Reprinted from the Journal of the American Chemical Society, 1984, *106*, 4653.


# Theoretical Study of the Metal Chemical Shift in Nuclear Magnetic Resonance. Ag, Cd, Cu, and Zn Complexes

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**Abstract:** The nuclear magnetic shielding constants of the metals in the Cu, Zn, Ag, and Cd complexes were studied theoretically by the ab initio finite perturbation SCF method. We investigated the origin of the metal chemical shifts for a general understanding of the electronic structure of the metal complexes and their metal NMR. The complexes studied were Cu complexes CuCl, $CuCl_4^{3-}$, $Cu(CN)_4^{3-}$, $Cu(NH_3)_2^+$, Zn complexes $Zn(H_2O)_6^{2+}$, $ZnCl_2$, $ZnCl_4^{2-}$, $Zn(CN)_4^{2-}$, $Zn(NH_3)_4^{2+}$, Ag complexes $Ag(H_2O)_6^+$, $AgF_4^{3-}$, $AgCl_2^-$, $AgCl_4^{3-}$, $Ag(CN)_4^{3-}$, $Ag(NH_3)_2^+$, and Cd complexes, $Cd(H_2O)_6^{2+}$, $CdCl_2$, $CdCl_4^{2-}$, $Cd(CN)_4^{2-}$, $Cd(CH_3)_2$. The metal chemical shifts are due mainly to the paramagnetic term. For the complexes of Cu, Zn, Ag, and Cd, whose electronic configurations are primarily $d^{10}s^{1-2}p^0$, the metal chemical shift is due to the electrons in the valence *n*p orbital and the holes in the valence $(n-1)$d orbital. For the Cu complexes, the d mechanism is predominant, so that the chemical shift increases with increasing electron acceptability of the ligand. For the Zn and Cd complexes, the p mechanism is more important than the d mechanism, so that the chemical shift increases with increasing electron-donating ability of the ligand. For the Ag complexes, the p and d mechanisms are competitive. These trends are understood from the atomic energy levels of the free metal atoms. For the diamagnetic term, which is smaller than the paramagnetic term for the chemical shift, we found a Pascal rule like formula. Thus, for the complexes of the 1B and 2B metals, a balance of the valence d and p contributions makes the metal chemical shift in a full variety.

Magnetic properties have long been a powerful tool for the studies of the electronic structures of transition-metal complexes. The theoretical basis for studying the properties of molecules in magnetic field has been well established.[2-8] Recently, experiments on the NMR properties of the metals are actively reported for various kinds of metal complexes.[9-15] We expect that they contain a lot of valuable information on the nature of the chemical bonds between metal and ligands and between metals. The magnetic properties of molecules reflect an angular momentum of the electron. The studies of the magnetic properties will bring us information on the roles of the electrons of higher angular momentum in these chemical bonds. For metal complexes, the roles of the d and f electrons of the metals are very interesting.

We report here an ab initio theoretical study on the chemical shifts of the nuclear magnetic resonance of the metals for Ag, Cd, Cu, and Zn complexes. The molecules studied are Ag complexes, $Ag(H_2O)_6^+$, $AgF_4^{3-}$, $AgCl_2^-$, $AgCl_4^{3-}$, $Ag(CN)_4^{3-}$, $Ag(NH_3)_2^+$, Cd complexes, $Cd(H_2O)_6^{2+}$, $CdCl_2$, $CdCl_4^{2-}$, $Cd(CN)_4^{2-}$, $Cd(CH_3)_2$, Cu complexes, CuCl, $CuCl_4^{3-}$, $Cu(CN)_4^{3-}$, $Cu(NH_3)_2^+$, and Zn complexes, $Zn(H_2O)_6^{2+}$, $ZnCl_2$, $ZnCl_4^{2-}$, $Zn(CN)_4^{2-}$, $Zn(NH_3)_4^{2+}$.

Experimental data for metal chemical shifts are now accumulated for several metal species.[12] For Ag complexes, Endo et al.[13] observed recently the metal chemical shifts of the $^{109}Ag$ complexes and discussed the relation between the chemical shift and the coordination number in aqueous solutions. For Cu complexes, Endo et al.[13] measured recently the metal chemical shifts

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0002-7863/84/1506-4653$01.50/0 

of the $^{63}Cu$ complexes in aqueous solution and of the solid. For Cd and Zn complexes, Cardin et al.[14] and Maciel et al.[14,15] reported the metal chemical shifts of the $^{113}Cd$ and $^{67}Zn$ complexes, respectively, in aqueous solutions and of the solid and discussed the effect of halide complexation of Cd and Zn.

We selected these metals because the roles of the d electrons, in comparison with those of the s, p electrons, are rather unclear for these formally $d^{10}$ metals. For transition metals with $d^n$ ($n < 10$) electrons, we give a report in a subsequent paper.[16] To the best of our knowledge, this is the first ab initio study on the metal chemical shift of the transition-metal complexes. We study the origin of the *metal* chemical shifts for a general understanding of the electronic structure of the metal complexes and the metal nuclear magnetic resonance.

## Method

We consider a molecule in an external magnetic field. The electronic Hamiltonian has the form

$$\mathcal{H} = (1/2m)\sum_j[-i\hbar\nabla_j + (e/c)A(r_j)]^2 - \sum_A\sum_j Z_A/r_{jA} + \sum_{i>j}1/r_{ij} \quad (1)$$

Here, $A(r_j)$ is the vector potential at the position of an electron $j$. For a molecule in a uniform magnetic field, $H$, the vector potential is given by

$$A(r_j) = (1/2)H \times r_j + \sum_A(\mu_A \times r_{jA})/r_{jA}^3 \quad (2)$$

where $\mu_A$ is a nuclear magnetic moment. Expanding the total Hamiltonian in powers of $H$ and $\mu_A$, we obtain

$$\mathcal{H} = \mathcal{H}_0 + \sum_t H_t\hat{H}_t^{(1,0)} + \sum_A\sum_t \mu_{At}\hat{H}_{At}^{(0,1)} + (1/2)\sum_A\sum_t\sum_u \mu_{At}\hat{H}_{Atu}^{(1,1)}H_u + \ldots \quad (3)$$

where $t$, $u$ denote $x$, $y$, $z$ axes, and

$$\hat{H}_0 = -(\hbar^2/2m)\sum_j\nabla_j^2 + V \quad (4a)$$

$$\hat{H}_t^{(1,0)} = -(i\hbar e/2mc)\sum_j(r_j \times \nabla_j)_t \quad (4b)$$

$$\hat{H}_{At}^{(0,1)} = -(i\hbar e/2mc)\sum_j(r_{Aj} \times \nabla_j)_t/r_A^3 \quad (4c)$$

$$\hat{H}_{Atu}^{(1,1)} = (e^2/4mc^2)\sum_j(r_j r_{Aj}\delta_{tu} - r_{jt}r_{Aju})/r_{Aj}^3 \quad (4d)$$

The nuclear magnetic shielding constant is given by

$$\sigma_{tu}^A = \left[\frac{\delta^2 E(H_u)}{\delta\mu_{At}\delta H_u}\right]_{\mu_A=H=0} \quad (5)$$

