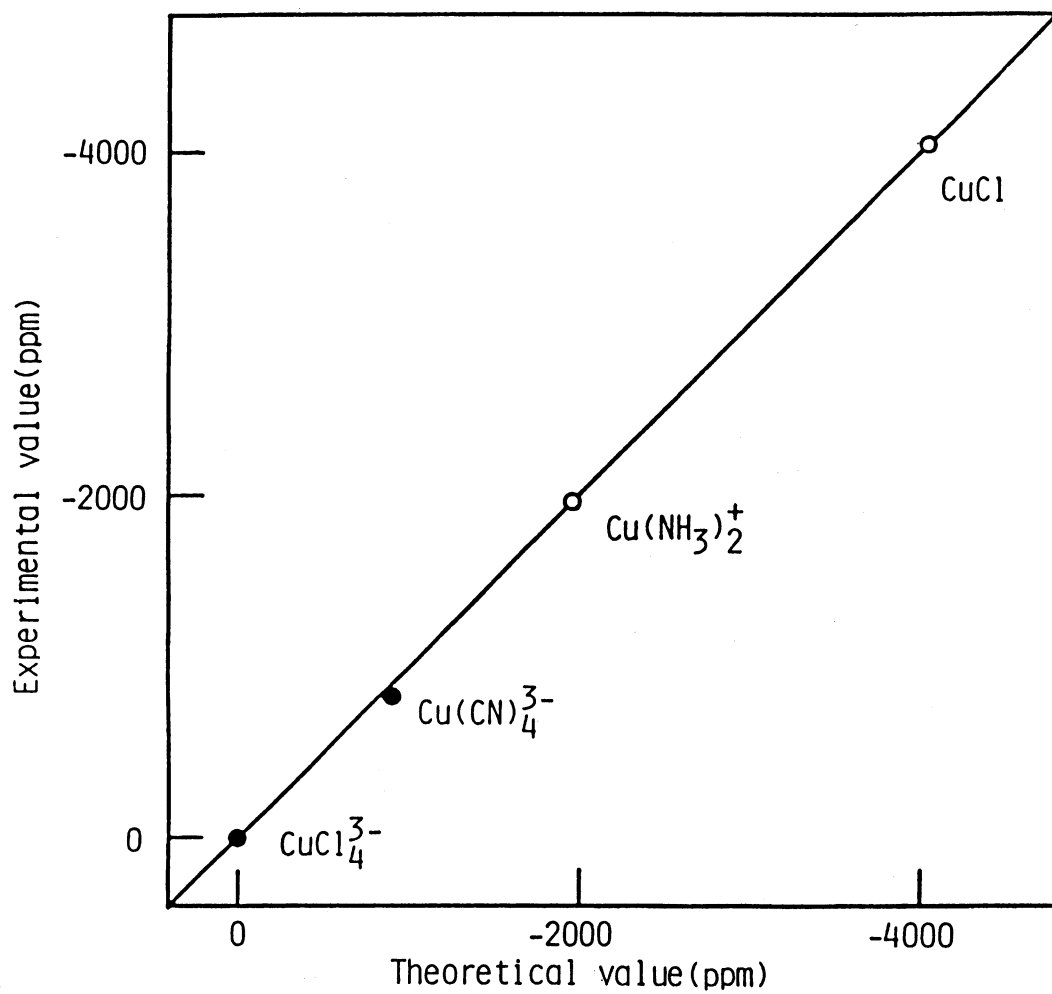


Figure 4. Comparison between theoretical and experimental values for the ^{63}Cu chemical shifts of the copper complexes.

