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Quantum Chemical Calculations of Cadmium Chemical Shifts in Inorganic Complexes

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This study reports a systematic approach of ab initio calculations of ^{113}Cd chemical shifts to understand the coordination chemistry of cadmium complexes. Cadmium-113 chemical shifts were calculated using Hartree−Fock (HF) and density functional theoretical (DFT) methods for cadmium complexes, dimethylcadmium ($CdMe_2$), diethylcadmium ($CdEt_2$), methylethylcadmium (CdMeEt), cadmium nitrate tetrahydrate [$Cd(NO_3)_2 \cdot 4H_2O$], and cadmium acetate dihydrate [$Cd(OAc)_2 \cdot 2H_2O$]. Theoretical and experimental chemical shift values are compared in order to determine the effectiveness of theoretical calculations in determining cadmium chemical shifts. We also determined the magnitude of the principal elements of the ^{113}Cd CSA tensor values for hydrated cadmium nitrate and cadmium acetate. The effect of different cadmium basis sets such as polarized double-ζ split valence, 3-21G, and uncontracted Sadlej on chemical shift values was also evaluated. The density functional calculations were found to match the experimental chemical shift values considerably better than the Hartree−Fock calculations. Further, the agreement between the theoretical and experimental values significantly improved with the inclusion of a sufficient number of water molecules. Cadmium-113 chemical shifts of several cadmium complexes with coordination number six were analyzed in order to examine the efficacy of the ab initio calculations. Theoretical results suggest that the Double-Zeta Valence Potential (DZVP) and Sadlej basis sets are better than the 3-21G basis set. Our calculations also show that ab initio calculations identify the coordination number of cadmium complexes.

Introduction

The chemical shift interaction contains valuable information about the local environment of a nucleus and therefore is useful in understanding the chemical bonding, conformation, and dynamics of molecules. For example, chemical shifts of metals in inorganic and biological complexes can provide insights into the nature of coordinating ligands, coordination number, and the coordination geometry. The direct detection of the most prevalent metals, such as zinc and calcium, using NMR experiments to determine their chemical shifts is rather difficult. Therefore, it becomes essential to use ^{113}Cd, which has spin I $= 1/2$, as a surrogate probe for zinc, calcium-containing biocomplexes.[1,2] Analogous experimental efforts are directed to elucidate and comprehend fundamental structural and electronic basis for the metal ion NMR parameters. Unlike ^{1}H, ^{13}C, and ^{15}N, ^{113}Cd spans a chemical shift range of 900 ppm, which makes it a valuable tool for distinguishing different metal coordination geometries and ligand types. On the other hand, there were instances when isotropic chemical shift was insufficient to understand the geometry and the effect of ligands. This can be overcome by determining the magnitude and orientations of the individual components of the chemical shift anisotropy. The ability of ^{113}Cd CSA to provide more information was seen in its capacity to differentiate cadmium alaninate and cadmium glycinate structures.[3] Similarly, Jakobsen et al. solid-state NMR experiments identified the compensatory effect of two tensor elements in mesotetraphenylporphyrin and its pyridyl adduct, which led to a small chemical shift difference of 33 ppm.[4] To further understand the chemical principles underlying the variation of the ^{113}Cd CSA tensor, solid-state NMR experiments can be supplemented with ab initio calculations. In this paper, we present quantum chemical approaches to calculate the ^{113}Cd CSA tensors that can be directly compared with the experimental data for further applications.

A number of density functional theory (DFT) methods have been developed for investigating geometries, vibrational frequencies, and reactivity of organic, inorganic, and biocomplexes.[5,6] DFT has also been extensively used to calculate isotropic and anisotropic chemical shift values for ^{13}C[7] and ^{15}N[8,9] nuclei. There are also a few studies on ^{13}C chemical shifts involving *d*-block metals such as Hg, Rh, Ru, Pt, Cr, and Os.[10−12] These theoretical calculations have provided insight on understanding the effects of geometry, on the variation of chemical shifts, and in identifying atoms coordinated to the metal. In the case of metal-containing peptides and proteins, performance of the metal shielding calculations are highly dependent on the basis set and the number of basis functions used. In addition, electron correlation plays a vital role and makes ab initio calculations demanding. Moreover, relativistic effects need to be taken into account for accurate chemical shift values. Recently, DFT[13,14] has been applied to estimate electric field gradients[15] and chemical shifts of metals in heavy metal complexes.[16] These investigations employed Perdew et al., and Yang et al.,[17] hybrid functions that take exchange and correlation integrals into account. Generally, inclusion of these functionals results in better estimation of theoretical parameters tending toward the experimental value.