Using the Hellmann–Feynman theorem, we obtain

$$\sigma_{tu}^A = \langle\Psi(0)|\hat{H}_{Atu}^{(1,1)}|\Psi(0)\rangle + \frac{\partial}{\partial H_u}[\langle\Psi(H_u)|\hat{H}_{At}^{(0,1)}|\Psi(H_u)\rangle]_{H=0} \quad (6)$$

Here $\Psi(0)$ is the unperturbed wave function and $\Psi(H_u)$ is the wave function in the presence of the $u$ component of the external magnetic field. The first term of eq 6 is the diamagnetic shielding tensor, and the second term is the paramagnetic shielding tensor. Here, we discuss only the isotropic terms of the shielding constants of the metal given by

$$\sigma^{dia}{}_M = (1/3)\{\sigma^{dia}{}_{xx} + \sigma^{dia}{}_{yy} + \sigma^{dia}{}_{zz}\} \quad (7a)$$

$$\sigma^{para}{}_M = (1/3)\{\sigma^{para}{}_{xx} + \sigma^{para}{}_{yy} + \sigma^{para}{}_{zz}\} \quad (7b)$$

where the subscript M denotes the metal species in question (Ag, Cd, Cu, or Zn).

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**Table I.** Exponents of the Additional p-Type Gaussians to the MIDI-1 Sets for Metals

| atom | exponent | |
|---|---|---|
| Cu | 0.11000 | 0.03223 |
| Zn | 0.16000 | 0.04382 |
| Ag | 0.15000 | 0.03800 |
| Cd | 0.16000 | 0.04094 |

**Table II.** Geometries of the Complexes Studied in the Present Calculations

| molecule | symmetry | parameter[a] | |
|---|---|---|---|
| $Cu(CN)_4^{3-}$ | $T_d$ | r(Cu–C) | 2.12[b] |
| $Cu(NH_3)_2^+$ | $D_{3d}$ | r(Cu–N) | 2.05[b] |
| CuCl | $C_{\infty v}$ | r(Cu–Cl) | 2.34[b] |
| $Zn(H_2O)_6^{2+}$ | $T_h$ | r(Zn–O) | 1.97[b] |
| $ZnCl_4^{2-}$ | $T_d$ | r(Zn–Cl) | 2.30[b] |
| $ZnCl_2$ | $D_{\infty h}$ | r(Zn–Cl) | 2.30[b] |
| $Zn(CN)_4^{2-}$ | $T_d$ | r(Zn–C) | 2.08[b] |
| $Zn(NH_3)_4^{2+}$ | $T_d$ | r(Zn–N) | 2.01[b] |
| $Ag(H_2O)_6^+$ | $T_h$ | r(Ag–O) | 2.18[b] |
| $Ag(NH_3)_2^+$ | $D_{3d}$ | r(Ag–N) | 2.22[b] |
| $AgCl_2^-$ | $D_{\infty h}$ | r(Ag–Cl) | 2.51[b] |
| $AgF_4^{3-}$ | $T_d$ | r(Ag–F) | 2.16[b] |
| $AgCl_4^{3-}$ | $T_d$ | r(Ag–Cl) | 2.51[b] |
| $Ag(CN)_4^{3-}$ | $T_d$ | r(Ag–C) | 2.29[b] |
| $Cd(H_2O)_6^{2+}$ | $T_h$ | r(Cd–O) | 2.14[b] |
| $CdCl_2$ | $D_{\infty h}$ | r(Cd–Cl) | 2.47[b] |
| $CdCl_4^{2-}$ | $T_d$ | r(Cd–Cl) | 2.47[b] |
| $Cd(CH_3)_2$ | $D_3d$ | r(Cd–C) | 2.25[b] |
| $Cd(CN)_4^{2-}$ | $T_d$ | r(Cd–C) | 2.25[b] |
| –CN | $C_{\infty v}$ | r(C–N) | 1.17[c] |
| $-NH_3$ | $C_{3v}$ | r(N–H) | 1.032[d] |
| | | ∠HNH | 109.5[d] |
| $-CH_3$ | $C_{3v}$ | r(C–H) | 1.094[e] |
| | | ∠HCH | 109.5[e] |
| $-OH_2$ | $C_{2v}$ | r(O–H) | 0.957[f] |
| | | ∠HOH | 104.5[f] |

[a] In angstroms for the lengths, and in degrees for the angles. [b] We assume that these lengths are the sums of the tetrahedral covalent radii.[26] [c] The C–N length in the CN radical.[33] [d] The N–H length and the HNH angle in the $NH4^+$ ion.[34] [e] The C–H length and the HCH angle in the $CH_4$ molecule.[34] [f] The O–H length and the HOH angle in the $H_2O$ molecule.[34]

In the present paper, we used the finite perturbation method[17,18] to get the perturbed wave function $\Psi(H_u)$. In the Hartree–Fock–Roothaan approximation, the Fock matrix in the magnetic field $H_u$ is given by

$$F_{\mu\nu}(H_u) = h_{\mu\nu} - iH_u(\hat{H}_{\mu\nu}^{(1,0)})_u + \sum_\tau\sum_\sigma P_{\tau\sigma}(H_u)[(\mu\nu|\tau\sigma) - (1/2)(\mu\sigma|\tau\nu)] \quad (8)$$

where

$$\hat{H}_{\mu\nu}^{(1,0)} = (e\hbar/2mc)\langle\phi_\mu|(r \times \nabla)|\phi_\nu\rangle \quad (9)$$

In actual calculations, we applied the *finite* external magnetic field of the order of $10^{-6}$–$10^{-3}$ au. The ab initio SCF MO's in the magnetic field were calculated with the use of the modified version of the HONDOG program.[19] The paramagnetic term was calculated as a gradient at zero external field as given by eq 5. The gauge origin was taken at the position of the metal nucleus. The basis set we used is the MIDI-1 set of Sakai, Takewaki, and Huzinaga[20]

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**Table III.** Diamagnetic and Paramagnetic Contributions, $\sigma^{dia}_M$ and $\sigma^{para}_M$, to the Metal Magnetic Shielding Constant $\sigma_M$ and Their Analyses into Core and Valence MO Contributions[a]