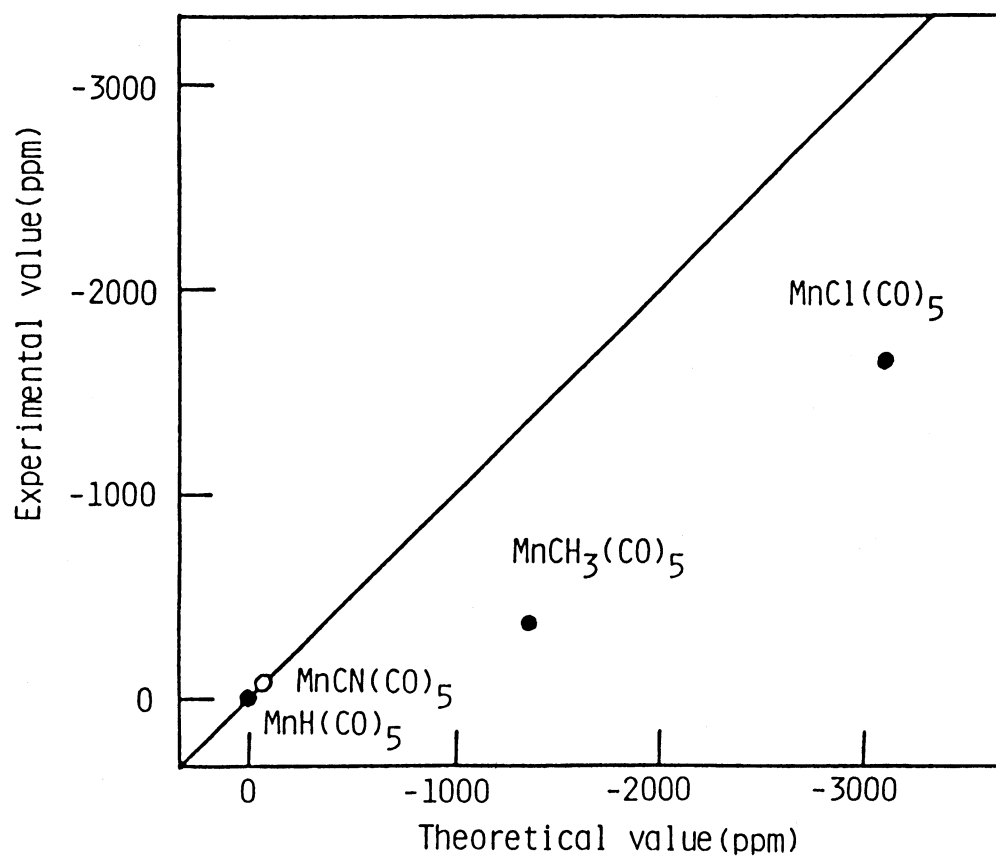


Figure 5. Comparison between theoretical and experimental values for the ^{55}Mn chemical shifts of the manganese complexes.

These factors are not considered in the calculations. For the complexes CdMe_2 , CdMeEt , CdEt_2 , and CdMe(OMe) , the effects of the solvent are expected to be small for the experimental conditions [8,10]. The parallelism between theory and experiment is especially excellent for these molecules. This fact is understood to show the reliability of the present theoretical results.

In Figures 2 and 3, we see that the correlation between theory and experiment are good for the silver and zinc complexes. This is rather surprising considering the ambiguity in the structure and solvation of these complexes in aqueous solutions. For the silver complexes, the experimental shift is larger for the iodide than for the bromide, and the calculated shift is larger for the chloride than for the fluoride. The ordering is natural and may be understood to suggest a small relativistic effect due to the heavy ligand atoms [5].

For the copper complexes, we have only two examples for which both experimental and theoretical values exist. These two points lie almost on the diagonal line, showing the reliability of the calculated values. Recently, Kitagawa and Munakata reported a systematic experimental study of the Cu chemical shift [23]. They reported that the copper chemical shift is larger for the ligand which is more π -electron withdrawing. This observation is very important and is explained clearly by the mechanism of the copper chemical shift, as shown in the next section.

For the Mn chemical shift, we have studied the complexes of the form $\text{Mn(CO)}_5\text{L}$ with $\text{L} = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}$. The correlation between theory and experiment is only fair. The calculated shifts are larger than the experimental values. Referring to Table 1, we notice that for the Mn shielding constant, the paramagnetic term is an order of magnitude larger than those of the Ib and IIb metal complexes. We will see later that this is due to the difference in the origin of the metal chemical shift for these complexes.

4. MECHANISM OF THE METAL CHEMICAL SHIFT OF THE Ib AND IIb METAL COMPLEXES

We now want to clarify the electronic origin of the metal chemical shift. Since the origin is very much different for complexes of the Ib and IIb metals and those of Mn, we will explain the origin separately. We want to identify an electronic mechanism that produces the metal chemical shift, which would be useful as a guiding principle for experimental chemists.

Referring to Table 1, we see that the chemical shifts are mostly due to the valence MO contributions to the paramagnetic term. We have shown in a previous paper [5] that the behavior of the valence electrons near the nucleus are observed as a chemical shift through NMR spectroscopy. The diamagnetic term itself is large but its contribution to the chemical shift is small. We therefore discuss the diamagnetic term separately in Section 6. In Tables 2 and 3, we have shown the metal AO contributions and the ligand contributions, respectively, to the paramagnetic term of the metal shielding constant. The definition of the AO contribution was given previously [5]. Comparing the numbers in Tables 2 and 3, we immediately understand that the ligand contributions are small and that the dominant term comes from the metal AO contributions. The metal s AO contribution is identically zero, because the s AO does not have angular momentum, so that the metal chemical shifts are primarily due to the metal p and d orbital contributions.

