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ELECTRONIC MECHANISM IN CADMIUM CHEMICAL SHIFT

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Cadmium chemical shifts are studied theoretically by the ab initio molecular orbital method. The compounds studied are $CdMe_2$, CdMeEt, $CdEt_2$,CdMe(OMe), $Cd(OMe)_2$, CdMe(SMe) and $Cd(SMe)_2$. The calculated values of the Cd chemical shifts agree excellently with the experimental values, showing quantitative reliability of the theoretical method used in this paper. The cadmium chemical shift is mainly due to the p mechanism in the paramagnetic term. The contribution of the d mechanism is small. Therefore, the metal chemical shift is proportional to the π-electron donating ability of the ligands. The diamagnetic contribution, which is determined solely by a structural factor, is small for the chemical shift. The difference between the methyl and ethyl ligands is attributed partly to the p mechanism (paramagnetic) and partly to the structural factor (diamagnetic). The outer d orbitals of the sulfur in the SMe ligand are unimportant for the Cd chemical shift.

1. Introduction

The understanding of the chemistry of compounds involving transition metals has been significantly advanced in this decade [1]. This is largely due to the knowledge of the electronic structures of organometallic compounds and metal complexes (see for example ref. [2]). The chemistry of transition metal complexes and organometallics is primarily distinguished by the involvement of d electrons, in comparison with the chemistry of the first-row atoms. It would be valuable if there was an experimental method that could clarify the role of the d electrons in chemical bonding in contrast to that of the s and p electrons. The nuclear magnetic resonance spectroscopy of metal nuclei [3–5] is one such method. This experiment observes a property which depends on the angular momentum of the electrons around the metal nucleus under considerations. Since the average values of the angular momentum of the electrons belonging to s, p and d orbitals are 0, 1 and 2, respectively, NMR experiments of metal nuclei give primarily information on the d electrons, secondary that of the p electrons, and that of the s electrons is projected out. Therefore, NMR spectroscopy is useful not only as a tool for analytical chemistry, but also for investigating the electronic structures of metal compounds and, especially, the role of the d electrons in the chemistry of transition metal compounds.

In this series of studies [6–8], we theoretically investigate *metal* chemical shifts in NMR spectroscopy with the ab initio molecular orbital theory. The purpose is twofold. One is to establish a reliable method for calculating metal chemical shifts of inorganic and organometallic compounds. The other is to elucidate the mechanism of the chemical shift based on the analysis of the calculated results. We want to give a guiding concept to experimental chemists which is useful for understanding and predicting the trends in metal chemical shifts. Although the electronic mechanisms of chemical shifts of the first-row nuclei are rather well understood, there seems to be no such electronic concept for the metal chemical shifts of the transition metal compounds, except for the one we have proposed previously [6–8].

The molecules we have studied so far are the Cu, Zn, Ag and Cd complexes [6], in which the

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metal atoms are characterized by the electronic configurations $d^{10}s^{1-2}p^0$ in their ground state, and the Mn complexes [7], in which the Mn atom has an open d subshell $d^5s^2p^0$ in its ground state. We have shown that the mechanism of the metal chemical shift is very different for these two classes of compounds because of the filled and half-filled nature of the valence d subshell [8].

For the Cu, Zn, Ag and Cd complexes, the p and d mechanisms are important as the origin of the metal chemical shift [6]. Fig. 1 is an illustration of these mechanisms. Because of the essentially closed-shell nature of the d subshell, the paramagnetic contribution of the p electrons donated to the metal becomes comparable to that of the d electrons. The d mechanism is due to the angular momentum of the hole produced in the valence d shell of the metal by electron-withdrawing ligands. (Type 1 and type 2 in fig. 1, will be explained later.) The p mechanism is due to the angular momentum of the electrons in the valence p orbitals of the metal transferred from electron-donating ligands. The electronic effect of the ligand is thus reversed for the p and d mechanisms. The relative importance of the p and d mechanisms is primarily determined by the atomic nature of the metal [6]; the p mechanism is more important than the d mechanism for the Zn and Cd complexes, the d mechanism is more important than the p mechanism for the Cu complexes, and the two mechanisms are comparable for the Ag complexes.