| | $\sigma^{dia}$ | | | | $\sigma^{para}$ | | | | $\sigma$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| molecule | core | valence | total | shift | core | valence | total | shift | total | shift |
| $CuCl_4^{3-}$ | 2292 | 375 | 2667 | 0 | −63 | −818 | −881 | 0 | 1786 | 0 |
| $Cu(CN)_4^{3-}$ | 2190 | 387 | 2577 | −90 | −103 | −1588 | −1691 | −810 | 886 | −900 |
| $Cu(NH_3)_2^{+}$ | 2150 | 314 | 2464 | −203 | −73 | −2582 | −2655 | −1774 | −191 | −1977 |
| CuCl | 2171 | 279 | 2450 | −217 | −79 | −4617 | −4696 | −3815 | −2246 | −4032 |
| $Zn(H_2O)_6^{2+}$ | 2266 | 486 | 2752 | 0 | −44 | −272 | −316 | 0 | 2436 | 0 |
| $ZnCl_4^{2-}$ | 2376 | 406 | 2782 | 30 | −55 | −447 | −502 | −186 | 2280 | −156 |
| $ZnCl_2$ | 2294 | 342 | 2636 | −116 | −42 | −414 | −456 | −140 | 2179 | −257 |
| $Zn(CN)_4^{2-}$ | 2272 | 420 | 2692 | −60 | −74 | −654 | −728 | −412 | 1964 | −472 |
| $Zn(NH_3)_4^{2+}$ | 2250 | 418 | 2668 | −84 | −75 | −711 | −786 | −470 | 1882 | −554 |
| $Ag(H_2O)_6^{+}$ | 4514 | 361 | 4875 | 0 | −41 | −431 | −472 | 0 | 4403 | 0 |
| $Ag(NH_3)_2^{+}$ | 4484 | 239 | 4722 | −153 | −33 | −628 | −661 | −189 | 4062 | −341 |
| $AgCl_2^{-}$ | 4549 | 241 | 4790 | −85 | −46 | −1001 | −1047 | −575 | 3742 | −661 |
| $AgF_4^{3-}$ | 4504 | 328 | 4832 | −43 | −75 | −1083 | −1158 | −686 | 3673 | −730 |
| $AgCl_4^{3-}$ | 4631 | 307 | 4938 | 63 | −76 | −1296 | −1372 | −900 | 3566 | −837 |
| $Ag(CN)_4^{3-}$ | 4521 | 308 | 4829 | −46 | −96 | −1416 | −1512 | −1040 | 3318 | −1085 |
| $Cd(H_2O)_6^{2+}$ | 4626 | 378 | 5004 | 0 | −33 | −442 | −475 | 0 | 4529 | 0 |
| $CdCl_2$ | 4655 | 253 | 4908 | −96 | −25 | −643 | −668 | −193 | 4240 | −286 |
| $CdCl_4^{2-}$ | 4731 | 314 | 5045 | 41 | −40 | −875 | −915 | −440 | 4129 | −400 |
| $Cd(CH_3)_2$ | 4595 | 256 | 4851 | −153 | −43 | −1047 | −1090 | −615 | 3761 | −768 |
| $Cd(CN)_4^{2-}$ | 4640 | 343 | 4983 | −21 | −95 | −1509 | −1604 | −1129 | 3378 | −1151 |

[a] Values in ppm.

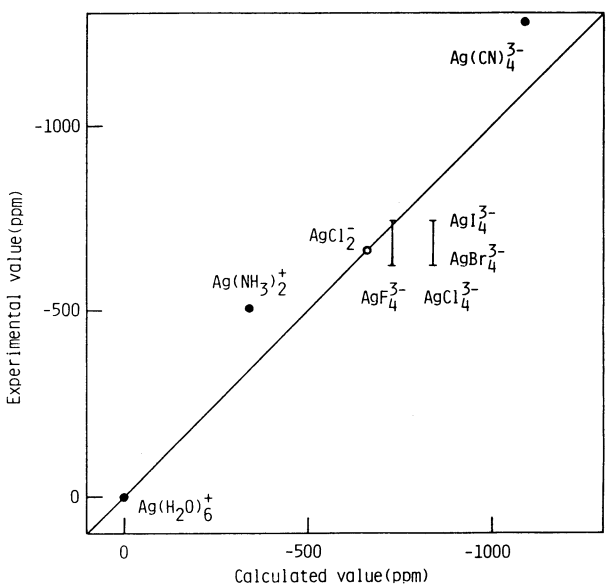


**Figure 1.** Comparison between experimental and calculated values for the $^{109}Ag$ chemical shifts of the silver complexes. For halides, the shifts were observed only for $AgBr_4^{3-}$ and $AgI_4^{3-}$. We have calculated $AgF_4^{3-}$ and $AgCl_4^{3-}$ and compared their shifts with those of $AgBr_4^{3-}$ and $AgI_4^{3-}$. For the linear $AgCl_2^{-}$ molecule, no experimental data are reported; the circle shows only the calculated value.

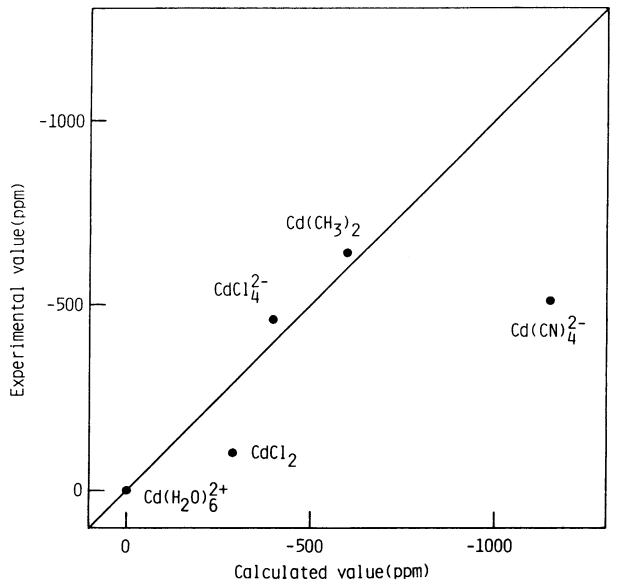


**Figure 2.** Comparison between experimental and calculated values for the $^{113}Cd$ chemical shifts of the cadmium complexes.

for both metals and ligands. This basis set is of double-$\zeta$ quality for valence orbitals. Further, we added two single-primitive Gaussians for the $np$ AO's of the central metals. They are shown in Table I.

The structural data of the complexes in aqueous solutions, where most of the experiments were performed, are very limited. Though the geometries of some complexes are known,[21-25] most of them are unknown. Therefore, we adopted Pauling's tetrahedral covalent radii,[26] for internal consistency, for all the metal–ligand distances. The aqueous solutions of the Zn and Cd ions are reported to be coordinated in an octahedral way by water.[21,23]

Table II summarizes the geometries of the complexes used in the present calculations. The geometries of the ligands are explained in the footnote of this table.

### Correlation of the Theoretical Values with Experiments

In Table III, we have summarized the nuclear magnetic shielding constants and the chemical shifts of the metals for all the molecules studied here. The shifts are given relative to the reference molecules, $CuCl_4^{3-}$, $Zn(H_2O)_6^{2+}$, $Ag(H_2O)_6^{+}$, and $Cd(H_2O)_6^{2+}$. The diamagnetic and paramagnetic terms are also given along with their analysis into the core and valence MO contributions, which will be discussed in detail below.