Looking at Table 2 in more detail, we notice that for the Cu chemical shift, the d orbital contribution is dominant, for the Zn and Cd chemical shifts; the p orbital contribution is more important than the d orbital contribution; and for the Ag chemical shift, the p and d orbital contributions are comparable. This observation is very important in understanding the trends in the chemical shift that are characteristic of metal species.

Now, how do these p and d orbital contributions arise? The Ib and IIb metals studied in this section have the electronic configurations $d^{10}s^1-2p^0$ in their ground state. As the perturbation

theory shows [24], the closed p and d subshells give no contributions to the paramagnetic term. Table 1 shows that these p and d contributions are due to the valence orbitals. Therefore, we conclude that these paramagnetic terms are caused by the donation of electrons from the ligands to the metal p orbitals and by the back-donation of electrons from the metal d orbitals to the ligands. In other words, the electrons in the valence p orbitals and the holes in the valence d orbitals produce angular momentum when the magnetic field is applied and give paramagnetic contributions to the metal nuclear shielding constants of the complexes. In Figure 6, we illustrated these two mechanisms, namely the p mechanism and the d mechanism. Though this figure is drawn for the π interactions, these mechanisms involve both σ and π interactions. For the p mechanism an electron donating ligand produces a larger metal chemical shift. On the other hand, for the d mechanism an electron-withdrawing ligand produces a larger metal chemical shift. Thus, the effect of the ligand is entirely different for the p and d mechanisms.

From Table 3, we see that the d mechanism is much more important than the p mechanism for the Cu complexes. This suggests that the d orbitals are important in forming the bond between copper and ligands. This further suggests that the Cu chemical shift would be parallel to the d-electron acceptability of the ligands, as long as the number of ligands is the same. This is supported by the recent ^{63}Cu NMR experiments of Kitagawa and Munakata [23]. They observed that the Cu chemical shift increases with increasing π -electron withdrawing ability of the ligand. For the Zn and Cd complexes, the p mechanism is calculated to be more important than the d mechanism. For these IIb metal complexes, the p orbitals are more important than the d orbitals for the chemical bonds between the metal and the ligands. For the CdL_2 complexes, the p mechanism is predominant. For the CdL_4 complexes, the d contribution increases though it is still smaller than the p contribution. This is in part due to the hybridization necessary for tetrahedral coordination. For the CdL_2 complexes, sp hybridization is dominant, but for the CdL_4 complexes,

Table 2. Metal AO contributions to the paramagnetic term of the metal shielding constant (In ppm.)^a.

Ligand	Cu		Zn		Ag		Cd	
	p	d	p	d	p	d	p	d
(H ₂ O) ₆	---	---	-195	-54	-204	-171	-291	-124
F ₄	---	---	---	---	-633	-489	---	---
Cl	-210	-4486	---	---	---	---	---	---
Cl ₂	---	---	-316	-128	-494	-540	-604	-52
Cl ₄	-305	-553	-373	-101	-851	-491	-723	-166
(CN) ₄	-290	-1360	-343	-335	-538	-925	-864	-687
(NH ₃) ₂	-165	-2475	---	---	-248	-390	---	---
(NH ₃) ₄	---	---	-420	-309	---	---	---	---
(CH ₃) ₂	---	---	---	---	---	---	-992	-68

Major contribution d p p,d p

^a The s orbital contribution is identically zero.

Table 3. Ligand contributions to the paramagnetic term of the metal shielding constant (In ppm.).