There are a few studies in the literature, which involved calculating cadmium chemical shifts. One study was done in

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TABLE 1: A List of Basis Functions and Computation Time Used in the Quantum Chemical Calculations of ^{113}Cd CSA Tensors for Various Cadmium Molecules[a]

cadmium complex	molecule	number of basis functions	number of primitive Gaussians	Cd-bs	N-bs	computation time (h)
cadmium nitrate	$Cd(NO_3)_2 \cdot 4H_2O$	305	604	S		9.5
cadmium nitrate	$Cd(NO_3)_2 \cdot 4H_2O$	264	508	D		3.5
cadmium nitrate (extended)	$Cd(NO_3)_2 \cdot 4H_2O + 13\ H_2O$	604	1204	S		43.5
cadmium nitrate (extended)	$Cd(NO_3)_2 \cdot 4H_2O + 13\ H_2O$	563	1028	D		26
cadmium acetate	$Cd(OAc)_3(H_2O)_2$	354	769	S		14.5
cadmium acetate (extended)	$Cd_2(OAc)_4 \cdot 4H_2O \cdot AcOH$	634	1408	S	S	95
cadmium acetate (extended)	$Cd_3(OAc)_6 \cdot 6H_2O \cdot AcOH$	668	1549	S	D	104.5
cadmium acetate (extended + H_2O)	$Cd_3(OAc)_6 \cdot 7H_2O \cdot AcOH$	934	2082	S	D	338.5

[a] Cd-bs: Basis set on the central cadmium atom; N-bs: Basis set on the neighboring cadmium atoms; S: Sadlej basis set; D: DZVP basis set.

1993 by Ellis et al., in determining the cadmium chemical shifts of diethylcadmium and dimethylcadmium using the Hartree−Fock (HF) method.[18] At that time, a large basis set like the Sadlej basis set was not available and density functional theory (DFT) was not well characterized. Later, Takuji et al. studied the same molecules by using improved basis sets in the HF/finite perturbation method.[19] These basis sets had higher angular momentum basis functions and were found to give better values than the previous study, but still there was a significant mismatch between theoretical and experimental values. One of the biggest limitations of the HF method is its inability to consider electron correlation. A slightly expensive DFT method, which combines HF, local, and gradient-corrected exchange terms, is usually employed to overcome this problem. With the advent of faster computers, running DFT calculations using a larger basis set has become a reality and this enabled us to examine the efficacy and accuracy of calculated ^{113}Cd chemical shifts using DFT methods.

This work also extends earlier studies[18−20] in analyzing the influence of bigger basis sets on chemical shift values. In addition, we have taken a new initiative in the field of ab initio calculations of metal complexes by studying principal shielding elements of experimentally well-characterized molecules, namely cadmium acetate[21,22] and cadmium nitrate.[23] Furthermore, we have also analyzed the effect of hydrogen bonding and coordinate bonds on the theoretical results. Many of the cadmium-containing bio-complexes show different coordination numbers varying from 4 to 8 and were found to form discrete cadmium−ligand coordination spheres. Our selection of molecules was influenced by this reason.

Computation Details

The calculations were performed with the *Gaussian98* program[24] on a Pentium III PC with 32, 64, and 256 MB RAM and varying clock speeds. Geometry for dimethylcadmium, diethylcadmium, and methylethylcadmium was optimized using *pm3mm* geometry optimization method. The second set of calculations was performed on the optimized complexes after fixing the Cd−C distances to that of the experimental values. The geometries of cadmium nitrate and cadmium acetate were obtained from the respective crystal structure[25,26] and the positions of hydrogens were further optimized using the *pm3mm* geometry optimization method.[27] The details of the structure are discussed in the Results section. The above molecules have uncommon coordination numbers of 2, 7, and 8 while the most common coordination number for cadmium is 6. We also determined ^{113}Cd chemical shifts for several hexacoordinated cadmium molecules such as cadmium benzoate, *p*-chloro cadmium benzoate, *p*-nitro cadmium benzoate, bis(2,2′-dipyridylamine)dinitratocadmium (CdPyr1), and bis-(aminomethylpyridine)dinitratocadmium (CdPyr2).

