514 Bull. Chem. Soc. Jpn. Vol. 83, No. 5, 514–519 (2010)

Calculations and Electronic Analyses of ^{55}Mn and ^{13}C Nuclear Magnetic Shielding Constants for $Mn(CO)_5X$ ($X = H$, F, Cl, Br, I, and CH_3) and $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+})

Hirotaka Tanimura,[1] Ayumi Kitahori,[1] Chie Kuzuoka,[1] Yasushi Honda,[1,2] and Masahiko Hada*[1,2]

[1]Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University,
1-1 Minami-Osawa, Hachioji, Tokyo 192-0397

[2]CREST, Japan Science and Technology (JST) Agency, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075

Received December 25, 2009; E-mail: hada@tmu.ac.jp

We calculated ^{55}Mn and ^{13}C magnetic shielding constants for $Mn(CO)_5X$ ($X = H$, F, Cl, Br, I, and CH_3) and $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+}), respectively. For the first molecular group, we compared the calculated ^{55}Mn chemical shifts with the experimental values, and clarified effects of the basis sets. The calculated magnetic shielding constants using the second-order Douglas–Kroll–Hess (DKH2) method showed good agreement with the experimental results. According to the atomic orbital (AO) contribution analysis, the origin of the chemical shifts was attributed to the d–d transitions of Mn. In particular, the 3dπ orbital mainly contributed to the paramagnetic term of the Mn chemical shift. For the second molecular group, the ^{13}C chemical shifts were dependent on the metal atoms. When the metal centers were Cr^{2+} or Fe^{2+}, lower field shifts were seen. When the metal centers were Cu^{+} or Zn^{2+}, upper field shifts were observed. These results were in good agreement with the experimental trends. The change of the paramagnetic term mainly depended on the d orbital configurations of the metal of centers, and the donation from the metal d orbital to the CO anti-bonding π^* orbitals is expected to affect the chemical shift.

Nuclear magnetic resonance (NMR) is a powerful tool to study electronic structures of molecules and has been actively applied to various systems, especially for transition-metal complexes.[1] Theoretical elucidation of the mechanism of NMR chemical shift is an interesting and important theme in chemistry. For metal complexes, several electronic mechanisms of chemical shifts on the metal nuclei have been proposed by analyzing shielding constants of various nuclei on the periodic table by Nakatsuji et al.[2] They clarified the following things. The metal chemical shifts are due to mainly to the paramagnetic term. For Cu, Zn, Ag, and Cd complexes, the main electronic configurations of the metal atoms are $d^{10}s^{1-2}p^0$, and the chemical shift is due to electrons and holes in the valence np and $(n-1)$d orbitals of the metals, respectively. These systems are understood by the atomic energy levels of the free metal atoms and are called the p mechanism and/or the d mechanism. On the other hand, the d–d transition mechanism has been proposed for complexes including typical transition metals such as Mn by Kanda et al.[3] They studied ^{55}Mn nuclear magnetic shielding constants of $Mn(CO)_5L$ ($L = H$, CN, CH_3, and Cl). For these molecules, the chemical shifts are determined by the electronic configurations of the metal d orbitals and perturbation effects of the ligand on these orbitals. However the agreement between calculated and experimental values was not very good.

In a living body, many kinds of enzymes are found. Their functions are different from each other even if the same metallic ions are included in the enzymes.[4] To clarify the mechanism that controls functions of enzymes, multi-nuclear NMR is a useful tool when small molecules can act as a model of the enzyme.[5] Recently, theoretical studies of the NMR properties of metals are actively reported for various kinds of metalloenzymes, however problems in accuracy remain in the calculations, and those studies have not always provided satisfying results.

In the former part of this article, we reexamined the ^{55}Mn NMR shielding constants of $Mn(CO)_5X$ ($X = H$, F, Cl, Br, I, and CH_3) in order to improve our previous data[3] quantitatively. In general, relativistic effects become indispensable when the target molecules include heavy atoms. Some of these molecules include heavy elements, and relativistic treatments are expected to be needed for the calculations. In the latter part, we will show the calculations of ^{13}C NMR shielding constants of $M(^{13}CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+}). These molecules can be simple models of enzymes in living bodies.[6] We analyzed the tendency of the chemical shifts by the Gordon decomposition, and we suggest that the origin of the chemical shifts is the electron configuration of d orbitals and the energy gap between d orbitals. In the final section, we summarized the conclusions.