Ligand	Cu	Zn	Ag	Cd
(H ₂ O) ₆	---	-67	-62	-60
F ₄	---	---	-37	---
Cl	-1	---	---	---
Cl ₂	---	-13	-13	-12
Cl ₄	-24	-27	-30	-27
(CN) ₄	-41	-50	-49	-53
(NH ₃) ₂	-15	---	-23	---
(NH ₃) ₄	---	-57	---	---
(CH ₃) ₂	---	---	---	-29

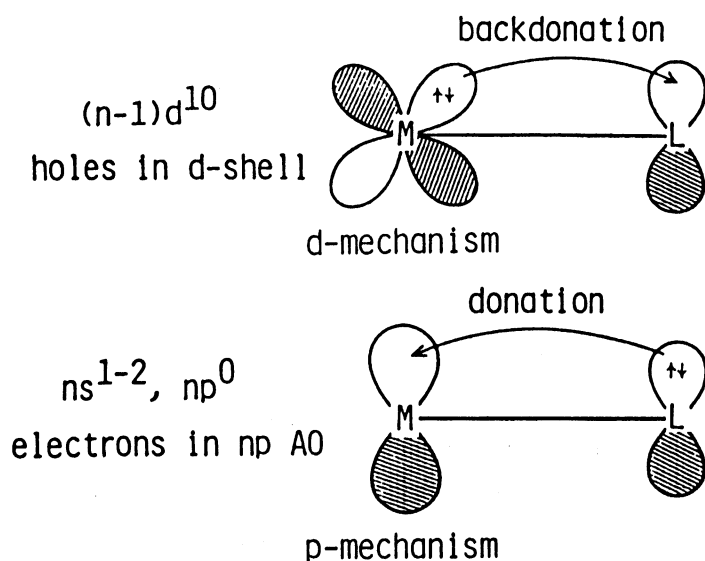


Figure 6. Illustration of the d and p mechanisms of the metal chemical shift. The holes in the d orbitals due to back-donation and the electrons in the p orbitals due to donation are the origin of the paramagnetic term of the metal chemical shift of the Ib and IIb metal complexes.

mixing of the sp^3 and sd^3 hybridizations occur. For the Zn complexes, we fail to see such a clear relation. Comparing the tetrahedral Cl and CN complexes, we see that the d mechanism is much facilitated by the CN ligand though the p contribution itself is larger than the d contribution. This is due to the π -withdrawing ability of the CN ligand through the $d_{\pi}(\text{metal}) - p_{\pi}(\text{ligand})$ conjugation. Further, the d mechanism is more effective than the p mechanism since the angular momentum is larger for the d orbital than for the p orbital. Lastly, for the Ag complexes, we see that the p and d mechanisms are competitive. The relative importance depends strongly on the number and the nature of the ligands. In Table 4, we summarize the major mechanisms for the chemical shifts of the Ib and IIb metal complexes and the roles expected of the ligands.

Now, why do these differences in the origin of the metal chemical shift occur? A possible answer is based on the atomic energy levels of the metal atoms. In Figure 7, we show the atomic energy levels of the Ib (Cu, Ag) and IIb (Zn, Cd) metal ions [25]. For these metals, the valence s AO is important for the metal-ligand bonds. For neutral species, the ns levels of these metals are close. Thus, we choose the ns levels as a standard in Figure 7. Note that the s AO does not contribute to the shielding constant, because it does not have any angular momentum. Looking at the differences between the $(n-1)d - ns$ and $ns - np$ level splittings, we see that the d - s splitting is smaller than the p - s splitting for Cu, the reverse relation for Zn and Cd, and the splittings are very close for Ag. In the Cu complex formation, the d orbitals of Cu would more easily mix with the metal-ligand bonds than the p orbitals. For the Zn and Cd complexes, the reverse relation is expected, and for the Ag complexes, the mixing tendency of the 4d and 5p AO's is expected to be similar. Thus, the relative importance of the p and d mechanisms in the metal chemical shift is attributed to the structures in the atomic energy levels of the metal atom itself.

Table 4. Summary of mechanisms which give major paramagnetic contributions to the metal chemical shifts.

Metal Complexes	p- or d-Mechanism	Role of ligand
Cu	holes in (n-1)d shell ↓ electrons in np AO	electron-acceptor ↓ electron-donor
Cd, Zn	electrons in np AO ↓ holes in (n-1)d shell	electron-donor ↓ (shift may be large)
Ag	electrons in np AO ↑↑ holes in (n-1)d shell	electron-donor ↑↑ electron-acceptor

Table 5. Analysis of the paramagnetic term, σ_{Mn}^{para} , of $Mn(CO)_5L$ complexes into metal AO and ligand contributions. (In ppm.)

