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Theoretical Study of Metal NMR Chemical Shifts. Selenium Compounds[#]

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The ^{77}Se chemical shifts of nine selenium compounds, SeRR′ (R, R′=H, Me, Et, Ph, SiH_3, GeH_3), are theoretically investigated by *ab initio* Hartree–Fock/finite perturbation method. The calculated values agree well with the experimental values. The Se chemical shift is dominated by the Se valence 4p AO contribution to the paramagnetic term, and shows a parallelism with the 4p-hole population and the net charge of the central Se atom. The Se chemical shift moves downfield as an increase of the hole in the 4p orbitals, and therefore, as an increase in the electron-withdrawing ability of the ligands attached to the selenium atom.

A lot of experimental data have been accumulated in recent year for transition-metal NMR chemical shifts.[1—4] However, the knowledge on the electronic origin of the chemical shifts is still limited. For understanding the trend and the meaning of the observed values, systematic theoretical study is necessary.

The purpose of this series of studies on the metal NMR chemical shift[5—18] is to clarify the electronic origins and mechanisms of the metal chemical shifts by analyzing the *ab initio* calculational results and thus to give a guiding concept to experimental chemists which is useful for understanding the trends in metal chemical shifts. We have investigated the complexes of the metals Cu, Ag, Zn, and Cd[8,9] whose electronic configurations are represented as $d^{10}s^{1-2}p^0$, the complexes of Sn[10,11] and Ge[12] which have the configurations $d^{10}s^2p^2$, the complexes of Ti,[13] Nb,[14] Mn,[15] and Mo[16,17] which have the configuration $d^{2-5}s^{1-2}$, and the complexes of Ga and In[18] which have the configuration $d^{10}s^2p^1$. Recently, Tossell[19,20] and Barfield et al.[21,22] have also studied the Zn and Mo chemical shifts, respectively. Our studies on the electronic mechanisms of the metal chemical shifts have been reviewed recently.[7]

We have classified the metal complexes into four groups, and revealed that the mechanisms of the metal chemical shifts are the intrinsic properties of the metal atoms and are mainly determined by the electronic configurations of the central metal atoms: They depend on the occupations of the valence nd and $(n+1)$p subshells. For the Cu, Ag, Zn, and Cd complexes, the d-hole or p-electron mechanism is the origin of the metal chemical shift. For the Si, Ge, and Sn compounds, the p-excitation mechanism is important. For the complexes of the Ti, Nb, Mn, and Mo atoms, which have open d subshells, the d-excitation mechanism is dominant and the shifts are parallel with the inverse of the magnetically allowed d-d* excitation energies of the complexes. The chemical shifts of the Ga and In complexes are unique in that they are mainly due to the diamagnetic term and therefore mainly depend on the structural factors, like bond distance and ligand nuclear charge, rather than the electronic factors.

In this paper, we report *ab initio* molecular orbital (MO) calculations of ^{77}Se NMR chemical shifts for nine selenium compounds, SeRR′ (R, R′=H, Me, Et, Ph, SiH_3, GeH_3), and clarify the electronic origin and the mechanism of the Se chemical shifts. We note that the valence electron configuration of the ground state Se atom is $4s^24p^4$.

Method of Calculations

The Se magnetic shielding constant σ and the Se chemical shift δ are calculated by the finite perturbation method.[23—29] The detail of the method was described in the first paper of this series.[8] Calculations of the unperturbated Hartree–Fock wave function were carried out with the HONDO7 program.[30] The gauge origin is placed at the position of the Se atom.

The basis sets are taken from the book of Huzinaga et al.[31] The Se basis is (13s10p4d)/[6s5p1d] plus two polarization d-functions (ζ=0.144, 0.489). For H, C, Si, and Ge atoms, the basis sets are (4s)/[2s],[32] (7s4p)/[3s2p], (10s7p)/[4s3p], and (13s10p4d)/[5s4p1d], respectively.

The geometries of the Se complexes calculated in this paper are summarized in Table 1. They are basically the experimental geometries[33—35] except for those that are not known experimentally.