Computational Details

The nuclear magnetic shielding tensor σ_{Ntu} (t, $u = x$, y, and z) of the nucleus N is expressed as a second-order derivative of the total energy[7–11] given by

$$\sigma_{Ntu} = \left.\frac{\partial^2 E}{\partial \mu_{Nt} \partial B_{0u}}\right|_{B_0=\mu_N} \qquad (t, u = x, y, z) \qquad (1)$$

where μ_{Nt} is the nuclear magnetic moment of the nucleus N in the t direction, and B_0 is the strength of an external magnetic field. The magnetic shielding tensor can be decomposed into the following two contributions as

$$\sigma_{Ntu} = \sigma(\mathrm{dia})_{Ntu} + \sigma(\mathrm{para})_{Ntu} \tag{2}$$

where the first and second terms are called the diamagnetic and paramagnetic shielding tensors, respectively. The $\sigma(\mathrm{dia})_{Ntu}$ can be expressed by

$$\begin{aligned}\sigma(\mathrm{dia})_{Ntu} &= \frac{e^2\mu_0}{4m_e}\langle 0|\frac{\mathbf{r}\cdot\mathbf{r}_N\delta_{tu} - r_t r_{Nu}}{r_N^3}|0\rangle \\ &= \frac{e^2\mu_0}{4m_e}\int \rho(\mathbf{r})\frac{\mathbf{r}\cdot\mathbf{r}_N\delta_{tu} - r_t r_{Nu}}{r_N^3}\,d\mathbf{r}\end{aligned} \tag{3}$$

where μ_0 is the permeability of vacuum. Equation 3 is composed by integration of the position operator $\mathbf{r}$ and the electron density $\rho(\mathbf{r})$. Therefore, $\sigma(\mathrm{dia})_{Ntu}$ depends on the electron density around the resonance nucleus. On the other hand, the $\sigma(\mathrm{para})_{Ntu}$ in the perturbative form can be expressed by

$$\sigma(\mathrm{para})_{Ntu} = \frac{e^2\mu_0}{2m_e^2}\sum_{m\neq 0}\frac{\langle 0|\hat{L}_t|m\rangle\langle m|\frac{\hat{L}_{Nu}}{r_N^3}|0\rangle}{E_0 - E_m} \tag{4}$$

where $|m\rangle$ runs over excited-state wave functions. The $\sigma(\mathrm{para})_{Ntu}$ includes the angular momentum operator L and has an anti-shielding effect through the magnetic response of the angular momentum. We mainly discuss isotropic averages of these two terms, $\sigma(\mathrm{dia})_N$ and $\sigma(\mathrm{para})_N$, defined by

$$\begin{aligned}\sigma(\mathrm{dia})_N &\equiv \sigma(\mathrm{dia})_{N,\mathrm{isotropic}} \\ &= \frac{1}{3}(\sigma(\mathrm{dia})_{Nxx} + \sigma(\mathrm{dia})_{Nyy} + \sigma(\mathrm{dia})_{Nzz})\end{aligned} \tag{5}$$

$$\begin{aligned}\sigma(\mathrm{para})_N &\equiv \sigma(\mathrm{para})_{N,\mathrm{isotropic}} \\ &= \frac{1}{3}(\sigma(\mathrm{para})_{Nxx} + \sigma(\mathrm{para})_{Nyy} + \sigma(\mathrm{para})_{Nzz})\end{aligned} \tag{6}$$

Furthermore, we hereafter omit the subscript N of the shielding constant for simplicity when the resonance nucleus is obvious. In usual cases, changes in magnetic shielding constants or chemical shifts are attributed to those in $\sigma(\mathrm{para})$. The chemical shift δ of the target molecule is defined using isotropic term $\sigma_N \equiv \sigma_{N,\mathrm{isotropic}} = \sigma(\mathrm{dia})_N + \sigma(\mathrm{para})_N$ as

$$\delta = \sigma_N[\mathrm{ref}] - \sigma_N \tag{7}$$

where $\sigma_N[\mathrm{ref}]$ is the σ_N value of the reference molecule. The reference molecules in this study are $^{55}Mn(CO)_5H$ for $Mn(CO)_5X$ and free ^{13}CO for $M(CO)(NH_3)_3$, respectively.