For the Mn chemical shift, the contribution of the d electrons is predominant, because of the active open-shell nature of the d orbitals. The perturbation theoretical viewpoint given previously [7] seems to be useful. The chemical shifts are understood in terms of the effects of the ligands on the occupied and unoccupied manifolds of these d orbitals.

Recently, the cadmium chemical shift has received much attention because of its extreme utility in the study of biologically active molecules [4]. In a previous paper [6], we studied the chemical shifts of some cadmium compounds, including $Cd(H_2O)_6^{2+}$, $CdCl_2$, $CdCl_4^{2-}$, $Cd(CN)_4^{2-}$ and $Cd(CH_3)_2$. For these system we have shown that the p mechanism is more important than the d mechanism, so that the ^{113}Cd chemical shift increases with increasing ability of electron donation from the attached ligands.

In this paper, we study in more detail the electronic mechanism of the cadmium chemical shift. We choose the following cadmium(II) compounds, including some organometallics: $CdMe_2$, CdMeEt, $CdEt_2$, CdMe(OMe), $Cd(OMe)_2$, CdMe(SMe) and $Cd(SMe)_2$ where $Me = CH_3$, Et $= C_2H_5$. For these molecules, solvent effects are expected to be smaller than for those studied previously. The purpose of the present study is fourfold. One is to test further the quantitative reliability of our ab initio method for the calculation of the metal chemical shift. Two is to examine the reliability of the model for the electronic mechanism of the ^{113}Cd chemical shift previously proposed [6]. Three is to understand the origin of the difference between methyl and ethyl ligands. Although these ligands are considered to be essentially the same in many aspects of chemistry, the Cd chemical shifts of $CdMe_2$ and $CdEt_2$ differ by

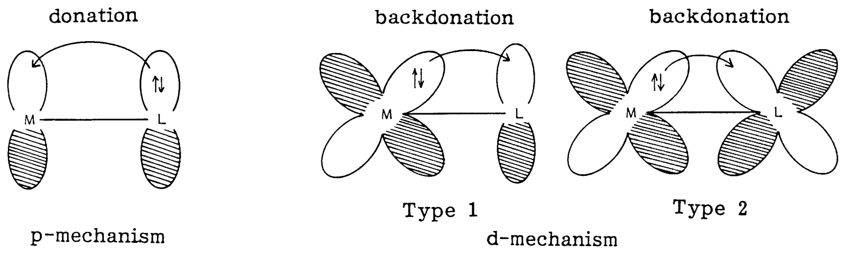

Fig. 1. Illustration of the p and d mechanisms of the metal chemical shift. They are due to the metal–ligand interactions which produce electrons in the outer valence np orbitals and holes in the valence $(n-1)$d shell, respectively. They are important as the origins of the paramagnetic terms of the metal chemical shifts of the compounds in which the metal atoms have almost closed d subshell.

about 100 ppm [3]. Four is to compare the chemical shift mechanism for the OMe and SMe ligands. Both of these ligands are π-electron donating. One interesting difference is that the sulfur ligand has low-lying vacant d orbitals but the oxygen does not. If the d orbitals of sulfur strongly participate in the Cd–S bond as illustrated by the type-2 d mechanism shown in fig. 1, the d electrons would be withdrawn from the cadmium, and the d mechanism would be largely enhanced. This would result in some abnormality for the chemical shifts of CdMe(SMe) and $Cd(SMe)_2$.

In the next section, we briefly explain the method of calculation. In section 3, we examine the correlation between the theoretical and experimental values. We then investigate the mechanism of the Cd chemical shift, the origin of the difference in the methyl and ethyl ligands, and the role of the outer d orbitals of the sulfur of the SMe ligand.