Correlation between Theory and Experiment

The calculated results of the Se nuclear magnetic shielding constant σ and the chemical shift δ are summarized in Table 2. The chemical shift is defined as the difference between the two magnetic shielding constant, that is

$$\delta = \sigma(\text{ref}) - \sigma, \qquad (1)$$

where σ (ref) denotes the magnetic shielding constant of the reference compound, which is $SeMe_2$ in this study. The shielding constant is the sum of the diamagnetic term σ^{dia} and the paramagnetic term σ^{para},

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}}, \qquad (2)$$

[#] This paper is dedicated to the memory of the late Professor Hiroshi Kato who has taught a lot to H. N. about quantum chemistry and about a research life.

Table 1. Geometries of the Se Compounds[a,b]

Molecule	Symmetry	Se–A	Se–H	C–C	A–H	∠ASeA	∠CSeH	∠HSeH	∠SeCC	∠SeAH	∠CCH	∠HCH	Torsion
$SePh_2$ [i]	C_2	1.920		1.390	1.080	106.00							38.00
$SeEt_2$ [j]	C_{2v}	1.943		1.539	1.100	96.18			113.60	108.80	110.40		
MeSeEt[g]	C_s	1.949(Me)		1.528	1.089[c]	98.03			110.96	107.36[c]			
					1.088[d]					110.51[d]			
		1.961(Et)			1.089					107.97	110.27[c]		
					1.092[c]						111.31[d]		
					1.091[d]								
PhSeH[g]	C_1	1.920	1.465	1.390	1.080		96.50						
$SeMe_2$	C_{2v}	1.945			1.088[c]	96.32				105.00[c]		109.87[e]	
					1.096[d]					110.33[d]		110.62[f]	
MeSeH	C_s	1.959	1.473		1.088		96.45					110.00	
SeH_2	C_{2v}		1.460					90.90					
$Se(GeH_3)_2$	C_{2v}	2.344			1.563	94.60				109.47[h]			
$Se(SiH_3)_2$	C_{2v}	2.274			1.516	96.60				108.50			

a) Length in angstrom and angle in degree. b) A is the atom directry bonded to the Se atom and is either C, Si, or Ge. c) H is on the σ plane. d) H is out of the σ plane. e) Both H atoms are out of the σ plane. f) One H atom is on the σ plane. g) Calculated and optimised values, since the experimental values are not available. h) Tetrahedral angle is assumed. i) Ref. 34. j) Ref. 35.

Table 2. Calculated Se Magnetic Shielding Constants and Their Breakdown into Core and Valence MO Contributions (ppm)

Molecule	Diamagnetic term σ^{dia}				Paramagnetic term σ^{para}				Magnetic Shielding σ constant	Chemical shift δ	
	Core	Valence	Total	Shift	Core	Valence	Total	Shift	Total	Calcd	Exptl
$SePh_2$	2998	235	3232	−161	−65	−1741	−1806	609	1426	448	402[a]
$SeEt_2$	2957	161	3119	−47	−44	−1391	−1435	238	1684	190	233[a]
MeSeEt	2951	145	3095	−24	−38	−1210	−1248	51	1847	27	108[a]
PhSeH	2961	155	3116	−45	−40	−1192	−1232	35	1884	−10	152[a]
$SeMe_2$	2944	127	3071	0	−36	−1162	−1197	0	1874	0	0 0
MeSeH	2935	102	3037	34	−29	−1043	−1072	−125	1965	−91	−116[a] −155[b]
SeH_2	2925	78	3003	68	−22	−863	−884	−313	2119	−245	−226[a] −345[b]
$Se(GeH_3)_2$	3149	113	3262	−191	−26	−729	−755	−443	2508	−634	−612[a]
$Se(SiH_3)_2$	3008	115	3122	−51	−20	−716	−737	−460	2385	−511	−666[a]

a) Liquid phase value. b) Gas phase value (Ref. 37).

where σ^{dia} and σ^{para} are the first-order and second-order terms, respectively, in the perturbation theory.[36]