Figure 1 shows the correlation between the present theoretical results and the experimental data[13] for the $^{109}Ag$ chemical shifts of the silver complexes. All of the experimental data were measured in aqueous solutions with the $AgNO_3$ solution as their reference for the chemical shifts. The calculated values are the shifts from the magnetic shielding constant of the $Ag(H_2O)_6^{+}$ complex. For halides, the shifts were observed only for the bromide and iodide, $AgBr_4^{3-}$ and $AgI_4^{3-}$. Theoretically, we have calculated only fluoride and chloride $AgF_4^{3-}$ and $AgCl_4^{3-}$, for simplicity, and compared their shifts with those of $AgBr_4^{3-}$ and $AgI_4^{3-}$. The theoretical Ag chemical shifts for $AgF_4^{3-}$ and $AgCl_4^{3-}$ are −730

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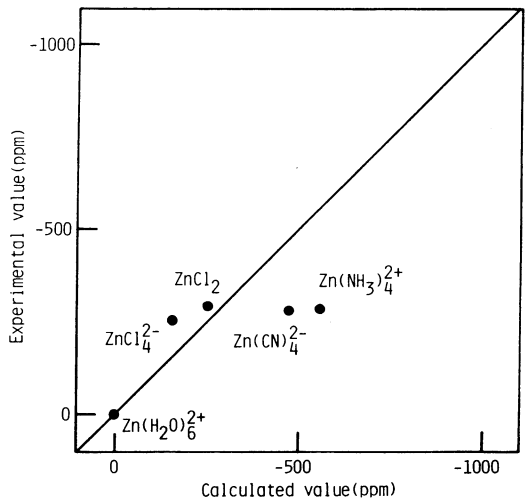


**Figure 3.** Comparison between experimental and calculated values for the $^{67}Zn$ chemical shifts of the zinc complexes.

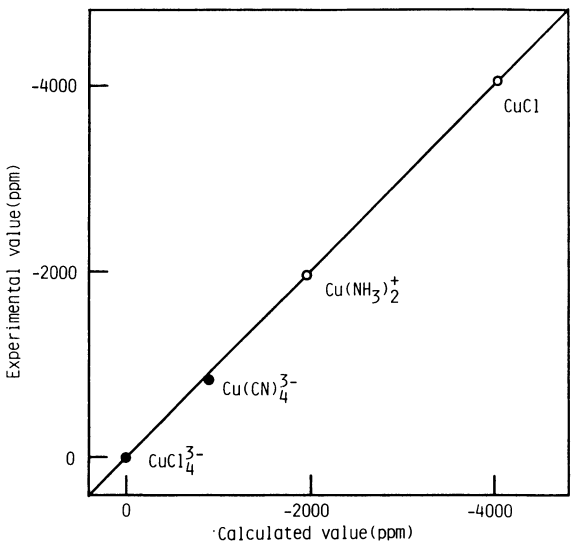


**Figure 4.** Comparison between experimental and calculated values for the $^{63}Cu$ chemical shifts of the copper complexes. For CuCl and $Cu(NH_3)_2^+$ complexes, the experimental data are not available. The circles show only the calculated values.

and −837 ppm, respectively, and the experimental Ag chemical shifts for $AgBr_4^{3-}$ and $AgI_4^{3-}$ are −623 and −739 ppm, respectively.[13a] For the complex $AgCl_2^-$, no experimental data are reported. We have calculated it to see the effect of the coordination number on the chemical shift of the central metal. From Figure 1, we may conclude that the present theoretical values are in good correlation with the experimental values. This is rather surprising, considering the uncertainties in the structures and solvations of these complexes in aqueous solution.

Figures 2 and 3 show the correlations between the theoretical and experimental values[14,15] of the $^{113}Cd$ and $^{67}Zn$ chemical shifts for the cadmium and zinc complexes, respectively. Experimentally, $Cd(CH_3)_2$ was measured neat, and $CdCl_4^{2-}$ was measured for the solid.[14] The rest are due to the aqueous solutions. Though the structures and the coordination numbers of the ligands are not known exactly, the present calculated values are in rather good correlation with the experimental data for most of the complexes. For the cadmium complexes, the cyanide $Cd(CN)_4^{2-}$ is far from the straight line. This is probably due to some solvation effects on the geometry and/or the coordination.

Figure 4 shows the correlation between the present results and the experimental data[13c] for the $^{63}Cu$ chemical shifts of the copper complexes. For CuCl and $Cu(NH_3)_2^+$ complexes, we could not get the experimental data. So, the circles in Figure 4 show only the calculated values. The $Cu(CN)_4^{3-}$ complex was measured in the aqueous solution and the $CuCl_4^{3-}$ complex for the solid. The points for $Cu(CN)_4^{3-}$ and $CuCl_4^{3-}$ are almost on the line of the gradient of 45°. It is expected that the present calculation would correspond well to the experimental values for other copper complexes, if they can be measured.

**Table IV.** AO Contributions to $\sigma^{dia}_{Cd}$ and $\sigma^{para}_{Cd}$ for $Cd(CH_3)_2$[a]

| AO | $\sigma^{dia}_{Cd}$ | $\sigma^{para}_{Cd}$ |
|---|---|---|
| Cd 1s | 1791 | 0 |
| 2s | 311 | 0 |
| 2p | 1265 | −1066 |
| 3s | 103 | 0 |
| 3p | 319 | 66 |
| 3d | 664 | −67 |
| 4s | 38 | 0 |
| 4p | 114 | 8 |
| 4d | 163 | −2 |
| 5s | 6 | 0 |
| 5p | 2 | 0 |
| $(-CH_3) \times 2$ | 75 | −29 |
| total | 4851 | −1090 |

[a] Values in ppm.

### Theoretical Analysis of the Metal Chemical Shifts

Table IV shows the contributions to the Cd magnetic shielding constant from Gaussian-type atomic orbitals (AO's) for $Cd(CH_3)_2$. The AO contributions are defined by the following formulas like Mulliken's population analysis

$$\sigma^{dia}{}_{tu}(N) = (e^2/4mc^2) \sum_{\mu \in N} \sum_{\nu}^{all} P_{\mu\nu}{}^{(0)} \langle \varphi_\mu | (r r_{Au} \delta_{tu} - r_t r_{Au}) r_A^{-3} | \varphi_\nu \rangle \quad (10a)$$

$$\sigma^{para}{}_{tu}(N) = (e\hbar/2mc) \frac{\partial}{\partial H_u} \sum_{\mu \in N} \sum_{\nu}^{all} P_{\mu\nu}{}^{Im}(H_u) \langle \phi_\mu | (r_A \times \nabla)_t r_A^{-3} | \phi_\nu \rangle \quad (10b)$$

where N denotes a Gaussian-type AO on metal or ligand. In Table IV, the ligand AO contributions were summed up for the ligand.

For the diamagnetic term, $\sigma^{dia}$, the contribution from the inner core AO's, i.e., 1s–4p AO's, of the metal is a major part of the total value. The contributions of the valence AO's (4d, 5s, 5p) and the ligand AO's are very small. Since the diamagnetic shielding operator involves the reciprocal of $r_A$, the contributions from the electrons near the nucleus are greater than those from the electrons far from the nucleus.

For the paramagnetic term, $\sigma^{para}$, the contributions of the s-type orbitals are 0, since an s electron has no angular momentum. The p- and d-type AO's give contributions. From Table IV we see that only the 2p and 3d core AO's give big contributions, in contrast to the nearly zero contributions from the valence AO's. This is, however, in contradiction with the perturbation theoretical consequence[6] that the *closed* p or d subshell gives no paramagnetic shielding.