2. Method of calculation

The Cd chemical shifts were calculated by the ab initio finite perturbation method [9,10]. The details of the method have been described in a previous paper [6]. For the SCF calculations, we used a modified version of the HONDOG program [11]. The gauge origin was taken at the position of the metal nucleus under consideration. The geometries of the complexes studied are shown in fig. 2. The lengths are in ångström and the angles in degree. Since experimental geometries of most of these complexes are not available, Pauling's tetrahedral covalent radii [12] were used for all the metal–ligand distances. For the geometries of the ligands, we used the geometries of the parent molecules. For example, the geometry of the OMe ligand was taken from that of the methyl alcohol [13]. The basis sets we used are MIDI-1 for cadmium and the atoms directly connected to

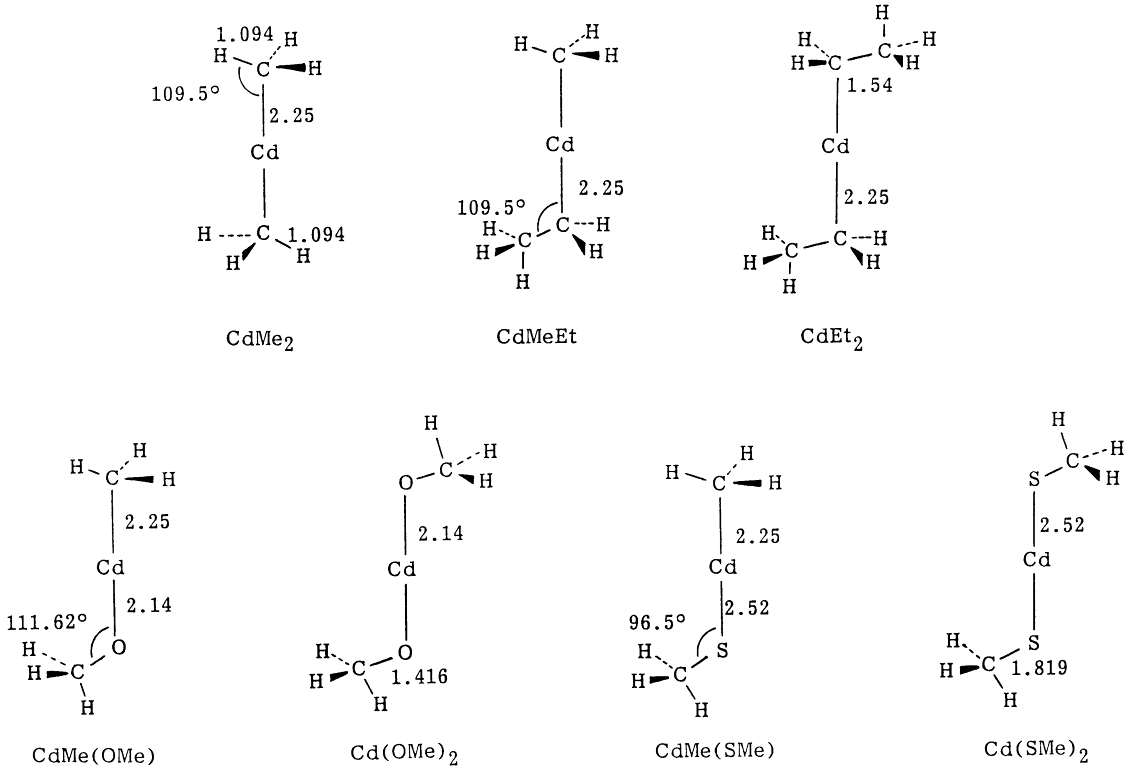

Fig. 2. Geometries of the complexes studied in the present calculations (lengths in ångström, and angles in degree).

cadmium, and MINI-1 for the other atoms [14]. For the cadmium 5p orbital two single-primitive Gaussians were added as in the previous study [6]. For the sulfur 3d orbital, we added a single-primitive Gaussian with an exponent of 0.141. This exponent was obtained by maximizing the overlap with the cadmium d orbitals as illustrated in type 2 of fig. 1. We also tested the 3d exponents of sulfur recommended for the Rydberg orbital ($\alpha = 0.015$) and for the polarization function ($\alpha = 0.540$) [15]. For consistency, we also added a d orbital (polarization function) on oxygen ($\alpha = 0.850$) [15]. The effects of the ligand d orbitals were estimated by comparison with the results obtained without including such d orbitals.