The correlation between the theoretical and experimental values of the Se chemical shifts are shown in Fig. 1. Our calculated results compare well with the experimental values. Most experimental values are obtained by liquid phase experiment. Ellis et al. reported the gas phase measurement for the chemical shifts of SeH_2, MeSeH, $SeMe_2$, and reported the chemical shifts to be −344.75 and −154.67 ppm for SeH_2 and MeSeH, respectively.[37] These values are larger than those due to the liquid phase values, −226 and −116 ppm, respectively. Figure 1 includes the results of both measurements. For $Se(SiH_3)_2$ and $Se(GeH_3)_2$, the order of the calculated values disagree with the one of the experimental values, though the order is reproduced in the paramagnetic term.

The absolute shielding constants of the Se compounds were obtained from the measurement of the spin-rotation constant by Jameson et al.[38] They are 2280 and 2069 ppm for SeH_2 and $SeMe_2$, respectively. Our results are 2119 and 1874 ppm, respectively. The values obtained by the *ab initio* calculations of Tossell et al. for SeH_2 is 2163.2 ppm.[39] The values calculated by the GIAO (gauge invariant atomic orbital) method[40—42] by Ellis et al. is 2133—2151 and 1932—2025 ppm, respectively, with different basis sets.[37] They pointed out a relatively large basis set dependence of the calculated values, which is now under study in our laboratory.

Mechanism of the Se Chemical Shift

The nuclear magnetic shielding constant consists of two contributions; the diamagnetic term σ^{dia} and the paramagnetic term σ^{para}. We analyze the calculated shielding constants into these contributions and the results are shown in Table 2. We see that the paramagnetic term is much more important than the diamagnetic term.

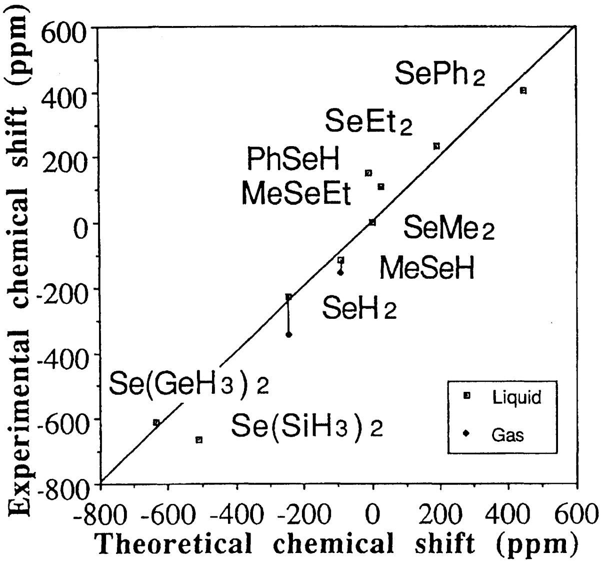

Fig. 1. Correlation between the calculated and experimental values of the Se chemical shifts of the Se compounds.

The diamagnetic and paramagnetic terms are further divided into core and valence molecular orbital (MO) contributions,[8] and the results are shown in Table 2. Here, the valence MOs are the higher occupied MOs composed of the Se 4s and 4p AOs and the ligand *ns* and *np* AOs. We observe that the valence MO contribution to the paramagnetic term is dominant for the Se chemical shifts. This result is natural since the chemical shift reflects the change in the electronic structure induced by the ligand substitution. We note that this is the change of the valence molecular orbital near the Se nucleus, as examined in some details in Ref. 8.

The paramagnetic and diamagnetic contributions are further analyzed into atomic orbital (AO) contributions,[8] and the results are shown in Tables 3 and 4, respectively. These tables show the Se AO contributions and the ligand contributions.

a. Paramagnetic Term. Referring to Table 3, we see that the Se p orbital contribution is predominant for the paramagnetic term: Both the absolute values and the changes are predominantly large. The s AO contribution is identically zero because the s AO does not have an angular momentum. The d-orbital contribution is small since the d orbitals of Se constitute the inner core. The ligand contributions are also small though they can not be ignored for the phenyl (Ph) and ethyl (Et) ligands. We thus conclude that the valence 4p contributions of the Se atom is the dominant origin of the Se chemical shift. The changes in the Se 4p electronic state induced by the ligand substitution is measured by the NMR technique as the Se chemical shift.