Three different basis sets, namely 3-21G,[28] DZVP,[29] and Sadlej,[30] were considered for the central cadmium atom. B3LYP and B3PW91 hybrid functionals were used for density functional calculations. Table 1 enlists the different cadmium nitrate and cadmium acetate molecules used for calculation, the total number of basis functions and basis sets considered, and the computation time taken by a 1 GHz Pentium III PC to complete these calculations. There is an addition of 41 basis functions when the DZVP basis set is replaced by the Sadlej basis set. This increase in primitive Gaussians slows down the calculation (Table 1).

Results are highly dependent on the number of atoms and type of basis functions used, and hence using a theoretically suitable reference is important for getting informative results. To start with, we referenced alkylcadmium compounds with respect to a free cadmium atom in order to avoid complications in ^{113}Cd chemical shift values as a result of Cd−ligand interaction. Later, for all Cd−O compounds, we referenced the chemical shift values by fixing the isotropic chemical shift value of an extended cadmium nitrate molecule to that of the experimental value (−102.2 ppm). Selection of cadmium nitrate as the reference was based on its highly defined central coordination sphere, very good comparison of the theoretically determined tensor values with the experimental ones, as well as reasonable matching in the theoretical and experimental isotropic chemical shift value with respect to a free cadmium atom. We have enumerated these issues in the Results section.

Gaussian calculations provide absolute shielding values, σ, and hence the chemical shift value of the complexes were obtained using the equation:

$$\sigma\,(\text{calc}) = -\sigma\,(\text{complex}) + \sigma\,(\text{ref})$$

Results and Discussion

The main purpose of this study is to address the following issues: (i) effect of DFT method on the ^{113}Cd chemical shifts; (ii) relationship between size of the basis set and the chemical shift value; (iii) determining coordination number of cadmium complexes using ab initio calculations; (iv) extrapolating this method for studying cadmium CSA tensors; and (v) influence of secondary effects such as hydrogen bonding and coordinate bonds on ^{113}Cd chemical shift tensors.

Ellis et al.[18] have done extensive experimental work on dimethylcadmium and diethylcadmium molecules. They found a distinct difference in the chemical shift values between the neat liquid and gaseous molecule as given in Table 2. Even though the pioneering computational work of Nakatsuji and co-workers[20] showed some similarities between theoretical and

TABLE 2: Experimental ^{113}Cd Chemical Shifts[a] Used To Compare with the Values Obtained from the ab Initio Calculations[b]

sample	chemical shift relative to 0.1 M $Cd(ClO_4)_2$ (ppm)	chemical shift relative to Cd atom (ppm)
$CdMe_2$, gas	705.0	1811.0
$CdEt_2$, gas	562.4	1668.4
$CdMe_2$, neat	642.9	1748.9
$CdEt_2$, neat	543.2	1649.2
CdMeEt, neat	692.9	1798.9

[a] Ref18. [b] δ[cadmium perchlorate − cadmium atom] = 1106 ppm.[35]

TABLE 3: Optimized Geometries of the Two Cadmium−Alkyl Complexes Using the *pm3mm* Method[a]

	R_{Cd-C} (Å)	R_{C-C} (Å)	R_{C-H} (Å)	θ_{CdCH} (degrees)	θ_{CdCC} (degrees)	θ_{CCH} (degrees)
$CdMe_2$	2.03		1.09	109.5		
experiment (g)	2.11		1.09	108.4		
$CdEt_2$	2.06	1.5	1.1	107.9	117.8	111.9
experiment (g)	2.13	1.5	1.1	108.8	116.2	114.4

[a] (g) − gaseous phase.

experimental values, the bond distances were fixed and not optimized using geometry optimization methods. This motivated Ellis et al.[18] to consider different basis sets for the geometry-optimized diethylcadmium and dimethylcadmium molecules. Cadmium chemical shifts obtained using these optimized geometries resulted in values quite different from the experimental values. They attributed the difference in values to the size of the basis set and failure to incorporate other effects such as spin−orbit coupling and electron correlation effects. In this study, we utilized bigger basis sets such as Sadlej and DZVP for determining cadmium chemical shifts. We also considered secondary effects such as hydrogen bonds and coordinate bonds, by extending the network to a greater number of molecules around the central coordination sphere, to understand the influence of these effects on chemical shifts.