3. Correlation between theory and experiments

The Cd nuclear magnetic shielding constants and the cadmium chemical shifts are summarized in table 1 for all the complexes studied here. The chemical shift of a molecule M is determined relative to the reference molecule, $CdMe_2$,

$$\Delta\sigma_M = \sigma(M) - \sigma(CdMe_2).$$

The nuclear magnetic shielding constant is the sum of the diamagnetic term, σ^{dia}, and the paramagnetic term, σ^{para}. Each term is decomposed into core and valence MO contributions. For the diamagnetic term, the core MO contributions are dominant. Therefore, the diamagnetic contribution to the chemical shift is small, as expected. For the paramagnetic term, on the other hand, the valence MO contributions are dominant, and the chemical shift is primarily determined by the change in these contributions. The experimental values are shown in the last column of table 1 [3,4,16–19]. For the CdMe(SMe) complex an experimental value is not available; the chemical shift is reported only for the hexamer, $[CdMe(SMe)]_6$ [19]. For the complex $Cd(SMe)_2$, the experimental value for $Cd(glutathione)_2$ is compared, since this compound is known experimentally to be the two coordination cadmium alkylthiolate complex [4,18]. For $Cd(OMe)_2$, no experimental value seems to be available.

The correlation between theory and experiment for the ^{113}Cd chemical shift is shown in fig. 3. Also included are the results for several other complexes taken from previous calculations [#1] [6]. Since the experimental values are not available for

Table 1
Diamagnetic and paramagnetic contributions, σ^{dia} and σ^{para}, to the ^{113}Cd nuclear magnetic shielding constant σ and their analysis into core and valence MO contributions (in ppm)

Compound	σ^{dia}				σ^{para}				σ		Exptl. shift
	core	valence	total	shift	core	valence	total	shift	total	shift	
$CdMe_2$	4595	256	4851	0	−43	−1047	−1090	0	3761	0	0
CdMeEt	4602	272	4874	23	−43	−1021	−1064	26	3810	49	50 [d]
$CdEt_2$	4607	289	4896	45	−43	−995	−1038	52	3858	97	94 [d]
CdMe(OMe)	4602	276	4878	27	−33	−755	−788	302	4090	329	323 [e]
CdMe(OMe) [a]	4602	276	4878	27	−34	−782	−816	274	4062	301	323 [e]
$Cd(OMe)_2$	4609	296	4905	54	−27	−590	−617	473	4288	527	–
CdMe(SMe)	4630	270	4900	49	−36	−898	−934	156	3966	205	–
CdMe(SMe) [b]	4630	270	4900	49	−40	−900	−940	150	3960	199	–
CdMe(SMe) [c]	4630	270	4900	49	−40	−932	−972	118	3928	167	–
$Cd(SMe)_2$	4665	284	4949	98	−31	−801	−832	258	4117	356	328 [f]
$Cd(SMe)_2$ [b]	4665	284	4949	98	−39	−802	−841	249	4108	347	328 [f]

[a] With d orbital on oxygen (polarization function).
[b] With 3d orbital on sulfur (optimized).
[c] With two d orbitals on sulfur (polarization function and Rydberg function).
[d] Ref. [16]. [e] Ref. [17]. [f] Ref. [18].

[#1] We have omitted the result for $Cd(CN)_4^{2-}$ [6], since in the NMR experimental condition [16], $Cd(CN)_4^{2-}$ seems to be in equilibrium with $Cd(CN)_3^-$ [20].