Molecules	Mn		Ligand		
	p	d	CO _{ax}	4xCO _{eq}	L
Mn(CO) ₅ H	-129	-12983	10	30	4
Mn(CO) ₅ CN	-75	-13138	7	24	3
Mn(CO) ₅ CH ₃	-106	-14385	9	27	-2
Mn(CO) ₅ Cl	1	-16276	8	24	3

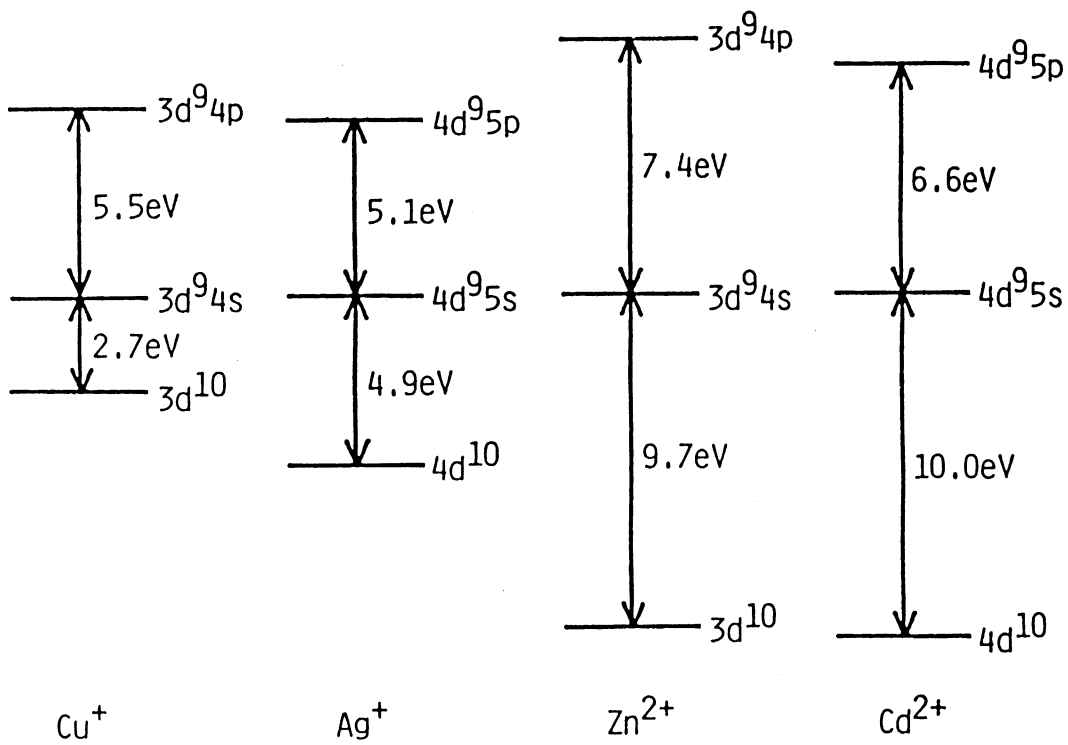


Figure 7. Atomic energy levels of the Ib (Cu, Ag) and IIb (Zn, Cd) metal ions. The energy levels of the d^9s^1 configurations are taken as a standard.

5. MECHANISM OF THE METAL CHEMICAL SHIFT OF THE Mn COMPLEXES

The mechanisms of the metal chemical shift of the Mn complexes are entirely different from those of the complexes of the Ib and IIb metals. Referring to Table 1, we see that the Mn chemical shifts are entirely due to the valence MO contributions to the paramagnetic term. In Table 5, we analyzed the paramagnetic term into the metal AO and ligand contributions. We immediately understand that the Mn chemical shifts are almost entirely due to the d AO contribution of the Mn atom.

The electronic configuration of the Mn atom is d^5s^2 in its ground state. The d orbitals are half-filled so that they enter strongly into the bonds with the ligands. In Table 6, we analyzed further the d contributions into the d_σ , d_π , and d_δ AO contributions, where σ refers to an axis along the Mn-L bond in the $Mn(CO)_5L$ complexes. Figure 8 shows an illustration of these 3d orbitals and some orbitals of the ligands. From Table 6, we see that the $3d_\sigma$ and the $3d_\pi$ orbitals give almost fifty-fifty contributions to the chemical shift. This is very reasonable, as seen below.