In order to resolve this paradox, we divided the paramagnetic term into the MO contributions rather than the AO contributions. The MO contributions are defined as follows.

$$\sigma^{dia}{}_{tu}(M) = (e^2/4mc^2) \sum_{i \in M} \sum_{\mu,\nu}^{all} 2 c_{\mu i}{}^{(0)} c_{\nu i}{}^{(0)} \langle \phi_\mu | (r r_{Au} \delta_{tu} - r_t r_{Au}) r_A^{-3} | \phi_\nu \rangle \quad (11a)$$

$$\sigma^{para}{}_{tu}(M) = (e\hbar/2mc)(\partial/\partial H_u) \sum_{i \in M} \sum_{\mu,\nu}^{all} \{ c_{\mu i}{}^{Im}(H_u) c_{\nu i}{}^{Re}(H_u) - c_{\mu i}{}^{Re}(H_u) c_{\nu i}{}^{Im}(H_u) \} \langle \phi_\mu | (r_A \times \nabla)_t r a^{-3} | \phi_\nu \rangle \quad (11b)$$

where M denotes an MO. Table V shows this analysis for the diamagnetic and the paramagnetic terms of $Cd(CH_3)_2$. The core MO's, which mainly consist of the cadmium 1s–4p and carbon 1s AO's, contribute only −43 ppm. The rest, which are the *valence* MO's, determine the paramagnetic shielding. In Table V, the assignments of the subdivided valence MO's are rough, because

**Table V.** MO Contributions to $\sigma^{dia}_{Cd}$ and $\sigma^{para}_{Cd}$ for $Cd(CH_3)_2$[a]

| MO | $\sigma^{dia}_{Cd}$ | $\sigma^{dia}_{Cd}$ |
|---|---|---|
| core MO | | |
| Cd 1s–4p | | |
| C 1s | 4595 | −43 |
| valence MO | | |
| $-CH_3$ | 48 | −591 |
| Cd 4d | 184 | 706 |
| Cd–C sym. | 13 | −138 |
| Cd–C asym. | 11 | −1024 |
| total | 4851 | −1090 |

[a] Values in ppm.

the valence MO's extend over the molecule and are closely spaced to each other. On the other hand, for the diamagnetic term, the core MO contribution is dominant in accordance with the AO analysis shown in Table IV.

Thus, it is shown that the paramagnetic term of the Cd chemical shift is determined, in the AO picture, by the *inner core* AO's, but in the MO picture, by the *outer valence* MO's. This apparent paradox for the paramagnetic term can be understood from the following mechanism of the metal chemical shift. Figure 5 shows the radial distribution functions of some hydrogenic p and d orbitals. The orbitals, except for the innermost AO's in each symmetry, have nodes for the orthogonality. The inner amplitudes of the outer MO's, e.g., for the 4p orbital the two small amplitudes in the regions of the 2p and 3p orbitals, are due to the orthogonality of the outer orbitals to the inner orbitals. Since the Gaussian orbitals we used are nodeless, these inner amplitudes are described by the GTO's of the inner shells. The paramagnetic shielding terms for metals are due to the valence MO's, as clearly shown by Table V, but due to these inner amplitudes of the valence AO's, as shown by Table IV. Since the operator of the paramagnetic term is $(r_A \times \nabla)_t r_A^{-3}$, the distributions of *the valence electrons near the nucleus* are observed through the nuclear magnetic resonance experiment.

Table III shows the diamagnetic and paramagnetic terms and their analyses into the core and valence MO contributions for all the complexes studied here. For the diamagnetic term, $\sigma^{dia}$, the core MO contributions are dominant. The valence MO contributions are only 5–18% of the total diamagnetic term. Though the absolute values of $\sigma^{dia}$ are large, their contributions to the chemical shifts are small. This is due to the constancy (transferability) of the inner shells independent of the chemical environments. We will show later that a Pascal rule like formula applies to the diamagnetic term because of this constancy.

For the paramagnetic terms, the valence MO contributions are about 10–100 times larger than those of the core MO contributions. This is in marked contrast to the case of the diamagnetic term. The total chemical shifts are primarily determined by the valence MO contributions of the paramagnetic term. Since the valence MO's are more sensible to the change in the ligand than the core MO's, the chemical shifts are mainly determined by the change in the valence MO contributions.

In the following sections, we analyze first the paramagnetic term in some detail and then the diamagnetic term.

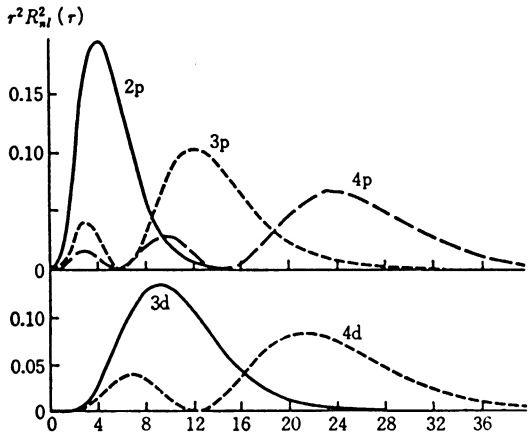


**Figure 5.** Radial distribution functions of the p- and d-type orbitals of the hydrogenic atom (modified from ref 35).

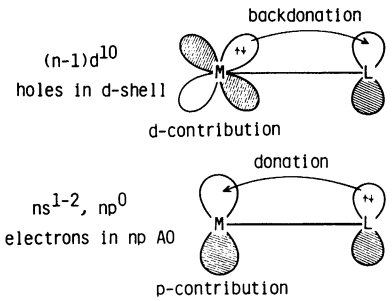


**Figure 6.** Illustration of the d and p mechanisms of the chemical shift. They are due to the metal–ligand interactions which produce respectively holes in the valence $(n-1)$d shell and electrons in the outer valence $n$p orbital. They are important as the origins of the paramagnetic term of the metal chemical shifts.

**A. Origin of the Paramagnetic Chemical Shift.** Table VI shows the contributions to the paramagnetic shielding constants of the metal from the metal AO's (in the sense discussed above). They show the sums of the contributions of the p- or d-type AO's. The contributions from the metal s orbitals are identically 0, so they are not shown in Table VI. Table VII shows the contributions to the paramagnetic terms of the metal from the ligands. We see that the ligand contributions are small for all the complexes. Therefore, we conclude that the metal chemical shifts are primarily due to the metal p and d orbital contributions.

The metals which are studied here are $d^{10}$ atoms, and as the perturbation theory[6] shows, the *closed* p and d subshells give no contribution to the paramagnetic term. Further, for the metals studied here, the outer valence p orbital is empty. Therefore, we further conclude that these paramagnetic terms are caused by the donation of electrons from the ligands to the metal outer p orbitals and by the back-donation of electrons from the metal d orbitals to the ligands. In other words, the electrons in the outer p orbitals and the holes in the valence d orbitals produce the metal chemical shifts of these complexes. Figure 6 is an illustration of these

**Table VI.** Contributions to the Paramagnetic Term of the Metal Shielding Constant, $\sigma^{para}_M$, from the Metal p and d AO's[a]

| | Cu | | Zn | | Ag | | Cd | |
|---|---|---|---|---|---|---|---|---|
| ligand | p | d | p | d | p | d | p | d |
| $(H_2O)_6$ | | | −195 | −54 | −240 | −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 | | | | |
| $(CH_o)_2$ | | | | | | | −992 | −68 |
| major contribution | d | | p | | p, d | | p | |

[a] Values in ppm.