^{113}Cd Chemical Shifts of Diethylcadmium and Dimethylcadmium. Optimization of dimethylcadmium resulted in a Cd−C bond distance of 2.03 Å compared to the experimental value of 2.112 Å.[31] Similarly, the Cd−C bond distance for diethylcadmium was found to be 2.06 Å compared to the experimental value of 2.133 Å.[32] Except for these values, the other distances (namely C−C and C−H bond distances) and the angles (CdCH, CdCC, and CCH) matched the experimental values (Table 3). ^{113}Cd chemical shielding values were calculated for these molecules using HF and DFT/B3PW91, B3LYP methods. These shielding values were compared with the absolute shielding values of a free cadmium atom to get a better perspective. The difference between free-atom and absolute shielding value of diethylcadmium and dimethylcadmium is given in Table 4. For all the complexes the isotropic chemical shift values calculated using hybrid functionals are greater than the corresponding values obtained using the HF method. The difference in the isotropic chemical shift values ranged from about 730 ppm to 1850 ppm for dimethylcadmium and 614 ppm to 1711 ppm for diethylcadmium. Experimental values for dimethylcadmium and diethylcadmium are 1811 and 1668 ppm, respectively. Both DZVP and Sadlej basis sets resulted in values closer to experimental ones. The effect of different basis sets on chemical shift values can be explained on the basis of the size of these basis sets. The split-valence basis set 3-21G contains a lower number of basis functions compared to the DZVP and Sadlej basis sets, resulting in an underestimated Cd chemical shift value.

Gaseous diethylcadmium and dimethylcadmium differ by 142.6 ppm, and our calculations using bigger basis sets and hybrid functionals resulted in values ranging from 133 to 160 ppm. As expected, the theoretical chemical shift value of methylethylcadmium falls between diethylcadmium and dimethylcadmium. We did not compare the theoretical methylethylcadmium value with the experimental value due to dissimilarity in the physical states.

To further validate the importance of these basis sets, we re-determined the chemical shift values for the *pm3mm* optimized dialkylcadmium molecules after fixing the Cd−C bond distances to that of the experimentally determined values. The absolute shielding values for the *pm3mm* optimized and experimentally fixed molecules differed by 100 to 200 ppm, but the δ value between dimethylcadmium and diethylcadmium for the experimentally fixed molecules positioned around 150−180 ppm as shown in Table 4 is similar to the δ value determined in the previous case. Based on this set of studies, we can clearly see an improvement in the current method. At the same time, it is inappropriate to draw a conclusion on the nature of the basis set using two molecules. Hence, we extended this method to other bigger molecules.

Chemical Shift Anisotropy in Cadmium Nitrate and Cadmium Acetate Hydrates. What is the quality of our calculation? To answer this question, we looked into two molecules, namely cadmium nitrate tetrahydrate and cadmium acetate dihydrate, for which the principal elements of the shielding tensor are available from experiments. Discrete neutral cadmium nitrate tetrahydrate was the immediate choice for our study rather than cadmium perchlorate for the same reasons mentioned before. To better understand this, the structure of cadmium nitrate[25] with (Figure 1b) and without hydrogen-bonded water molecules (Figure 1a) are considered in the calculations. The geometry around Cd in $Cd(NO_3)_2{\cdot}4H_2O$ is a distorted dodecahedron with four water molecules and two nitrates. Nitrates coordinate in a bidendate fashion to a cadmium atom. A single-crystal solid-state NMR study of a cadmium nitrate molecule shows the presence of two indistinguishable shielding tensors.[23] Honkonen et al.[23] rationalized the number

TABLE 4: Cadmium-113 Isotropic Chemical Shifts in ppm for Dimethylcadmium, Methylethylcadmium, and Diethyl Cadmium Molecules Obtained from *ab Initio* Calculations[a,b]