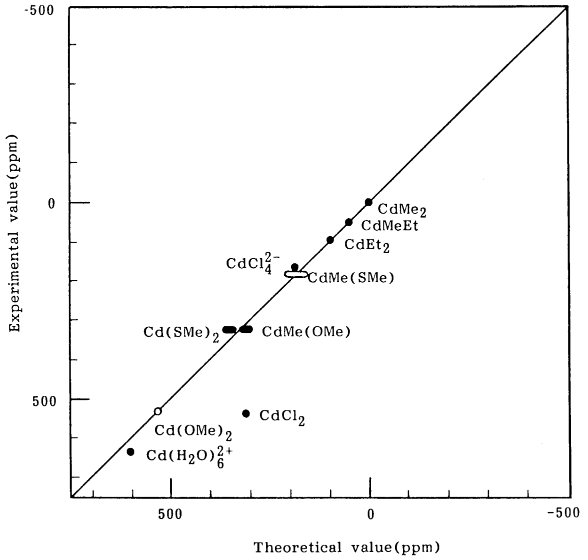

Fig. 3. Comparison between experimental and theoretical values for the ^{113}Cd chemical shifts of the cadmium complexes. For $Cd(OMe)_2$ and CdMe(SMe) complexes experimental data are not available so that the open circle shows only the theoretical value. For CdMe(SMe), CdMe(OMe) and $Cd(SMe)_2$, the theoretical values are given with the width obtained with and without including the d functions on the sulfur or oxygen atoms of the ligands.

$Cd(OMe)_2$ and CdMe(SMe), only the theoretical values are shown as open circles. At a first glance we see that the agreement between theory and experiment is quite good. This is especially so for the organometallic cadmium complexes studied here for which the solvent effect is expected to be small; some experimental values were obtained with neat samples [3,4]. We then conclude that the present ab initio theoretical method gives quantitatively reliable values for the metal chemical shifts of the cadmium complexes.

4. Mechanism of the Cd chemical shift

The paramagnetic contribution to the Cd nuclear shielding constant may be broken down into the metal orbital contributions and ligand contributions. The method for this analysis was described in a previous paper [6]. The result is given in table 2. The dominant contribution comes from the Cd p AO contribution. The d contribution is much smaller, and the ligand contribution is very small. The Cd s AO contribution vanishes identically because the s AO does not have angu-

Table 2
Contributions to the paramagnetic term of the ^{113}Cd nuclear magnetic shielding constant σ^{para} from the cadmium p and d AOs and the ligands (in ppm)

Compound	Cd [a]					Ligand				
	p	shift	d	shift	effect of d on ligand	Me	Et	OMe	SMe	shift
$CdMe_2$	−992	0	−68	0	–	−15	–	–	–	0
CdMeEt	−958	34	−71	−3	–	−15	−21	–	–	−6
$CdEt_2$	−923	69	−74	−6	–	–	−21	–	–	−12
CdMe(OMe)	−656	336	−101	−33	0	−14	–	−16	–	0
CdMe(OMe) [b]	−666	326	−105	−37	−14	−14	–	−31	–	−15
$Cd(OMe)_2$	−460	532	−125	−57	–	–	–	−16	–	−2
CdMe(SMe)	−850	142	−56	12	0	−15	–	–	−14	1
CdMe(SMe) [c]	−816	176	−83	−15	7	−15	–	–	−26	−11
CdMe(SMe) [d]	−867	125	−67	1	−28	−15	–	–	−23	−8
$Cd(SMe)_2$	−766	226	−38	30	0	–	–	–	−14	2
$Cd(SMe)_2$ [c]	−695	297	−95	−27	14	–	–	–	−25	−20

[a] The s AO contribution of Cd is zero.
[b] With d orbital on oxygen (polarization function).
[c] With 3d orbital on sulfur (optimized).
[d] With two d orbital on sulfur (polarization function and Rydberg function).

lar momentum. This result confirms the conclusion of the previous study [6] that the Cd chemical shift is mainly due to the p mechanism and the contribution of the d mechanism is small.

In the p mechanism, the chemical shift increases with increasing ability of electron donation of the ligand. Therefore, the order should be OMe > SMe > Et > Me as confirmed by the present calculation. This is the order of the π-electron donating ability of the ligands [21,22].