**Table VII.** Contributions to the Paramagnetic Term of the Metal Shielding Constant, $\sigma^{para}_M$, from the Ligands[a]

| ligand | Cu | Zn | Ag | Cd |
|---|---|---|---|---|
| $(H_2O)_6$ | | −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 |

[a] Values in ppm.

mechanisms. Though this figure is written for the $\pi$ interactions, these mechanisms involve both $\sigma$ and $\pi$ interactions.

Now, which of the contributions are larger, either p contribution or d contribution? This depends primarily on the metal and then on the number and the nature of the ligands. From Table VI, we see that for the Cu complexes the d contributions are always much larger than the p contributions; for the Zn complexes and especially for the Cd complexes, the p contributions are larger than the d contributions, and for the Ag complexes the p and d contributions are relatively close and competitive. In Table VIII, we have given a summary of the mechanism.

In order to see the effects of the ligands, let us compare the tetrahedral complexes with the Cl and CN ligands, which were calculated for all the metal species studied here. The ligand $Cl^-$ is a so-called hard base, and $CN^-$ is a soft base. By replacing the Cl ligand with the CN ligand, the d contribution increases very much, though the p contribution is relatively unaffected except for the Ag complexes. Between the Cl and CN ligands, the $\pi$-effects are completely reverse. The ligand Cl is $\pi$-donating, but CN is $\pi$-withdrawing. Since the electronic configuration of the metal studied here is primarily $d^{10}s^{1-2}p^0$, the CN ligand withdraws the d electrons from the metal through the $d_\pi$(metal)–$p_\pi$(ligand) overlap, as shown in Figure 6, producing a hole in the metal d-subshell. For the Cl ligand, this interaction should be small since the d orbitals of the metal are already fully occupied. Instead, the $\pi$ electron of the Cl is transferred to the empty p orbital of the metal. This interaction is, however, not as favorable as the $d_\pi$(M)–$p_\pi$(L) interaction because of the shape and the diffuse nature of the metal p orbital. Thus, between the Cl and CN ligands, the d contribution to $\sigma_M^{para}$ is much larger for the CN ligand than for the Cl ligand. Conversely, the p contribution is larger for the Cl ligand than for the CN ligands. (An exception is seen for the Cd complex.) The d effects are larger than the p effects because the angular momentum included in the chemical shift operator is larger for the d orbital than for the p orbital and because the $d_\pi$(M)–$p_\pi$(L) interaction in the CN complexes should be larger than the $p_\pi$(M)–$p_\pi$(L) interaction in the Cl complexes. For the $\sigma$ interactions, the Cl and CN ligands are similar and both are electronegative. The group electronegativity is 3.03 and 3.3 for the Cl and CN ligands, respectively.[27] The CN ligand withdraws more $\sigma$ electrons from the fully occupied $d_\sigma$ orbitals of the metal than the Cl ligand. This $\sigma$ effect of the CN ligand is cooperative with the $\pi$ effect, in contrast to that of the Cl ligand, and further facilitates the d mechanism of the chemical shift. This is why the CN ligand is very effective for the d mechanism. In conclusion, the interaction which produces the holes in the $(n-1)$d shell of the metal facilitates the d mechanism and the interaction which gives an electron in the $n$p AO of the metal facilitates the p mechanism. This is valid for both $\sigma$ and $\pi$ interactions with the ligand.

For the copper complexes, the d contribution is much larger than the p contribution (Table VI). This suggests the importance of the d orbitals of the copper in forming the bond with the ligands. This further suggests that the Cu chemical shifts should be determined primarily by the electron acceptability of the ligands so far as the number of the ligands is the same. This fact corresponds well to the recent experimental results of the $^{63}Cu$ NMR analysis due to Kitagawa et al.[28] They obtained the result that the more $\pi$ acceptable the ligand is, the greater is the chemical shift.

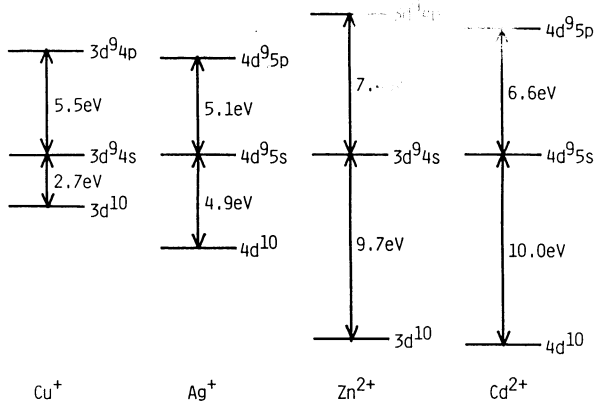


**Figure 7.** Atomic energy levels of the 1B (Cu, Ag) and 2B (Zn, Cd) metal ions. The energy levels of the $d^9s^1$ configurations are taken as a standard.

From Table VI, we see a trend that the d contribution decreases and the p contribution increases with increasing the number of the ligand, so long as the ligands are the same. However, for a general conclusion, more extensive studies are necessary, since the number of the complexes studied here is very limited.

For $Cd(CH_3)_2$, which is the only organometallic compound in the present study, the d contribution is small, because the bonds between the metal and ligands are made of the metal s and p orbitals and the $\sigma$ orbitals of the $CH_3$ group.

We summarize the general trends in the paramagnetic contributions of the metal chemical shifts in Table VIII.

For the copper complexes, the d mechanism is a major source of the paramagnetic term, so the chemical shift is determined primarily by the electron acceptability of the ligand.

For the Zn and Cd complexes, which belong to the 2B group, the p mechanism is larger than the d mechanism, so the chemical shift reflects the ability of the electron donation of the ligand to the $n$p orbital of the metal. The $\pi$ acceptability of the ligand, of course, contributes to the chemical shift, as seen for the CN ligand, since the angular momentum is larger for the d electrons than for the p electrons.

For the silver complexes, the p and d mechanisms are competitive, so the chemical shift is due to the sum of the p and d effects of the ligands.

Now why do these differences in the origin of the metal chemical shift occur? A possible answer is given based on the atomic energy levels of the metals. Figure 7 shows the atomic energy levels of the 1B ($Cu^+$, $Ag^+$) and 2B ($Zn^{2+}$, $Cd^{2+}$) metal ions.[29] As for the interactions between the metal and ligands, we consider the donation of the ligand electrons to the metal $n$p orbital and the back donation of the electrons from the metal $(n-1)d^{10}$ orbital to the ligands. The electrons in the metal s orbital, which are important for bonding between these metals and ligands, do not contribute to the shielding constant. For the monovalent 1B metals, the $(n-1)$d–$n$s and $n$s–$n$p level splittings are 2.7 and 5.5 eV, respectively, for $Cu^+$ and 4.9 and 5.1 eV for $Ag^+$. For the divalent 2B metals, the corresponding d–s and s–p splittings are 9.7 and 7.4 eV, respectively, for $Zn^{2+}$ and 10.0 and 6.6 eV for $Cd^{2+}$. For neutral species, the $n$s levels of Cu and Ag and also of Zn and Cd are similar.[29] Therefore, we understand that the d orbitals of Cu more easily mix with the metal–ligand bond than the p orbitals. In Ag, this mixing tendency of the 4d and 5p AO's is expected to be close, relative to that of the 5s AO. For the 2B metals, the mixing tendency of the $n$p AO, relative to that of the $n$s AO, should be larger than that of the $(n-1)$d AO. Thus, the

(27) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111.