	3-21G			DZVP			Sadlej		
	RHF	B3PW91	B3LYP	RHF	B3PW91	B3LYP	RHF	B3PW91	B3LYP
$CdMe_2$	735	838	850	1554	1828	1850	1592	1806	1830
$CdEt_2$	614	697	701	1442	1695	1711	1458	1653	1670
CdMeEt	669	760	768	1499	1764	1784	1527	1733	1754
δ	121	141	149	112	133	139	134	153	160
δ1	177	184	155	137	143	114	156	161	134

[a] $\delta = \sigma(CdMe_2) - \sigma(CdEt_2)$; experimental gas phase δ value is 142.6 ppm; $\sigma(CdMe_2\text{-gas}) = 1811$ ppm; $\sigma(CdEt_2\text{-gas}) = 1668.4$ ppm; $\sigma(CdMeEt\text{-liq}) = 1798.9$ ppm. [b] δ1: $\sigma(CdMe_2) - \sigma(CdEt_2)$: chemical shift difference for fixed Cd−C distances.

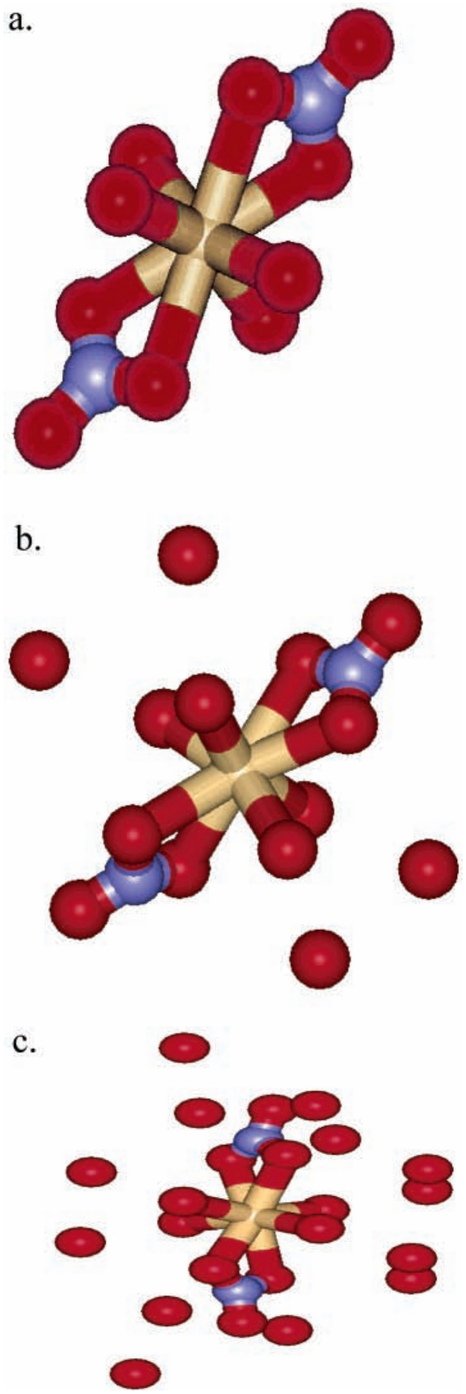

Figure 1. Structure of cadmium nitrate molecule considered in the ab initio calculations of ^{113}Cd CSA tensors. (a) The central coordination sphere taken from the crystal structure of cadmium nitrate.[25] (b) Addition of 13 water molecules to the crystal structure shown in (a) in order to consider the effects of hydrogen bonding in ab initio calculations of ^{113}Cd nuclei.

TABLE 5: Cadmium-113 Chemical Shift Values for Cadmium Nitrate Obtained Using Two Different Basis Sets in the ab Initio Calculations Relative to Free Cadmium Atom[a]

	3-21G	DZVP	Sadlej
$Cd(NO_3)_2 \cdot 4H_2O$	−2	771	954
$Cd(NO_3)_2 \cdot 4H_2O$ with 13 waters	24	750	964

[a] The experimental value is 1004 ppm relative to the free cadmium atom.