From the MO analysis, we see that the $3d_\pi$ and $3d_{\delta_1}$ orbitals lie in the occupied MO's and the $3d_\sigma$ and $3d_{\delta_2}$ orbitals lie in the unoccupied MO's. The reason for this ordering is qualitatively given in the semiempirical treatment of Gray et. al. [26]. In the picture of second-order perturbation theory as given by Eqn. (5), the paramagnetic term is expressed as a sum of the contributions of various excitations. Among the d orbitals shown in Figure 8, there are four types of d-d transitions. They belong to the symmetry $A_2(3d_{\delta_1} \rightarrow 3d_{\delta_2})$, $B_2(3d_{\delta_1} \rightarrow 3d_\sigma)$, $E(3d_\pi \rightarrow 3d_\sigma)$, and $E(3d_\pi \rightarrow 3d_{\delta_2})$. Among these, the B_2 excitations do not contribute, because the angular momentum operator belongs to the $A_2(l_z) + E(l_x, l_y)$ symmetry. Further, for the complexes studied here, no δ bond exists between Mn and the axial ligand L. The MO's of δ symmetry give only a secondary contribution to the chemical shift. Thus, the Mn chemical shift of the $Mn(CO)_5L$ complexes is due primarily to the $3d_\pi \rightarrow 3d_\sigma$ transitions. This is why the $3d_\pi$ and $3d_\sigma$ orbitals give almost fifty-fifty contributions to the chemical shift as analyzed in Table 6.

Table 6. Analysis of the Mn 3d contributions to the paramagnetic term^a (In ppm.).

Molecules	$3d_{\sigma}$		$3d_{\pi}$		$3d_{\delta 1}$	
	Value	Shift	Value	Shift	Value	Shift
Mn(CO) ₅ H	-2669	0	-5313	0	-2453	0
Mn(CO) ₅ CN	-3009	-340	-5272	41	-2262	191
Mn(CO) ₅ CH ₃	-3295	-626	-5988	-675	-2460	-7
Mn(CO) ₅ Cl	-4361	-1692	-6865	-1552	-2318	135

Molecules	$3d_{\delta 2}$		Total	
	Value	Shift	Value	Shift
Mn(CO) ₅ H	-2548	0	-12983	0
Mn(CO) ₅ CN	-2595	-47	-13138	-155
Mn(CO) ₅ CH ₃	-2641	-93	-14384	-1401
Mn(CO) ₅ Cl	-2732	-184	-16276	-3293

^a $3d_{\sigma} = 3d_z^2$; $3d_{\pi} = 3d_{xz}, 3d_{yz}$; $3d_{\delta 1} = 3d_{xy}$; $3d_{\delta 2} = 3d_x^2 - y^2$, in the coordinate system shown in Fig. 8.

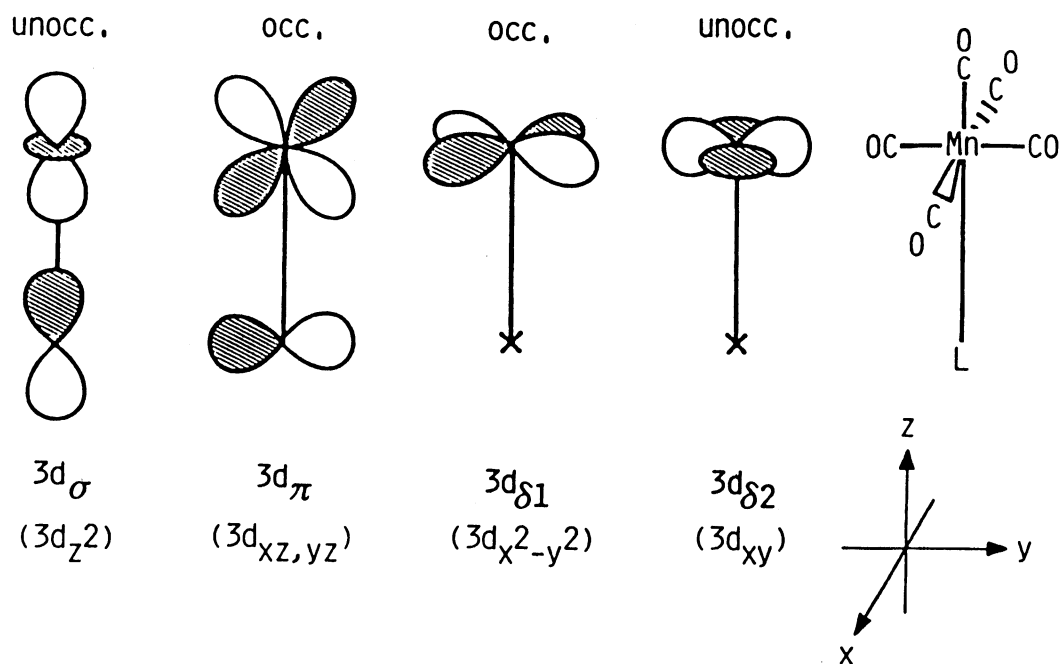


Figure 8. Illustration of the manganese 3d orbitals.