The diamagnetic term, on the other hand, is accurately determined by the structural factors alone. Flygare and Goodisman found that the diamagnetic term is expressed to a good approximation as [23]

$$\sigma^{\text{dia}} = \sigma^{\text{dia}}(\text{free atom } M) + \frac{e^2}{3mc^2}\sum_{\alpha}\frac{Z_\alpha}{r_\alpha}, \qquad (1)$$

where σ^{dia}(free atom M) is the free-atom diamagnetic susceptibility of the atom M, α runs over all nuclei except M, Z_α is the atomic number, and r_α is the distance between the nuclei M and α. In the previous paper [7], we showed that the diamagnetic terms follow a Pascal-rule-like formula given by

$$\sigma^{\text{dia}} = \sigma^{\text{dia}}(M) + \sum_{L} n_L \sigma^{\text{dia}}(L), \qquad (2)$$

where $\sigma^{\text{dia}}(M)$ is essentially the same as σ^{dia}(free atom M) in eq. (1), $\sigma^{\text{dia}}(L)$ is the contribution of the ligand L, and n_L is the number of ligands L attached to M. Eq. (2) is obtained from eq. (1) if the M–L length and the geometry of L are assumed to be constant. In table 3 are shown the values of σ^{dia}(Cd) and $\sigma^{\text{dia}}(L)$ for the complexes studied here. Two values are given for $\sigma^{\text{dia}}(L)$; one calculated from the present ab initio results by a least-squares fitting method based on eq. (2) and the other from the second term of eq. (1). The difference Δ is very small. Thus, the diamagnetic term is determined solely by the structural factors. The contribution of the diamagnetic term to the chemical shift is small.

5. Difference in the methyl and ethyl ligands

Though methyl and ethyl groups are chemically very similar, the ^{113}Cd chemical shifts of CdMe_2 and CdEt_2 are different by as much as 94 ppm [3]. Furthermore, CdPr^{n}_2, CdPr^{i}_2 and CdBu^{n}_2 exhibit chemical shifts of 139, 207 and 154 ppm [3] relative to CdMe_2. (Pr^{n}, Pr^{i} and Bu^{n} represent *n*-propyl, iso-propyl and *n*-butyl, respectively.) In order to understand the origin of these differences, we have calculated the Cd chemical shifts of CdMe_2, CdMeEt and CdEt_2.

In table 1 we see that the Cd chemical shifts of CdMe_2, CdMeEt and CdEt_2 are calculated to be 0, 49 and 97 ppm, in excellent agreement with the experimental values of 0, 50 and 94 ppm [3]. We further see that the origin of this chemical shift is 45% diamagnetic and 55% paramagnetic.

The diamagnetic difference is attributed to the difference in the ligand contribution, $\sigma^{\text{dia}}(L)$, as shown in table 3. The ligand contributions of 37 ppm for CH_3 and 60 ppm for C_2H_5 certainly explain the difference in the diamagnetic term shown in table 1. This is strictly the structural factor. The paramagnetic difference, however, is attributed to the difference in the valence electronic structure of the metal. More details are available in table 2, which gives an analysis of the paramagnetic shielding in terms of the metal AO and ligand contributions. We see from table 2 that the paramagnetic difference is mostly attributable to the difference in the p mechanism. The d mechanism and the ligand contribution give a reverse effect. Thus, the origin of the paramagnetic difference lies in the fact that the ethyl group is more strongly π-electron donating (hyperconjugative) than the methyl group.

In conclusion, the origin of the difference in the methyl and ethyl ligands is partly due to the

Table 3
Central metal and ligand contributions to the diamagnetic term of the ^{113}Cd nuclear magnetic shielding constant (in ppm)

Contribution	Ab initio	From eq. (1)	Difference
σ^{dia}(Cd)	4775	–	–
σ^{dia}(Me)	37	35	2
σ^{dia}(Et)	60	58	2
σ^{dia}(OMe)	66	63	3
σ^{dia}(SMe)	88	85	3
$\sigma^{\text{dia}}(\text{Pr}^{\text{n}})$	–	73	–
$\sigma^{\text{dia}}(\text{Pr}^{\text{n}})$	–	81	–
$\sigma^{\text{dia}}(\text{Bu}^{\text{n}})$	–	86	–

structural factor (diamagnetic) and partly due to the electronic factor (paramagnetic), i.e. the p mechanism.