TABLE 6: A Comparison between Theoretical and Experimental Chemical Shift Tensor Values of Cadmium Nitrate Tetrahydrate

	σ_{iso} (ppm)	σ_{33} (ppm)	σ_{22} (ppm)	σ_{11} (ppm)
$Cd(NO_3)_2 \cdot 4H_2O$	−112.7	23.9	−179.4	−182.5
$Cd(NO_3)_2 \cdot 4H_2O$ with 4 waters	−107.5	20.3	−159.6	−183.3
$Cd(NO_3)_2 \cdot 4H_2O$ with 13 waters	−102.2	25.5	−158.8	−173.3
experiment	−102.2	22.2	−154.3	−174.4

of CSA tensors to the *mm2* point group of a cadmium nitrate molecule. They also reported the magnitudes of the principal elements of the CSA tensors to be 22.2 ppm, −154.3 ppm, and −174.4 ppm with respect to solid cadmium perchlorate. Further, they showed the orientation of these tensor elements to be highly dependent on the Cd−O bond distances. The most deshielded element (σ_{33}) is oriented normal to the water oxygen plane, whereas the other two shielded elements, σ_{11} and σ_{22}, lie in the water−oxygen plane making 88° and 84° angles, respectively, with the plane containing Cd and 4 oxygens. Before looking at the CSA tensors in our theoretical studies, we wanted to compare the shielding values with that of the free cadmium atom. In the two structures of cadmium nitrate shown in Figure 1, the first one (Figure 1a) led to a chemical shift value of 954 ppm compared to the experimental value of 1004 ppm using the Sadlej basis set (see Table 5). Now consideration of hydrogen bonds by putting in 13 water molecules resulted in a value of 964 ppm (Figure 1b). Unlike the Sadlej basis set, the DZVP basis set led to an underestimated value of 750 ppm. Due to reasonable matching in the two values using the Sadlej basis set as well as to simplify things, we set the theoretical isotropic chemical shift value of cadmium nitrate tetrahydrate (extended) to the experimental value of −102.2 ppm for the remaining studies. Use of the Sadlej basis set on cadmium and 6-311+G on other atoms led to shielding values of −182.5 ppm, −179.4 ppm, and 23.9 ppm for the unextended network as shown in Table 6. The four water molecules and two nitrates present around the central cadmium atom can form hydrogen bonds with nine other water molecules present in the crystal lattice. Addition of water molecules improved the value from −182.5 ppm to −173.3 ppm for σ_{11} and −179.4 ppm to 158.8 ppm for σ_{22}. The value of σ_{33} changed by 1 ppm. As mentioned before, σ_{33} lies in a plane normal to the water plane and is least affected by adding water molecules. Also, we determined the shielding tensor values for a molecule, which considered a lower number of hydrogen bonds around the central coordination sphere. There is a distinct difference in shielding tensors between structures (b) and (c) given in Figure 1. To make sure that the results obtained by using bigger basis sets and hybrid functionals are not fortuitous, we considered cadmium acetate dihydrate complex in our calculations.

The structure of cadmium acetate dihydrate, shown in Figure 2, has an orthorhombic system with a $P2_12_12_1$ space group.[26] Cadmium is located in a distorted square-based trigonal capped polyhedron environment and the cadmium atom is surrounded by seven oxygen atoms—two from water, four from the acetates, and the last one from the bridging acetate. A solid-state NMR experimental study[23,24] on this molecule resulted in an isotropic chemical shift value of −51.6 ppm. In addition, three principal CSA values were found to be 33.5 ppm, −69.5 ppm, and −118.7 ppm, going from the most deshielded to the most shielded. Orientations determined in the same study showed that the σ_{33} axis is oriented 9° away from the Cd−O (one of the bidendate acetates) longest bond. The σ_{11} axis is directed 89° away from the same Cd−O bond and lies along the water plane. Similarly, the σ_{22} axis is 7° away from the water plane and tilted at an angle of 81° from the longest Cd−O bond. The orientations of