In the former part of this work, the target molecules are $Mn(CO)_5X$ (X = H, F, Cl, Br, I, and CH_3). The molecular geometries were optimized by second-order Møller–Plesset (MP2)[12]/6-311G(d,p)[13,14] method. For the calculations of ^{55}Mn nuclear magnetic shielding constants, we employed the restricted Hartree–Fock (RHF) and the spin-free second-order Douglas–Kroll–Hess (DKH2) methods.[15–18] The basis set we used were 6-311G(d,p). In the latter part of this work, the target molecules are $M(CO)(NH_3)_3$ ($M = Cr^{2+}, Fe^{2+}, Cu^{+}$, and Zn^{2+}). Optimization of the molecular geometries and calculations of ^{13}C nuclear magnetic shielding constants were performed at the B3LYP level. The basis sets were (14s11p5d4f)/[6s5p3d1f] for the metal atoms, (11s6p1d)/[4s3p1d] for the C, N, and O atoms, and (4s)/[1s] for the H atoms, respectively.[19]

We used gauge-including atomic orbital (GIAO) method in order to avoid the gauge-origin dependence problem for the NMR calculations. Since the decomposition of $\sigma(\mathrm{dia})$ and $\sigma(\mathrm{para})$ depends slightly on the gauge origin even in the GIAO method, we set the gauge origin on the resonance atoms, i.e., the Mn and C atoms for $Mn(CO)_5X$ and $M(CO)(NH_3)_3$, respectively. All the calculations were performed by the Gaussian 03 program package.[20]

Results and Discussion

^{55}Mn Magnetic Shielding Constants for $Mn(CO)_5X$. Figure 1 shows the molecular structure of $Mn(CO)_5X$ (X = F, Cl, Br, I, and CH_3) optimized at the MP2/6-311G(d,p) level. All the molecules are octahedral with the Mn centers. The CO(ax) and CO(eq) mean CO ligands at the axial and equatorial positions, respectively. The molecular geometry parameters of these molecules are shown in Table 1. In the case that X is a halogen atom, the bond length tended to be longer as X is heavier. The Mn–CO(ax) bond length is shorter than the Mn–CO(eq). In the case of X = H and Cl, the experimental values for the bond lengths are reported.[21,22] The calculated Mn–X and Mn–CO bond lengths were ca. 0.1 Å shorter than the corresponding experimental values. However, considering the test calculations of NMR chemical shift, we adopted these calculated values.

Figure 2 shows comparison between the RHF-calculated and experimental[23] chemical shifts of the Mn complexes, although no experimental data were found for $Mn(CO)_5F$. The reference molecule is $Mn(CO)_5H$. The basis set of Mn in the previous study[3] was MIDI + diffuse and those of the ligands were

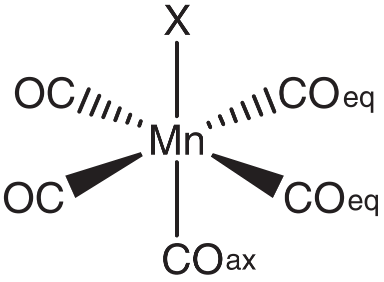

Figure 1. Molecular structure of $Mn(CO)_5X$ (X = F, Cl, Br, I, and CH_3).

Table 1. Calculated Molecular Geometry Parameters for $Mn(CO)_5X$ (X = H, F, Cl, Br, I, and CH_3)[a)]

X	Mn–X	Mn–CO(ax)	Mn–CO(eq)
H	1.46 (1.57)[b)]	1.74 (1.85)[b)]	1.76 (1.86)[b)]
F	1.89	1.69	1.80
Cl	2.28 (2.37)[c)]	1.68 (1.81)[c)]	1.78 (1.89)[c)]
Br	2.42	1.68	1.78
I	2.60	1.67	1.77
CH_3	2.08	1.70	1.76

a) The numbers in parentheses are the corresponding experimental values. All the values are given in Å. b) Ref. 21. c) Ref. 22.

MINI, while we used 6-311G(d,p) in this study. As shown in Figure 2, the Mn magnetic shielding constants are much improved in comparison with the previous values by employing the extended basis sets. It is noted that this change is due to just improvement of the basis set, not the theoretical method. On the other hand, low magnetic field shift is observed from $Mn(CO)_5I$ to $Mn(CO)_5F$. This shift is due to electronegativity of the ligand atoms (F, Cl, Br, and I). When the ligand has high electronegativity such as fluoride, the electron density of the Mn center was robbed by the ligand and the shielding effect of electrons is expected to become smaller, and it gives the lower field shift. However, the main origin of the chemical shift is not diamagnetic but paramagnetic effects on the Mn, and it is discussed later. For $Mn(CO)_5I$, the result of the Mn chemical shift is somewhat deviated from the 45° line. This would be due to the lack of relativistic and/or electron correlation effects.

To analyze the calculation results in detail, we decomposed the nuclear magnetic shielding constants to the diamagnetic and paramagnetic terms in the non-relativistic calculations. The results are shown in Table 2. The diamagnetic terms are almost constant for every molecule. Since the σ(dia) depends on the electron density around the resonance nucleus, the electron density surrounding the Mn center is expected to be almost unchanged. On the other hand, the paramagnetic term largely changed depending on the ligands because of changes in the angular momenta of the p and d orbitals of Mn. Therefore, the chemical shifts for these molecules are attributed to changes in the σ(para), and we discuss this term hereafter.