Based on this analysis, it is possible to discuss the chemical shifts of $CdPr^n_2$, $CdPr^i_2$, and $CdBu^n_2$. Since the diamagnetic term is given by eq. (1), we can calculate the ligand contributions $\sigma^{dia}(L)$ from the structural data alone [13], which are given in table 3. The diamagnetic contributions to the chemical shifts calculated in this approximation are 76, 92 and 102 ppm, respectively, for $CdPr^n_2$, $CdPr^i_2$ and $CdBu^n_2$. Since the experimental values of the chemical shifts are 139, 207 and 154 ppm, respectively, we can estimate the paramagnetic terms to be 63, 115 and 62 ppm, respectively. This result indicates that the π-electron donating ability of the Pr^n ligand is slightly larger than that of the Et ligand, but that of Bu^n is almost the same as that of Pr^n, viz. the π-electron donating ability is saturated at about Pr^n. On the other hand, that of Pr^i is larger than that of Pr^n, in accordance with the empirical fact that the secondary alkyl group is more hyperconjugative than the primary alkyl group [22].

6. Role of the outer d orbitals of the SMe ligand

Lastly we want to analyze the difference in the Cd chemical shift for the OMe and SMe ligands. In particular, we want to examine the role of the outer d orbitals of the sulfur in the SMe ligand. It is seen from table 1 and fig. 3 that the agreement between theory and experiment is good for the series $CdMe_2$, CdMe(OMe) and $Cd(OMe)_2$, and also for the series $CdMe_2$, CdMe(SMe) and $Cd(SMe)_2$. In both of these series, the chemical shift is explained by the p mechanism for the paramagnetic term (see table 2).

To see the effect of the outer 3d orbital on the sulfur of the SMe ligand, we carried out the calculations with and without the 3d orbital on sulfur. Two kinds of sulfur 3d orbitals were used. One is a single Gaussian d orbital which has maximum d–d overlap with the cadmium 4d orbital. This is referred to as the d(opt) orbital. The other consists of two Gaussian d orbitals which are the so called Rydberg 3d orbital and polarization function. Referring to table 1, we see that the chemical shifts of $CdMe_2$, CdMe(SMe) and $Cd(SMe)_2$ are calculated to be 0, 205 and 356 ppm without the d orbitals, 0, 199 and 347 with the d(opt) orbital. When both d(pol) and d(Ryd) orbitals are used, we obtain 0 and 167 ppm for $CdMe_2$ and CdMe(SMe), respectively. In fig. 3, the calculated values are shown with this width. Although the polarization d plus Rydberg d calculation cause a shift of 32 ppm, this is the same order as the effect of the polarization d function on the oxygen of the OMe ligand, which is 28 ppm as seen from table 1. Although the effects of the d(opt) orbital on the p and d contributions are larger than those of the d(pol) + d(Ryd) orbitals (table 2), they tend to cancel so that the d(opt) orbital gives smaller final effect on the Cd chemical shift.

We thus conclude that the effect of the outer d orbitals of the sulfur on the Cd chemical shift is small, so that it causes no appreciable abnormality for the Cd chemical shift. The sulfur d orbital does not appreciably participate in the Cd–S bond.

7. Conclusions

In this paper, we have studied theoretically the cadmium chemical shifts of the cadmium complexes including organocadmium compounds, $CdMe_2$, CdMeEt, $CdEt_2$, $CdMe(OMe)_2$, CdMe (SMe) and $Cd(SMe)_2$. The conclusions of the present study are as follows:

(1) The calculated Cd chemical shifts agree excellently with the experimental values. Therefore, the ab initio theoretical methods used in this paper, such as the finite perturbation method, the choice of the basis set, etc., are reliable quantitatively to study the cadmium chemical shift.

(2) The cadmium chemical shift is mainly governed by the p mechanism in the paramagnetic term. The contribution of the d mechanism is small. The diamagnetic term, although dominant in the screening constant, is small for the chemical shift, and is determined solely by the structural factor. These results support the conclusion of the previous study [6].

(3) The difference of the methyl, ethyl and other alkyl ligands in the Cd chemical shift is

attributed partly to the structural factor (diamagnetic term) and partly to the electronic factor (paramagnetic term). Since the ethyl group is more π-electron donating than the methyl group, it facilitates the p mechanism more than the methyl group.

(4) The outer d orbitals on the sulfur of the SMe ligand are not important for the Cd–S bond and so have only a small influence on the Cd chemical shift.

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