(28) Kitagawa, S.; Munakata, M., private communication.

(29) Moore, C. E. "Atomic Energy Levels" National Bureau of Standard: Washington, 1971; Vol. 2, 3.

**Table VIII.** Summary for the Mechanisms of the Paramagnetic Terms Which Give the Major Contributions to the Metal Chemical Shifts

| metal complexes | mechanism in metal AO contribution | role of ligand |
|---|---|---|
| Cu | holes in $(n-1)$d shell $\gg$ electrons in $n$p AO | electron acceptor $\gg$ electron donor |
| Cd, Zn | electrons in $n$p AO > holes in $(n-1)$d shell | electron donor > electron acceptor (shift may be large) |
| Ag | electrons in $n$p AO $\fallingdotseq$ holes in $(n-1)$d shell | electron donor $\fallingdotseq$ electron acceptor |

**Table IX.** Metal AO Contributions to the Diamagnetic Term of the Metal Shielding Constant, $\sigma^{dia}_M$, Used in the Pascal Rule Like Formula, Eq 12[a]

| contribution | Cu | Zn | Ag | Cd |
|---|---|---|---|---|
| $\sigma^{dia}(s_M)$ | 1297 ± 3 | 1343 ± 2 | 2195 ± 2 | 2246 ± 4 |
| $\sigma^{dia}(p_M)$ | 843 ± 3 | 880 ± 2 | 1656 ± 3 | 1701 ± 3 |
| $\sigma^{dia}(d_M)$ | 239 ± 4 | 269 ± 2 | 794 ± 2 | 828 ± 2 |
| $\sigma^{dia}(M)$ | 2380 ± 4 | 2491 ± 2 | 4645 ± 3 | 4775 ± 2 |

[a] $\sigma^{dia}(M) = \sigma^{dia}(s_M) + \sigma^{dia}(p_M) + \sigma^{dia}(d_M)$. Values in ppm.

**Table X.** Contributions to the Diamagnetic Term of the Metal Shielding Constant, $\sigma^{dia}_M$, from the Ligands

| ligand | Cu | Zn | Ag | Cd |
|---|---|---|---|---|
| $(H_2O)_6$ | | 261 | 231 | 231 |
| $F_4$ | | | 185 | |
| Cl | 70 | | | |
| $Cl_2$ | | 143 | 145 | 133 |
| $Cl_4$ | 285 | 289 | 291 | 269 |
| $(CN)_4$ | 200 | 203 | 185 | 209 |
| $(NH_3)_2$ | 87 | | 80 | |
| $(NH_3)_4$ | | 177 | | |
| $(CH_3)_2$ | | | | 74 |

qualitative predictions based on the atomic energy levels agree well with the above summary of the trends in the metal chemical shifts.

**B. Diamagnetic Term.** We will now discuss the diamagnetic terms of the shielding constants of the metals. Table IX shows the diamagnetic contributions from the metal AO's. This table shows the ranges of the terms, since for all the complexes calculated here, the metal AO contributions were nearly constant independent of the change of the ligands. Since the diamagnetic terms are primarily determined by the inner-shell MO's, as shown in Table III, this constancy is a reflection of the transferability of the core electrons from molecule to molecule.

The isotropic average of the diamagnetic shielding tensor is equal to the electronic part of the potential, $\langle 1/r_M \rangle$, so that the contributions to the diamagnetic term from the metal AO's increase with increasing nuclear charge of the central atoms. In fact, the ratios between the contributions from the metal AO's are nearly equal to the ratios between the nuclear charges.

We note that for the Cu and Zn complexes the d contribution $\sigma^{dia}(d)$ shown in Table IX is actually the valence contribution. Therefore, the range of the values is relatively wide, especially for the Cu complexes.

Table X shows the diamagnetic contributions from the ligands. The contribution per unit ligand is almost a constant independent of the central metal atom to which the ligand is bonded. For example, for the $Cl_4$ ligand, the term is 285 ppm for the Cu complex, 289 ppm for the Zn complex, 291 ppm for the Ag complex, and 269 ppm for the Cd complex. Furthermore, the contribution of the four $Cl^-$ ligands in $MCl_4$ is twice as large as the contribution of the two $Cl^-$ ligands in $MCl_2$. The reason for this linearity is that the core orbitals of the ligand atoms, which are almost the same distances from the metals, give the predominant contributions to the diamagnetic shielding constants.

It is concluded from the above analysis that the diamagnetic term of the metal can be expressed in the following Pascal rule like formula

$$\sigma^{dia}_M = \sigma^{dia}(s_M) + \sigma^{dia}(p_M) + \sigma^{dia}(d_M) + \sum_L n_L \sigma^{dia}(L) = \sigma^{dia}(M) + \sum_L n_L \sigma^{dia}(L) \quad (12)$$

**Table XI.** Single Ligand Contributions to the Diamagnetic Term $\sigma^{dia}(L)$ Used in the Pascal Rule Like Formula, Eq 12[a]

| ligand | $\sigma^{dia}_M(L)$ | ligand | $\sigma^{dia}_M(L)$ |
|---|---|---|---|
| $CH_3$ | 37 | $OH_2$ | 40 |
| CN | 50 | F | 46 |
| $NH_3$ | 43 | Cl | 71 |

[a] Values in ppm.

**Table XII.** Comparison of the Diamagnetic Terms Calculated by the ab Initio Calculations with Those Calculated through the Pascal Rule Like Formula Given by Eq 12

| complex | $\sigma^{dia}$ ab initio | $\sigma^{dia}$ eq 12 | Δ |
|---|---|---|---|
| $CuCl_4^{3-}$ | 2667 | 2663 | −4 |
| $Cu(CN)_4^{3-}$ | 2577 | 2579 | +2 |
| $Cu(NH_3)_2^+$ | 2464 | 2465 | +1 |
| CuCl | 2450 | 2450 | 0 |
| $Zn(H_2O)_6^{2+}$ | 2752 | 2732 | −20 |
| $ZnCl_4^{2-}$ | 2782 | 2776 | −6 |
| $ZnCl_2$ | 2636 | 2634 | −2 |
| $Zn(CN)_4^{2-}$ | 2692 | 2692 | 0 |
| $Zn(NH_3)_4^{2+}$ | 2668 | 2664 | −4 |
| $Ag(H_2O)_6^+$ | 4875 | 4885 | +10 |
| $Ag(NH_3)_2^+$ | 4722 | 4731 | +9 |
| $AgCl_2^-$ | 4790 | 4787 | −3 |
| $AgF_4^{3-}$ | 4832 | 4829 | −3 |
| $AgCl_4^{3-}$ | 4938 | 4929 | −9 |
| $Ag(CN)_4^{3-}$ | 4829 | 4845 | +16 |
| $Cd(H_2O)_6^{2+}$ | 5004 | 5015 | +11 |
| $CdCl_2$ | 4908 | 4917 | +9 |
| $CdCl_4^{2-}$ | 5045 | 5059 | +14 |
| $Cd(CH_3)_2$ | 4851 | 4849 | −2 |
| $Cd(CN)_4^{2-}$ | 4983 | 4975 | −8 |