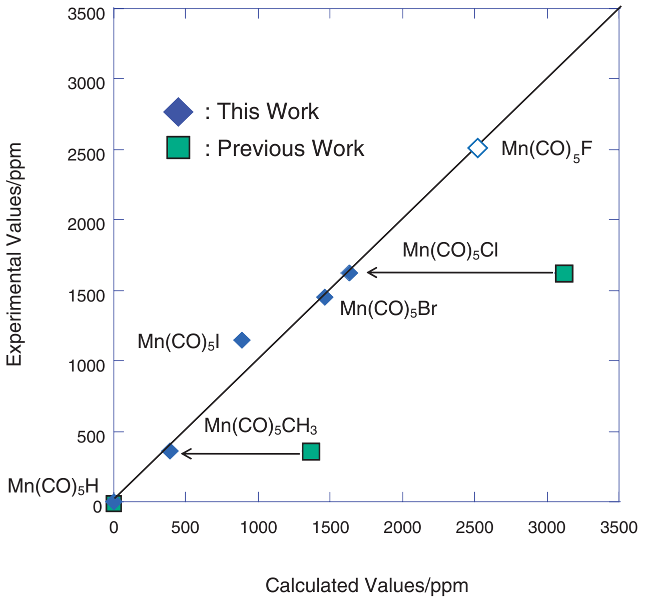

Figure 2. Comparison between the calculated and experimental values of ^{55}Mn NMR chemical shifts of the Mn complexes in this and a previous study. The experimental values are taken from Ref. 23, while no experimental data are available for $Mn(CO)_5F$.

The atomic orbital (AO) contributions to the paramagnetic term are listed in Table 3. Interestingly, it shows that even the AO contributions of X (X = H, F, Cl, Br, I, and CH_3) themselves are relatively small and do not depend on X largely. This indicates that the tendency of the chemical shift is independent of the contributions of the ligands themselves. Focusing on the p and d orbitals of the Mn nucleus, one can see that the d orbitals overwhelmingly contribute to the paramagnetic terms compared to the p orbitals. Thus, the contributions of the Mn d orbitals are essential to the chemical shifts in these systems.

We further decompose the AO contributions of the Mn 3d orbitals into several components in order to investigate the paramagnetic effects of these orbitals in detail, and the results are listed in Table 4. It indicates that the 3dπ orbitals mainly contribute to the paramagnetic terms of the Mn chemical shifts. Although the 3dσ and 3dδ_2 orbitals also contribute to the σ(para) values, they cancel each other consequently. The contributions of the 3dδ_2 orbitals are small. The molecular orbitals (MO) derived from the Mn 3d orbitals in $Mn(CO)_5X$ are shown in Figure 3. The 3dσ(3d$_{z^2}$) and 3dδ_1(3d$_{xy}$) are unoccupied orbitals, and the 3dπ(3d$_{xz,yz}$) and 3dδ_2(3d$_{x^2-y^2}$) orbitals are occupied. These results indicate that the chemical shifts for these molecules are attributed to the d–d transition from the 3dπ(3d$_{xz,yz}$) to the 3dσ(3d$_{z^2}$) and 3dδ_1(3d$_{xy}$) orbitals of the Mn atom.

Table 2. Diamagnetic and Paramagnetic Contributions to the Mn Magnetic Shielding Constants Calculated by RHF/6-311G(d,p) for $Mn(CO)_5X$ (X = H, F, Cl, Br, I, and CH_3)[a]

Molecules	σ(dia)	σ(para)	σ(total)	δ(calc)	δ(exp)[b]
$Mn(CO)_5H$	1906	−4707	−2801	0	0
$Mn(CO)_5F$	1908	−7150	−5242	2441	
$Mn(CO)_5Cl$	1905	−6331	−4426	1625	1626
$Mn(CO)_5Br$	1904	−6148	−4244	1443	1470
$Mn(CO)_5I$	1905	−5528	−3623	822	1145
$Mn(CO)_5CH_3$	1903	−5089	−3186	385	365

a) All the values are given in ppm. b) Ref. 23.