To understand the nature of the p AO contribution, we made the Mulliken AO population analysis for Se and the result is summarized in Table 5. We understand that the net charge on Se is influenced by the Se 4p population: an approximate linear relation is seen in Fig. 2 between the Se net charge and the 4p population. The Se 4s and 4d populations show only small changes and their changes are not monotonous. These results show that the electron-withdrawing ability increases in the order of $SiH_3 < GeH_3 < H < Me < Et < Ph$. This order agrees with the order of the atomic electronegativity, $Si < Ge < H < C$, and the order of the empirical group negatively, $SiH_3 < H < Me < Ph$, summarized by Wells.[43]

Figure 3 shows the dependence of the paramagnetic shielding constant on the Se 4p AO population. The paramagnetic shielding constant increases as the decrease of the Se 4p electron population, that is, as the increase of the 4p-hole population, due to the electron-withdrawing ligands. From this fact, we conclude that the Se chemical shift is due to the p-hole mechanism. The Se chemical shift moves downfield as an increase of the electron-withdrawing ability of the ligands.

McFarlane et al. pointed out experimentally that an increase in the electron-withdrawing ability of the ligands attached to the selenium atom should result in a negative increase of the selenium shielding.[44] In Fig. 4 we show the dependence of the paramagnetic shielding constant on the Se net charge of the Se compounds. The paramagnetic shielding constants negatively increase as an increase of the Se net charge. Our theoretical results thus reproduce the experimental trend.

We note that the dependence of the paramagnetic term on the Se 4p-hole population, rather than the 4p-electron population, is due to the fact that the 4p occupation of the Se atom is larger than three, a half

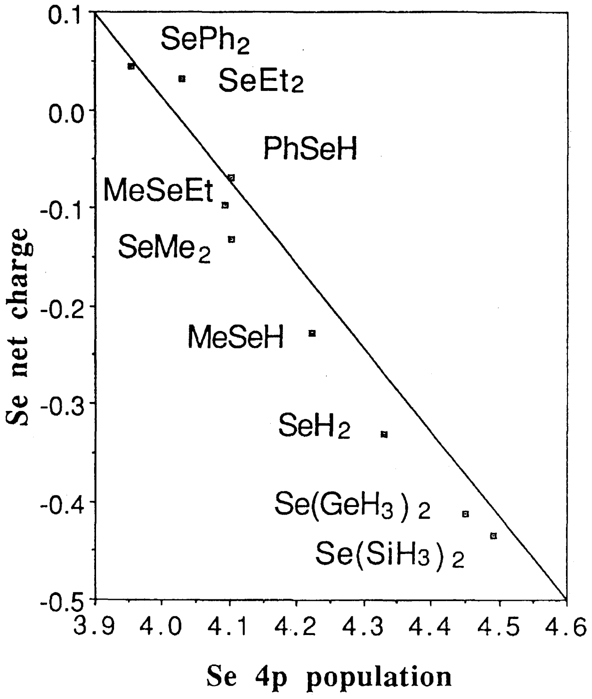

Fig. 2. Correlation between the net charge and the 4p population of the Se atom.

Table 3. AO Contributions to the Se Paramagnetic Term σ^{para} (ppm)

Molecule	Se				Ligand							σ^{para}
	s	p	d	Total	Ph	Et	Me	H	SiH_3	GeH_3	Total	Total
$SePh_2$	0	−1687	−24	−1711	−47						−95	−1806
$SeEt_2$	0	−1369	−21	−1391		−22					−44	−1435
MeSeEt	0	−1187	−24	−1211		−25	−13				−38	−1248
PhSeH	0	−1165	−22	−1188	−46			1.8			−44	−1232
$SeMe_2$	0	−1146	−26	−1172			−13				−25	−1197
MeSeH	0	−1042	−21	−1062			−12	2.4			−9.8	−1072
SeH_2	0	−873	−17	−890				2.8			5.5	−884
$Se(GeH_3)_2$	0	−729	−8	−737						−8.9	−18	−755
$Se(SiH_3)_2$	0	−713	−10	−723					−6.9		−14	−737