The $3d_{\pi}$ orbital of Mn lies in the HOMO region and its weight should increase as the ligand L becomes more π -donating. In Figure 9 we give an illustration in order to explain the mechanism of the Mn chemical shift in the $\text{Mn}(\text{CO})_5\text{L}$ complexes. The $3d_{\pi}$ contribution would increase (become more negative) in the order of $\text{CN} < \text{H} < \text{CH}_3 < \text{Cl}$, which is the empirical order of an π -donating ability. This agrees with the order given in Table 6. The $3d_{\sigma}$ orbital lies in the unoccupied MO region. Its weight would increase as the interaction between the $3d_{\sigma}$ AO and the ligand increases, because of the delocalization of the $3d_{\sigma}$ orbital. $\text{Mn}(\text{CO})_5^+$ is a typical soft Lewis acid [27]. So, the interaction with the ligand L would increase as the softness of the ligand base increases. Then, the $3d_{\sigma}$ contribution to the chemical shift is expected to increase (become more negative) as the softness of the ligand L decreases, namely, in the order of $\text{H}^- \sim \text{CN}^- < \text{CH}_3^- < \text{Cl}^-$. In Table 6, the order of the $3d_{\sigma}$ contribution is $\text{H} < \text{CN} < \text{CH}_3 < \text{Cl}$, which reflects this ordering. For the unoccupied $3d_{\sigma}$ orbital, static properties are useless as a measure because only the occupied orbitals contribute to such properties. The "softness" or the "hardness" is a property which is a result of the chemical interaction [27] so that it is more appropriate for describing the property of the unoccupied orbitals. Calderazzo et. al. [14] explained the trend in the Mn chemical shift from the effects of the ligands on the excitation energies between the d orbitals.

The Mn atom in the $\text{Mn}(\text{CO})_5\text{L}$ complexes has the electronic configuration $3d^{5.2}4s^04p^{0.2}$. In comparison with the electronic structure of the free atom, $3d^54s^24p^0$, the 4s electrons are donated completely to the ligands and the 3d and 4p orbitals accept electrons from ligands. The net charge of Mn is $+1.4 \sim +1.8$ in comparison with the formal charge of 1.0.

6. DIAMAGNETIC TERM

The diamagnetic term itself is large but its contribution to the chemical shift is small as seen from Table 1. It increases with in-

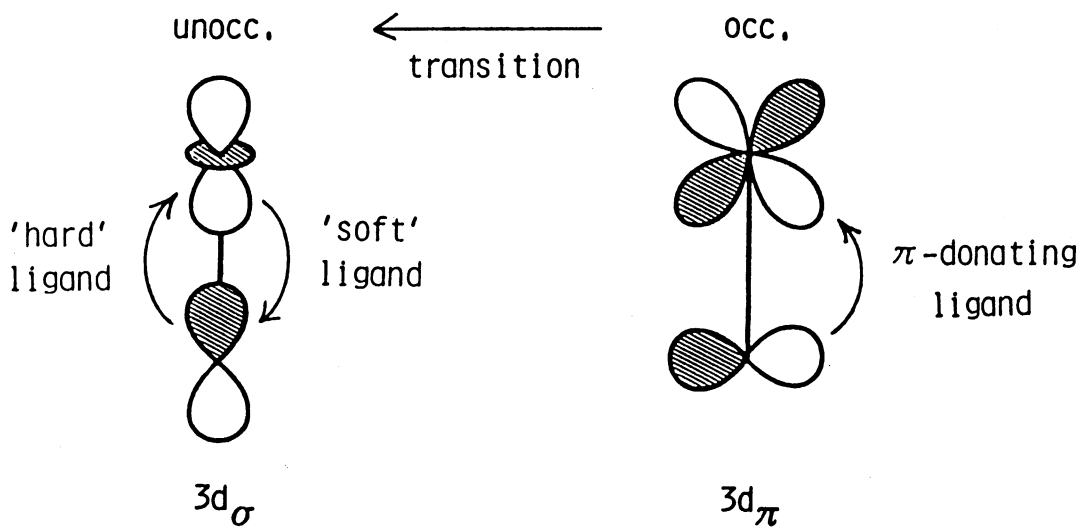


Figure 9. Illustration of the mechanism of the Mn chemical shift in the Mn(CO)₅L complexes which shows that the chemical shift should be larger with increasing π-donating ability and the hardness of the ligand.