Table 3. AO Contributions to the Paramagnetic Terms for $Mn(CO)_5X$ (X = H, F, Cl, Br, I, and CH_3)[a]

Molecules	Mn		Ligands			Others	Total
	p	d	CO(ax)	CO(eq) × 4	X		σ(para)
$Mn(CO)_5H$	−122.5	−4644.3	19.9	48.6	9.2	−17.9	−4707
$Mn(CO)_5F$	−40.8	−7857.4	22.7	38.2	9.4	677.9	−7150
$Mn(CO)_5Cl$	−39.7	−6915.9	24.1	40.1	8.0	552.4	−6331
$Mn(CO)_5Br$	−34.0	−6616.6	25.0	42.8	8.9	425.9	−6148
$Mn(CO)_5I$	−21.2	−6038.5	25.3	43.7	8.5	454.2	−5528
$Mn(CO)_5CH_3$	−107.8	−5220.0	23.0	45.7	11.2	158.9	−5089

a) All the values are given in ppm.

Table 4. The 3d AO Contributions of the Mn Atom to the Paramagnetic Terms for $Mn(CO)_5X$ (X = H, F, Cl, Br, I, and CH_3)[a)]

Molecules	3dσ	3dπ × 2	3dδ_1	3dδ_2	Total
$Mn(CO)_5H$	−1018	−2312	−263	1052	−2541
$Mn(CO)_5F$	−1779	−3911	−426	1741	−4375
$Mn(CO)_5Cl$	−1571	−3443	−379	1523	−3870
$Mn(CO)_5Br$	−1482	−3294	−377	1464	−3689
$Mn(CO)_5I$	−1345	−3006	−246	1342	−3355
$Mn(CO)_5CH_3$	−1111	−2598	−337	1174	−2872

a) All the values are given in ppm.

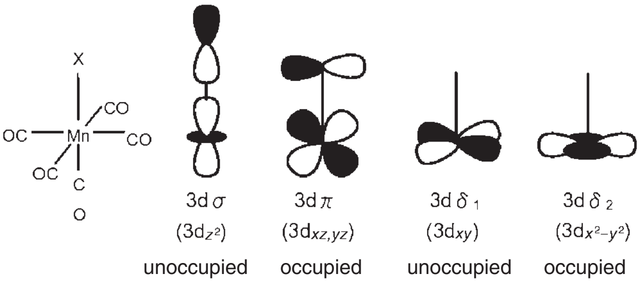

Figure 3. Shapes of Mn 3d orbitals for $Mn(CO)_5X$.

Table 5. Diamagnetic and Paramagnetic Contributions to the Mn Magnetic Shielding Constants Calculated by DKH2/6-311G(d,p) for $Mn(CO)_5X$ (X = H, F, Cl, Br, I, and CH_3)[a)]

Molecules	σ(dia)	σ(para)	σ(total)	δ(calc)	δ(exp)[b)]
$Mn(CO)_5H$	1932	−4628	−2695	0	0
$Mn(CO)_5F$	1936	−7086	−5150	2455	
$Mn(CO)_5Cl$	1932	−6253	−4321	1626	1626
$Mn(CO)_5Br$	1933	−6088	−4155	1460	1470
$Mn(CO)_5I$	1932	−5846	−3942	1134	1145
$Mn(CO)_5CH_3$	1931	−5015	−3084	388	365

a) All the values are given in ppm. b) Ref. 23.

Table 5 shows the results calculated by the DKH2 method which includes the relativistic effects. The DKH2 calculations improved the chemical shifts compared to RHF. Their results are in agreement with the experimental values, and all the errors between the calculated and experimental values are less than 6.3%. It indicates that the effect of spin–orbit interaction is not critical for these molecules, because only the spin free relativistic (SFR) terms were considered as the relativistic effects in this study. Also for the DKH2 calculations, σ(dia) were almost constant for variation of the molecules (from 1931 to 1936 ppm), whereas σ(para) changed greatly (from −4628 to −7086 ppm), indicating that the chemical shifts for these molecules are due to the σ(para) terms again.

To obtain more precise results, consideration of the higher-order relativistic and electron correlation effects are important. In the future, we want to calculate the shielding constants using the infinite order DKH (IODKH) method[24] combined with electron correlation theories such as coupled cluster singles and doubles (CCSD) and symmetry adapted cluster configuration interaction (SAC-CI)[25,26] methods, because it is known that the coupling effect between the relativistic and the electron correlation treatments is non-negligible.[27]

Table 6. Molecular Geometry Parameters for $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+})[a)]

Metal	Metal–C	C–O
Cr^{2+}	1.94	1.14
Fe^{2+}	2.28	1.03
Cu^{+}	1.85	1.14
Zn^{2+}	2.21	1.13

a) All the values are given in Å.