where $n_L$ is the number of the ligand L attached to the metal. The term $\sigma^{dia}(s_M)$ means the diamagnetic contribution from the metal s AO, and $\sigma^{dia}(L)$ means the diamagnetic contribution from the single ligand, L. $\sigma^{dia}(s_M)$, $\sigma^{dia}(p_M)$, and $\sigma^{dia}(d_M)$ are shown in Table IX, and $\sigma^{dia}(L)$ is given in Table XI for several ligands. The terms $\sigma^{dia}(s_M)$, $\sigma^{dia}(p_M)$, and $\sigma^{dia}(d_M)$ are constant depending on the metal species M, so that these terms are summed up as $\sigma^{dia}(M)$. We note that $\sigma^{dia}(L)$ is independent of the metals to which the ligand L coordinates.

Now, how well does the Pascal rule like formula (12) reproduce the diamagnetic term? In Table XII we compare the diamagnetic terms calculated by eq 12 with the values cited from Table III. It is seen that eq 12 works very well, giving the values which agree to within ±0.7% with those given in Table III. The largest difference is seen for $Zn(H_2O)_6^{2+}$ and is due to the difference of the $\sigma^{dia}(H_2O)$ from the average value (Table X).

Here we note a unique example where the chemical shifts are determined by the diamagnetic term. In Figure 3, the experimental and theoretical chemical shift of $ZnCl_2$ is more negative than that of $ZnCl_4^{2-}$. In Table III, however, the paramagnetic term of $ZnCl_2$ is more positive than that of $ZnCl_4^{2-}$. Referring to Table X we see that the observed trend is due to the diamagnetic term: namely, the diamagnetic term from the ligands for $ZnCl_4^{2-}$ is positive and twice as large as that for $ZnCl_2$, as the Pascal rule like formula indicates.

Lastly, we comment briefly upon the relativistic effects on the chemical shifts,[30] which are neglected in the present calculations. For the central metals, we may estimate the effects referring to

(30) (a) Pyykkö, P. *Chem. Phys.* **1983**, *74*, 1. (b) Pyper, N. C. *Chem. Phys. Lett.* **1983**, *96*, 204.

the relativistic calculations of the shielding constants of atoms by Kolb et al.[31] They are positive and about 7% of the shielding constant for Cu and Zn and about 16% for Ag and Cd. They increase up to about 41% for Au and Hg. However, since the effects of relativity are large for electrons in the inner core AO's, the relativistic effects on the chemical shifts are probably much smaller than these. Some of the effects would be incorporated within the form of the Pascal rule like formula given by eq 12.

A theory of chemical shift in which spin–orbit coupling is introduced through perturbation theory has been applied to hydrogen halides and halomethanes.[32] These results may be used to estimate the relativistic effects due to ligands. They show that the effects are positive for the shielding constant (shift to a higher field). As seen from Figure 1, the experimental chemical shifts of $AgBr_4^{3-}$ and $AgI_4^{3-}$ are −623 and −739 ppm, respectively.[12a] This change is reverse to that expected from the relativistic effect. In the present calculations, the heaviest ligand is the Cl atom, so the effects should be small.

## Conclusion

In this paper, we studied the nuclear magnetic shielding constants of the metals in the Ag, Cd, Cu, and Zn complexes. The results of the ab initio calculations compare well with the experimental chemical shifts. Table III summarizes the results of the present calculations. The paramagnetic term is a major part of the chemical shift, and the diamagnetic term is a minor part. For the paramagnetic term the inner amplitudes of the valence MO's of the metal are important (e.g., see Figure 5), and for the diamagnetic term the core MO's give a dominant contribution.

Table VIII shows a summary of the mechanisms of the metal chemical shift. For the complexes of the metals whose electronic configuration is primarily $d^{10}s^{1-2}p^0$, the paramagnetic term is due to the electrons in the outer valence *n*p orbital and the holes in the valence $(n-1)$d orbital of the metal. These electrons and holes are produced by the interactions between metal and ligands as illustrated in Figure 6. For the copper complexes, the metal chemical shift is due primarily to the d contributions so that it increases with increasing electron acceptability of the ligand. For the zinc and cadmium complexes, the p contribution is larger than the d contribution, so that the chemical shift is most affected by the ability of the electron donation of the ligand. However, the d contribution also becomes important when the ligand is a good electron acceptor like $CN^-$, because the d electrons have larger angular momentum than the p electrons. For the silver complexes, the p and d contributions are competitive. Therefore, both of the donating and withdrawing properties of the ligand are important. It is shown that these differences in the origin of the chemical shifts of the 1B and 2B metals are understood from the atomic energy levels of the metals.

The diamagnetic term is a minor part of the chemical shift. But the equation like Pascal's rule, as expressed by eq 12, is derived. So the diamagnetic term can be estimated very accurately at least for the series of the complexes calculated here.

The complexes studied here have the transition metals Cu, Ag, Zn, and Cd, which have the electronic structure $d^{10}s^{1-2}p^0$. So the balance of the valence d and p contributions makes the chemical shift in a full variety. The mechanism of the chemical shift for the complexes of the metals with incomplete d-valence shells should be different from those of the complexes studied here. Such study will be published in a forthcoming paper.

**Acknowledgment.** The calculation was carried out with the HITAC M200H and FACOM M382 computers at the Institute for Molecular Science and at the Data Processing Center of Kyoto University, respectively. We thank these computer centers for the grants of computing time. We also thank Dr. K. Futaki of Mitsubishi Paper Mills for his interest and support. Part of this study was supported by the Japan Society for the Promotion of Science.

**Registry No.** CuCl, 7758-89-6; $CuCl_4^{3-}$, 15444-92-5; $Cu(CN)_4^{3-}$, 19441-11-3; $Cu(NH_3)_2^+$, 16089-31-9; $Zn(H_2O)_6^{2+}$, 15906-01-1; $ZnCl_2$, 7646-85-7; $ZnCl_4^{2-}$, 15201-05-5; $Zn(CN)_4^{2-}$, 19440-55-2; $Zn(NH_3)_4^{2+}$, 17095-57-7; $Ag(H_2O)_6^+$, 42566-53-0; $AgF_4^{3-}$, 90605-28-0; $AgCl_2^-$, 15955-35-8; $AgCl_4^{3-}$, 15723-80-5; $Ag(CN)_4^{3-}$, 16743-34-3; $Ag(NH_3)_2^+$, 16972-61-5; $Cd(H_2O)_6^{2+}$, 14752-06-8; $CdCl_2$, 10108-64-2; $CdCl_4^{2-}$, 15974-49-9; $Cd(CN)_4^{2-}$, 16041-14-8; $Cd(CH_3)_2$, 506-82-1.

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