creasing nuclear charge [4] as expected from its operator given by Eqn. (2c). Flygare and Goodisman [28] have shown that the isotropic term of the diamagnetic shielding constant is written to a good approximation as

$$\sigma_A^{\text{dia}} = \sigma_A^{\text{dia}}(\text{free atom}) + \frac{e^2}{3mc^2} \sum_{B(\neq A)} Z_B/R_{AB} \quad (8)$$

where $\sigma_A^{\text{dia}}(\text{free atom})$ is the free-atom diamagnetic susceptibility, B denotes the nucleus other than A, Z_B its nuclear charge, and R_{AB} the internuclear distance. The free atom term $\sigma_A^{\text{dia}}(\text{free atom})$ is available from the literature [29,30]. This equation means that the diamagnetic contribution to the chemical shift is determined by the geometry and the ligand species of the complexes. A knowledge of the molecular electronic wavefunction is unnecessary.

In the previous two papers [5,6] on the metal chemical shift we reported that the diamagnetic term is expressed in the following Pascal-rule-like formula

$$\sigma_A^{\text{dia}} = \sigma^{\text{dia}}(\text{A}) + \sum_L n_L \sigma^{\text{dia}}(\text{L}), \quad (9)$$

where $\sigma^{\text{dia}}(\text{A})$ is an atomic contribution, $\sigma^{\text{dia}}(\text{L})$ the contribution from the single ligand L, and n_L the number of the ligands L. We calculated $\sigma^{\text{dia}}(\text{A})$ and $\sigma^{\text{dia}}(\text{L})$ by a least-squares fitting method from the diamagnetic terms shown in Table 1 and found that Eqn. (9) is accurate to within $\pm 0.7\%$. It is evident that the formula given by Eqn. (9) is easily derivable from Eqn. (8), if we assume fixed metal-ligand length and fixed ligand geometry. We certainly adopted such an approximation in the previous calculations [5,6]. Thus, the validity of Eqn. (9) seems to support the validity of Eqn. (8), although we weren't aware of the relation given by Eqn. (8) when we wrote these papers. Thus, we conclude that the diamagnetic contribution to the chemical shift is determined by the geometry and the ligand species of the complexes. However, the diamagnetic contribution itself reflects

mainly the variations in the paramagnetic term which is discussed in the previous sections.

7. CONCLUDING REMARKS

In this article, we wanted to show that the metal chemical shift is an important property which includes valuable information about the electronic structures and bonding in metal complexes. This property is especially suited to clarifying the role of the d electrons, relative to those of the s and p electrons. Further, we wanted to show that ab initio molecular orbital theory gives reliable and useful information not only in guessing the magnitude of the metal chemical shift but also in investigating the electronic origin of the chemical shift which reflects the nature of the bonds between the metal and the ligands in the complexes. We think the latter role is very important since our aim is to construct an intuitive concept which is useful as a guide for experimental chemists.

The metal chemical shift is a sum of two terms, the diamagnetic term and paramagnetic term. The diamagnetic term has only a minor effect which is determined by the molecular geometry and the species of the ligands. The paramagnetic term is the major term and reflects the valence electronic structure near the metal atom.

For complexes of the Ib (Cu, Ag) and IIb (Zn, Cd) metals, the p and d mechanisms are shown to be the two major mechanisms. For the Cu complexes, the p mechanism is more important than the d mechanism, and for the Ag complexes, the two mechanisms are competitive. These differences are attributed to the differences in the atomic energy levels of the free metal atoms. Further, these mechanisms suffer different substituent effects from the ligand. The d mechanism is facilitated by the electron-withdrawing substituent and the p mechanism is facilitated by electron-donating substituents.

For the Mn complexes, $Mn(CO)_5L$, the transitions from the d_{π} orbitals to the d_{σ} orbital are shown to be the main source of the Mn chemical shift from a perturbation theoretic point of view. The effects of the ligand L on the occupied d_{π} orbitals and on the unoccupied d_{σ}

orbitals are therefore important in an investigation of the trends in chemical shifts. We have summarized these effects in terms of the π -donating ability and hardness of the ligands.

For metal chemical shifts, many interesting subjects remain to be studied. There are many nuclear species for which the electronic origin is not yet clarified. Systematic studies, both theoretical and experimental, on the effects of the ligands on metal chemical shifts are necessary for thorough understanding. Relativity effects should be studied for complexes of heavy metals such as Pt, Hg, and Pb. For all of these studies, active collaborations between theory and experiment should be most fruitful.

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