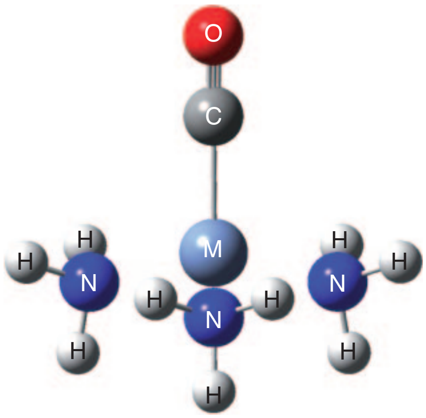

Figure 4. Molecular structure of $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+}).

Table 7. ^{13}C Magnetic Shielding Constants and Chemical Shifts for $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+})[a)]

Metal	σ(dia)	σ(para)	σ(total)	δ[b)]
Cr^{2+}	266.91	−443.13	−170.69	170.99
Fe^{2+}	266.91	−325.55	−58.64	58.94
Cu^{+}	265.58	−244.72	20.86	−20.56
Zn^{2+}	269.25	−243.72	25.53	−25.23
Free CO	271.00	−270.70	0.30	0.00

a) All the values are given in ppm. b) Reference substance is free CO.

^{13}C Magnetic Shielding Constants for $M(CO)(NH_3)_3$. Table 6 shows molecular geometry parameters of $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+}). The molecular structure of $M(CO)(NH_3)_3$ is illustrated in Figure 4. Since no experimental values for these molecules are available, we used these structures to calculate ^{13}C magnetic shielding constants.

Table 7 shows the calculation results of ^{13}C nuclear magnetic constants and the chemical shifts. The lower field shifts were observed for $M = Cr^{2+}$ and Fe^{2+}, and the higher field shifts for $M = Cu^{+}$ and Zn^{2+} compared to free CO. These results are in accordance with the experiment tendency.[28] The diamagnetic terms are almost constant for all complexes. On the other hand, the paramagnetic terms change greatly and are the origin of the chemical shifts, similarly to the molecules in the previous section.

MO contribution analysis of the paramagnetic shielding constants is shown in Table 8. There is little substantial difference in the carbonyl MO contributions between the molecules. On the other hand, the contributions of the metal atom changes are variant to change in the total shielding constants and are expected to be the origin of the chemical shifts in these systems. The contributions of the dπ and dσ orbitals are the largest for Cr^{2+}. However, they decrease for Fe^{2+}, and are very small values for Cu^+ and Zn^{2+}. These changes would be attributed to difference in the electron configuration of each metal. From eq 4, σ(para) for these systems is approximately represented as

$$\sigma(\text{para})_{\mathrm{N}tu} = \frac{e^2\mu_0}{2m_e^2} \sum_{\mathit{all}\ d\to d\ \mathit{transitions}} \frac{\langle 0|\hat{L}_t|d\to d\rangle\langle d\to d|\dfrac{\hat{L}_{\mathrm{N}u}}{r_{\mathrm{N}}^3}|0\rangle}{E_0 - E_{d\to d}} \tag{8}$$

The contributions through the excitations other than the d–d transitions can be ignored because they have higher energies, i.e., large denominators compared to the d–d transitions. Equation 8 means that the magnitude of σ(para) is associated with the excitation energy of the d–d transitions. Figure 5 shows electron configurations of the d orbitals for each metal ion. For Cr^{2+}, the d electrons are accommodated to only the dπ orbitals, and the dσ orbital is the LUMO. The energy gap between the dπ and dσ orbitals was calculated to be 14.7 eV. On the other hand, the d electrons occupy the dπ and dσ orbitals for Fe^{2+}. The energy difference between the dσ and dδ (LUMO) orbitals was 16.0 eV. Taking eq 8 into account, the magnitude of the σ(para) for the Cr complex is expected to be larger than that for the Fe complex. Furthermore, this trend is supported in terms of the difference of the angular momentum quantum number $\Delta\Lambda$ along the principal axis. The $\Delta\Lambda$ between the dσ and dδ orbitals is 2, while that between the dπ and dσ orbitals is 1. Therefore, the magnetic transition from the dσ to dδ orbitals for the Fe complex will become small compared to the dπ–dσ transition for the Cr complex. For Cu^+ and Zn^{2+}, no d–d transitions can occur because all the d orbitals are occupied, and therefore, the values of σ(para) are expected to be very small.