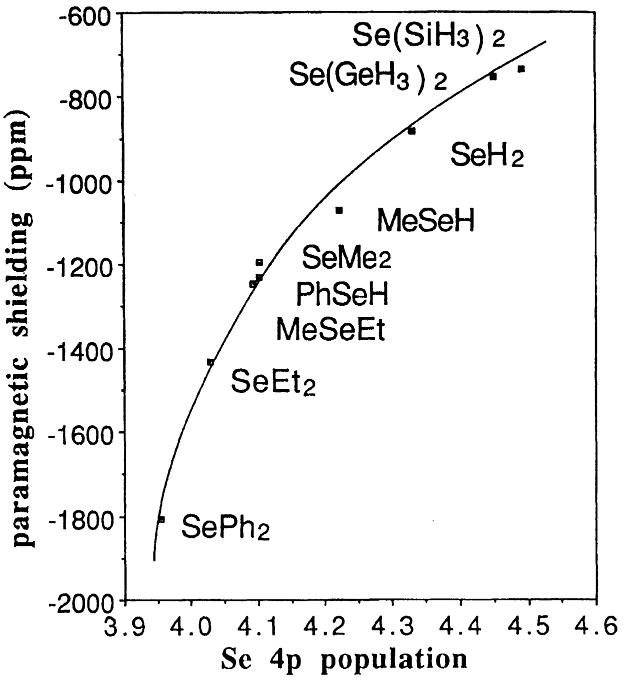

Fig. 3. Correlation between the Se paramagnetic shielding constant and the Se 4p population.

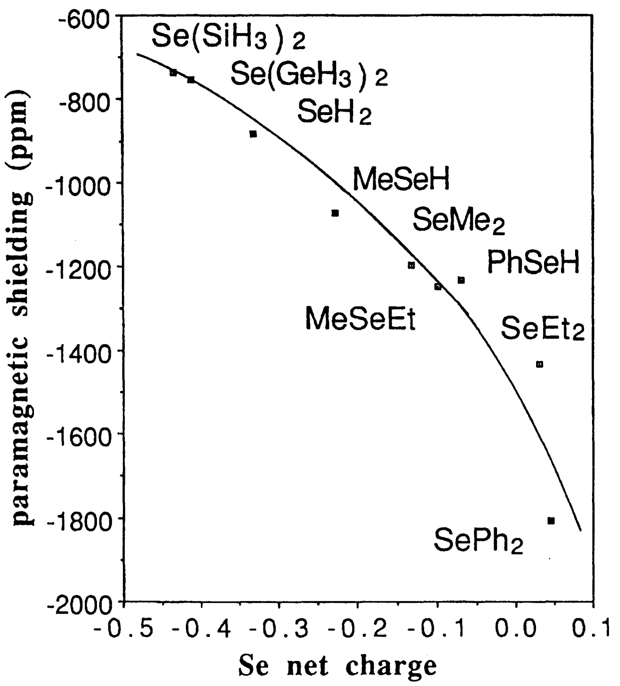

Fig. 4. Correlation between the Se paramagnetic shielding constant and the Se net charge.

of the full occupation. Further, the dependence is not linear, but approximately parabolic. These facts are understood from the equation derived previously (Eq. 9 of Ref. 11) for the analysis of the Sn chemical shifts. We also refer to the equation derived by Karplus and Das.[45)]

We show in Fig. 5 the orbital energy levels of the Se compounds, SeR_2 (R=H, Me, Et). The symmetries and the natures of the MOs are given in the figure and the numbering is for the valence MOs. We see that the orbital energy differences between higher occupied and lower vacant MOs decreases as the ligand changes from H to Me to Et. Assuming that the excitation energy is parallel to the orbital energy difference, we understand that the change in the excitation energy is also parallel to the change in the paramagnetic term. Cullen et al.[46)] and Poleschner et al.[47)] have pointed out from the experimental analysis that the Se chemical shifts of the compounds having C=Se double bond correlate linearly with the inverse of the excitation energy of the n→π* transition.