Table 8. MO Contributions to the Paramagnetic Shielding Constants for $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^+, and Zn^{2+})[a)]

		Cr^{2+}	Fe^{2+}	Cu^+	Zn^{2+}	Free CO
CO	σ	−269.37	−230.08	−237.50	−202.14	−253.43
	π	−20.80	−14.06	−14.96	−13.41	−17.24
	Total	−290.17	−244.14	−252.46	−215.55	−270.67
M	dπ	−148.22	−44.80	−10.92	−1.37	
	dσ	0.00	−35.83	20.47	−22.83	
	dδ	0.00	0.00	−0.60	0.24	
	Total	−148.22	−80.63	8.95	−23.96	
$(NH_3)_3$		−5.15	−0.84	−1.14	−4.17	
Grand total		−443.13	−325.55	−244.72	−243.72	−270.70

a) All the values are given in ppm.

Table 9 shows AO contribution analysis of the paramagnetic shielding constants. Obviously, the shielding is mainly caused by the 2p orbitals of the carbonyls. As we see Table 8 again, the total σ(para) values ascribed to the CO ligands are larger than those of the metal d orbitals. However, the degree of the change in the σ(para) strongly depends on the d orbitals of metal as discussed above. Considering these results together, we suggest that the origin of the chemical shift for these complexes is attributed to the MOs with the slightly donating character from the metal d orbital to the CO π^* orbital, as showed in Figure 6.

Conclusion

Calculations and electronic analyses of NMR chemical shifts for $Mn(CO)_5X$ (X = H, F, Cl, Br, I, and CH_3) and $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^+, and Zn^{2+}) were performed. Basis set enlargements for the first molecular group dramatically improved the results compared with the previous study, and the calculated chemical shifts were in good agreement with the experimental values. It was shown that

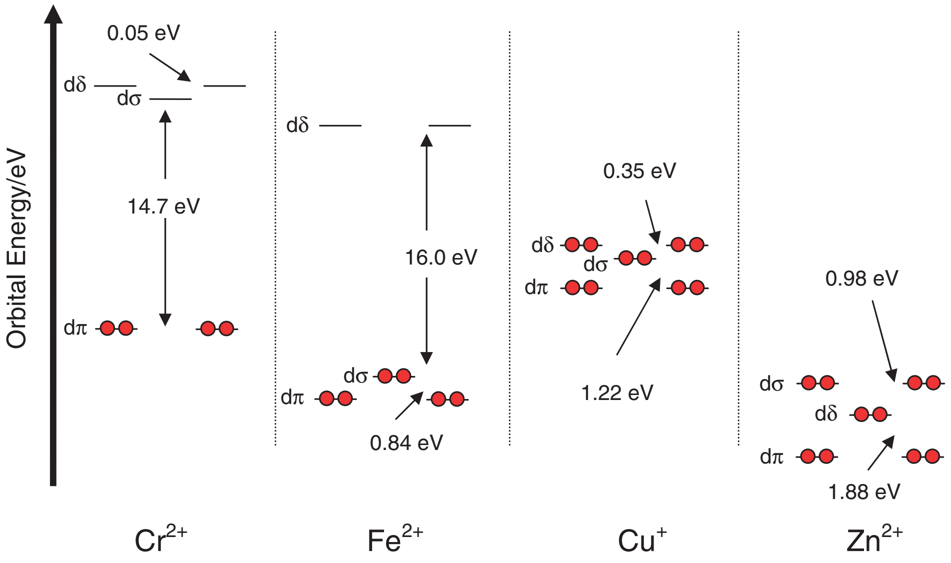

Figure 5. Electron configurations of the metal d orbitals for $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^+, and Zn^{2+}).

Table 9. AO Contributions to the Paramagnetic Shielding Constants for $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+})[a)]

		Free CO	Co^{2+}	Fe^{2+}	Cu^{+}	Zn^{2+}
CO	s	11.59	4.39	3.95	10.20	9.26
	$p_x + p_y$	−1.34	−97.87	177.36	−22.49	−3.59
	p_z	−278.16	−376.50	−372.46	−237.50	−251.28
	p total	−279.50	−474.36	−195.10	−259.99	−254.87
M	s		0.00	0.00	0.00	0.00
	$p_x + p_y$		−3.11	−3.34	−0.29	−0.40
	p_z		0.12	−0.44	−0.15	0.34
	d		6.12	−43.96	2.55	−0.55
$(NH_3)_3$			4.51	2.05	2.86	0.14
Grand total		−270.70	−443.13	−325.55	−244.72	−243.72

a) All the values are given in ppm.