Therefore, we think that both of the excitation energy and the density factor are important for the Se chemical shifts.

b. Diamagnetic Term. The diamagnetic term is a minor origin of the chemical shift, as seen from Table 2, but its analysis would clarify the physical meaning of the diamagnetic term. Table 4 shows that the Se atom contribution is almost constant for all the complexes studied here and so the shift in the diamagnetic term is entirely due to the ligand contribution.

It is almost an established fact that the diamagnetic term is determined solely by the structural factor rather than the electronic factor. Flygare and Goodisman re-

Table 4. AO Contributions to the Se Diamagnetic Term σ^{dia} (ppm)

Molecule	Se				Ligand							σ^{dia}
	s	p	d	Total	Ph	Et	Me	H	SiH_3	GeH_3	Total	Total
$SePh_2$	1558	1073	359	2990	121						242	3232
$SeEt_2$	1558	1074	359	2991		64					128	3119
MeSeEt	1558	1074	359	2991		64	40				104	3095
PhSeH	1558	1073	360	2991	120			5.7			126	3116
$SeMe_2$	1558	1074	359	2991			40				80	3071
MeSeH	1558	1074	359	2992			40	5.7			45	3037
SeH_2	1557	1075	360	2992				5.6			11	3003
$Se(GeH_3)_2$	1560	1076	357	2993						135	269	3262
$Se(SiH_3)_2$	1560	1076	357	2994					64		129	3122

Table 5. Mulliken AO Population Analysis for Se

Molecule	4s	4p	4d[a)]	Se net charge
$SePh_2$	1.913	3.954	0.194	0.045
$SeEt_2$	1.945	4.029	0.100	0.031
MeSeEt	1.937	4.092	0.174	−0.098
PhSeH	1.859	4.102	0.213	−0.069
$SeMe_2$	1.944	4.103	0.179	−0.132
MeSeH	1.897	4.221	0.214	−0.228
SeH_2	1.846	4.331	0.261	−0.331
$Se(GeH_3)_2$	2.150	4.451	−0.084	−0.412
$Se(SiH_3)_2$	2.149	4.492	−0.100	−0.434

a) d-polarization function.

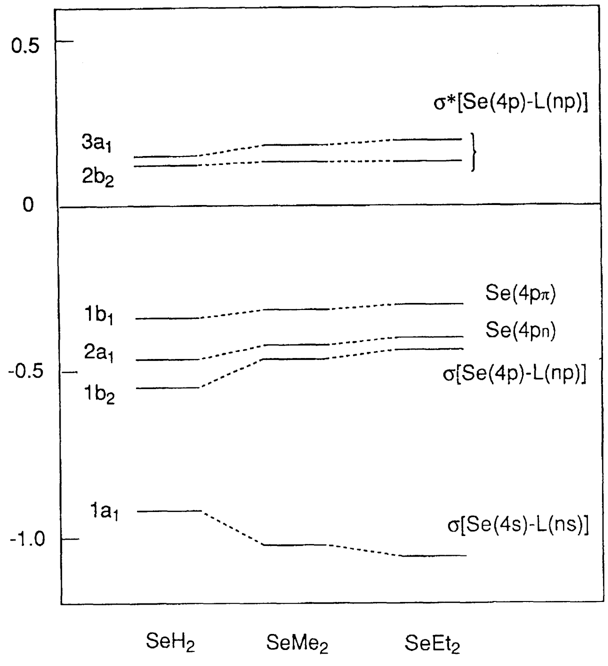

Fig. 5. Orbital energy diagram for SeR_2 (R=H, Me, Et).

ported that the diamagnetic term is expressed to a good approximation as[48)]

$$\sigma^{\mathrm{dia}} = \sigma^{\mathrm{dia}}(\text{free atom M}) + \frac{e^2}{3mc^2}\sum_{\alpha}\frac{Z_\alpha}{r_\alpha} \qquad (3)$$

where σ^{dia} (free atom M) is the diamagnetic constant for the free atom M, α runs over all nuclei except for M, Z_α is the atomic number of the nuclei α, and r_α is the distance between M and α. In our previous paper, we showed that the diamagnetic term is expressed in the Pascal-rule-like formula,[8)]

$$\sigma^{\mathrm{dia}} = \sigma^{\mathrm{dia}}(\mathrm{Se}) + \sum_{\mathrm{L}} n_{\mathrm{L}}\sigma^{\mathrm{dia}}(\mathrm{L}) \qquad (4)$$

which is derived from Eq. 3 if we neglect variations of the M–L bonds. In Eq. 4, σ^{dia} (Se) is the sum of the Se AO contributions, and σ^{dia} (L) and n_{L} denotes the ligand contribution and the number of the ligand L, respectively.

In this study, the average calculated value of σ^{dia} (Se) is 2991.6 ppm, which is close to the free atom value given by Malli and Froese,[49)] 2998.4 ppm. Thus, as understood from Eq. 4, the diamagnetic contribution to the chemical shift is due to the ligand contributions. As seen from Eq. 3, the ligand contribution is relatively large for GeH_3 and phenyl ligands since they have a heavy element and a number of nuclei, respectively.

Conclusion

In this paper, we have investigated the electronic origin of the Se NMR chemical shifts for the nine Se compounds, SeRR′ (R, R′=H, Me, Et, Ph, SiH_3, GeH_3) by the *ab initio* Hartree–Fock/finite perturbation method. The results are as follows:

(1) The Se chemical shift is mainly determined by the Se valence 4p contribution to the paramagnetic term.

(2) The Se chemical shift is due to the p-hole mechanism. The angular momentum of the valence 4p holes induced by the applied magnetic field is the origin of the paramagnetic term.

(3) The Se chemical shift moves downfield, therefore, as the electron-withdrawing ability of the ligand increases, since then the 4p-hole population increases.

(4) The diamagnetic contribution is small for the Se chemical shifts.

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References

1) "NMR and the Periodic Table," ed by R. K. Harris and B. E. Mann, Academic, London (1978).

2) "Multinuclear NMR," ed by J. Mason, Plenum, New York (1987).

3) J. Mason, *Chem. Rev.*, **87**, 1299 (1987).

4) M. Munakata, S. Kitagawa, and S. Shibata, "Introduction to the Multinuclear NMR Approach to the State Analysis," Kodansya Scientific, Tokyo (1991)(in Japanese).

5) H. Nakatsuji, in "Comparisons of Ab Initio Quantum Chemistry with Experiment: State of the Art," ed by R. J. Bartlett, Reidel, Dordrecht, Netherlands (1985).

6) H. Nakatsuji, in "Modern Chemistry, Supplement 11, High Resolution NMR Spectroscopy," ed by H. Saito and I. Morishima, Tokyo Kagaku Dojin, Tokyo (1987), p. 237 (in Japanese).

7) H. Nakatsuji, in "Nuclear Magnetic Shieldings and Molecular Structure," ed by J. A. Tossell, Kluwer Academic Pub., Hague (1993), p. 263.

8) H. Nakatsuji, K. Kanda, K. Endo, and T. Yonezawa, *J. Am. Chem. Soc.*, **106**, 4653 (1984).

9) H. Nakatsuji, T. Nakao, and K. Kanda, *Chem. Phys.*, **115**, 25 (1987).

10) H. Nakatsuji, T. Nakao, and T. Inoue, *Chem. Phys. Lett.*, **167**, 111 (1990).

11) H. Nakatsuji, T. Inoue, and T. Nakao, *J. Phys. Chem.*, **96**, 7953 (1992).

12) H. Nakatsuji and T. Nakao, *Int. J. Quantum Chem.*, submitted.

13) H. Nakatsuji and T. Nakao, *Chem. Phys. Lett.*, **167**, 571 (1990).

14) M. Sugimoto, M. Kanayama, and H. Nakatsuji, *J. Phys. Chem.*, **96**, 4375 (1992).