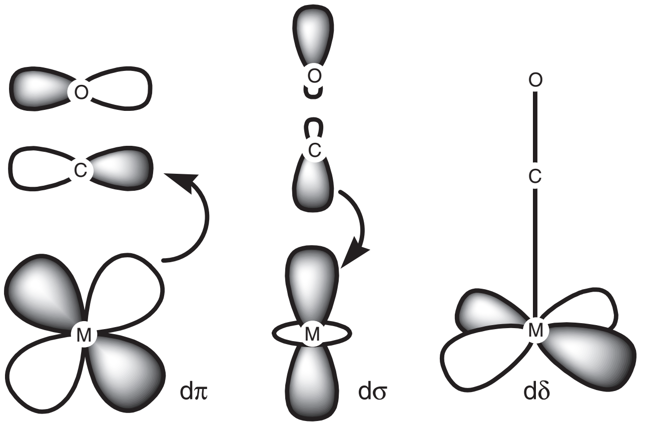

Figure 6. The d orbitals of M and π orbitals of CO in $M(CO)(NH_3)_3$ ($M = Cr^{2+}$, Fe^{2+}, Cu^{+}, and Zn^{2+}).

the d–d transitions of the Mn atom contributed mainly to the ^{55}Mn chemical shift. The present result supported the traditional analysis. The DKH2 calculations improved the values of the shielding constants further in spite of the fact that only the SFR terms were considered in this study. Also for the second molecular group, we reproduced the experimental tendency of the shielding constants. We propose that the origin of the chemical shifts for $M(CO)(NH_3)_3$ is due to the difference in the electron configuration of the metal ions. The larger σ(para) for $M = Cr^{2+}$ compared to $M = Fe^{2+}$ is accounted for in terms of the difference of the angular momentum quantum number and the energy gap between the occupied and unoccupied d orbitals. Especially for $M = Cu^{+}$ and Zn^{2+}, the d orbitals are fully occupied, and the σ(para) values become very small for these complexes.

This work was supported by the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists. The authors thank Dr. Hiroshi Fujii at the Institute of Molecular Science (IMS) for his valuable discussion and comments.

References

1 J. Mason, *Multinuclear NMR*, PLENUM, **1987**.

2 H. Nakatsuji, K. Kanda, K. Endo, T. Yonezawa, *J. Am. Chem. Soc.* **1984**, *106*, 4653.

3 K. Kanda, H. Nakatsuji, T. Yonezawa, *J. Am. Chem. Soc.* **1984**, *106*, 5888.

4 I. Bertini, R. S. Drago, in *The Coordination Chemistry of Metalloenzymes*, ed. by C. Luchinat, D. Reidel Publishing Company, Dordrecht, Holland, **1983**.

5 M. Hada, *J. Am. Chem. Soc.* **2004**, *126*, 486.

6 M. Kujime, H. Fujii, *Tetrahedron Lett.* **2005**, *46*, 2809.

7 L. L. Foldy, S. A. Wouthuysen, *Phys. Rev.* **1950**, *78*, 29.

8 N. F. Ramsey, *Phys. Rev.* **1950**, *77*, 567.

9 N. F. Ramsey, *Phys. Rev.* **1950**, *78*, 699.

10 N. F. Ramsey, *Phys. Rev.* **1951**, *83*, 540.

11 N. F. Ramsey, *Phys. Rev.* **1952**, *86*, 243.

12 C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618.

13 D. Feller, *J. Comput. Chem.* **1996**, *17*, 1571.

14 K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045.

15 M. Douglas, N. M. Kroll, *Ann. Phys.* **1974**, *82*, 89.

16 B. A. Hess, *Phys. Rev. A* **1985**, *32*, 756.

17 B. A. Hess, *Phys. Rev. A* **1986**, *33*, 3742.

18 C. C. Ballard, M. Hada, H. Kaneko, H. Nakatsuji, *Chem. Phys. Lett.* **1996**, *254*, 170.

19 R. Poirier, R. Kari, I. G. Csizmadia, *Handbook of Gaussian Basis Sets*, Elsevier, **1985**.

20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision B.01*, Gaussian, Inc., Pittsburgh PA, **2003**.

21 E. A. McNeill, F. R. Scholer, *J. Am. Chem. Soc.* **1977**, *99*, 6243.

22 P. T. Greene, R. F. Bryan, *J. Chem. Soc., A* **1971**, 1559.

23 R. G. Kidd, R. J. Goodfellow, in *NMR and the Periodical Table*, ed. by R. K. Harris, B. E. Mann, Academic Press, NY, **1978**.

24 M. Barysz, A. J. Sadlej, *J. Chem. Phys.* **2002**, *116*, 2696.

25 H. Nakatsuji, *Chem. Phys. Lett.* **1978**, *59*, 362.

26 H. Nakatsuji, *Chem. Phys. Lett.* **1979**, *67*, 329.

27 H. Tanimura, M. Hada, *J. Comput. Chem., Jpn.* **2004**, *3*, 153.

28 H. Fujii, private communication.