15) K. Kanda, H. Nakatsuji, and T. Yonezawa, *J. Am. Chem. Soc.*, **106**, 5888 (1984).

16) H. Nakatsuji and M. Sugimoto, *Inorg. Chem.*, **29**, 1221 (1990).

17) H. Nakatsuji, M. Sugimoto, and S. Saito, *Inorg. Chem.*, **29**, 3095 (1990).

18) M. Sugimoto, M. Kanayama, and H. Nakatsuji, *J. Phys. Chem.*, **97**, 5868 (1993).

19) J. A. Tossell, *Chem. Phys. Lett.*, **169**, 145 (1990).

20) J. A. Tossell, *J. Phys. Chem.*, **95**, 366 (1991).

21) J. E. Combariza, J. H. Enemark, M. Barfield, and J. C. Facelli, *J. Am. Chem. Soc.*, **111**, 7619 (1989).

22) J. E. Combariza, M. Barfield, and J. H. Enemark, *J. Phys. Chem.*, **95**, 5463 (1991).

23) H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.*, **43**, S34 (1965).

24) H. D. Cohen, *J. Chem. Phys.*, **43**, 3558 (1965).

25) H. D. Cohen, *J. Chem. Phys.*, **45**, 10 (1966).

26) J. A. Pople, J. W. McIver, and N. S. Ostlund, *Chem. Phys. Lett.*, **1**, 465 (1967).

27) J. A. Pople, J. W. McIver, and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960 (1968).

28) R. Ditchfield, D. P. Miller, and J. A. Pople, *J. Chem. Phys.*, **53**, 613 (1970).

29) H. Nakatsuji, K. Hirao, and T. Yonezawa, *Chem. Phys. Lett.*, **6**, 541 (1970).

30) M. Dupuis, J. D. Watts, H. O. Villar, and G. J. B. Hurst, "Program Library HONDO7 (No. 1501)," Computer Center of Institute for Molecular Science, (1989).

31) S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, "Gaussian Basis Sets for Molecular Calculations," Elsevier, Amsterdam (1984).

32) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).

33) "Landolt–Börnstein," ed by K. -H. Hellwege and A. M. Hellwege, Springer-Verlag, Berlin, Vol. II7 and II15.

34) V. Galasso, G. D. Alti, and A. Bigotto, *Tetrahedron*, **27**, 6151 (1971).

35) H. Matsuura and H. Murata, *Bull. Chem. Soc. Jpn.*, **52**, 3515 (1979).

36) N. F. Ramsey, *Phys. Rev.*, **77**, 567 (1950); **78**, 699 (1950); **83**, 540 (1951); **86**, 243 (1952).

37) P. D. Ellis, J. D. Odom, A. S. Lipton, Q. Chen, and J. M. Gulick, in "Nuclear Magnetic Shieldings and Molecular Structure," ed by J. A. Tossell, Kluwer Academic Pub., Hague (1993), p. 539.

38) C. J. Jameson and A. K. Jameson, *Chem. Phys. Lett.*, **135**, 254 (1987).

39) J. A. Tossell and P. Lazzeretti, *J. Magn. Reson.*, **80**, 39 (1988).

40) F. London, *J. Phys. Radium*, **8**, 397 (1937).

41) R. Ditchfield, *Mol. Phys.*, **27**, 789 (1974).

42) K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.*, **112**, 8251 (1990).

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

44) W. McFarlane and R. J. Wood, *J. Chem. Soc., Dalton Trans.*, **1972**, 1397.

45) M. Karplus and T. P. Das, *J. Chem. Phys.*, **34**, 1683 (1961).

46) E. R. Cullen, F. S. Guziec, C. J. Murphy, T. C. Wong, and K. K. Andersen, *J. Am. Chem. Soc.*, **103**, 7055 (1981).

47) H. Poleschner, R. Radeglia, and H. Meyer, *Org. Magn. Reson.*, **22**, 480 (1984).

48) W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, **49**, 3122 (1968).

49) G. Malli and C. Froese, *Int. J. Quantum Chem., Symp.*, **1**, 95 (1967).