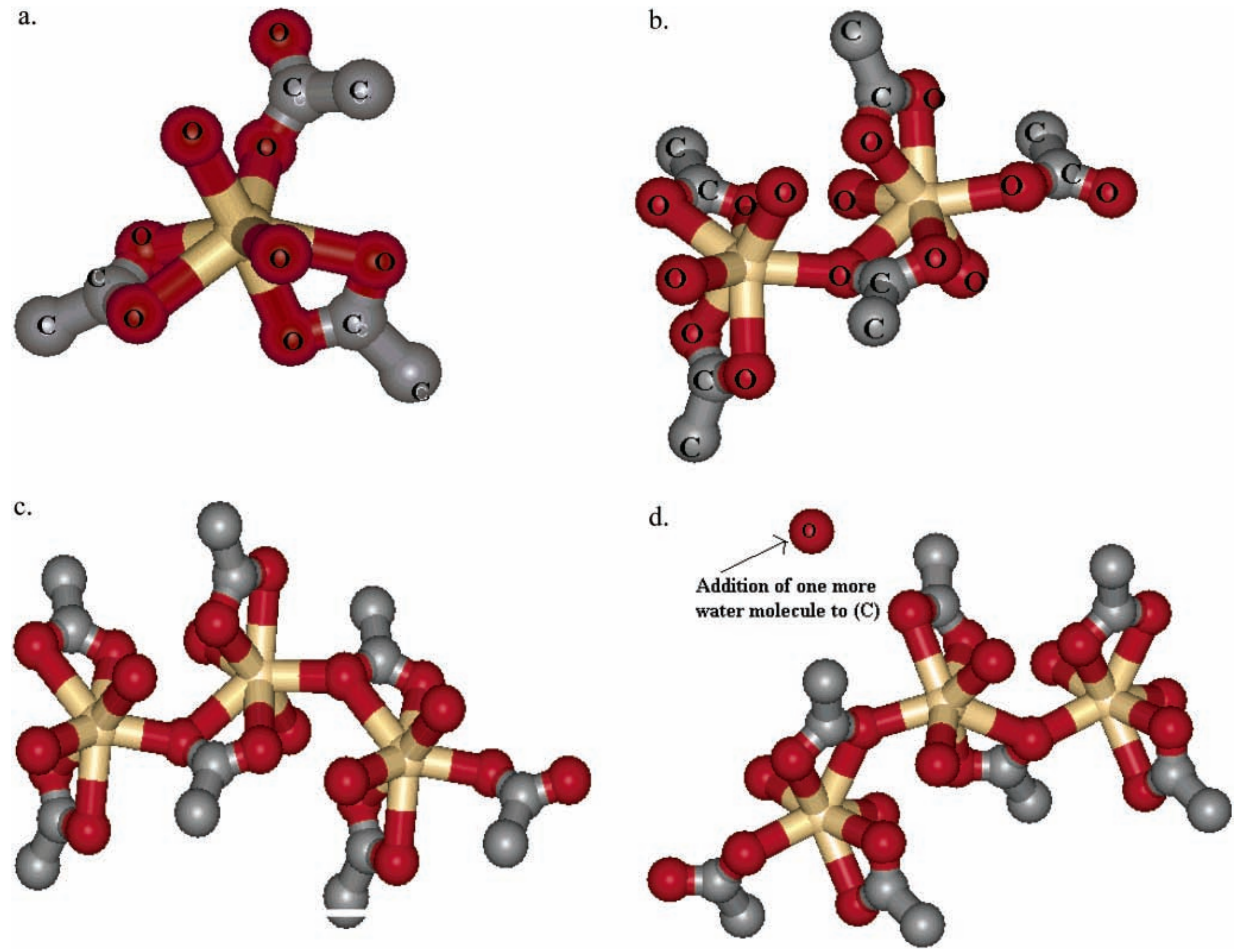

Figure 2. Structures of cadmium acetate network considered in the ab initio calculations of ^{113}Cd CSA tensors. (a) The central coordination sphere taken from the crystal structure of cadmium acetate.[26] (b) Extension of the network with the addition of one more cadmium acetate moiety to the central coordination sphere shown in (a). (c) Extension of the network with the addition of two cadmium acetate moieties to the central coordination sphere shown in (a). (d) Addition of one water molecule to the structure shown in (c) in order to calculate the effects of the hydrogen bonding.

the shielding elements were highly dominated by the position of the longest Cd−O bond and also on the position of the Cd−water oxygens. Unlike a cadmium nitrate molecule, cadmium acetate has a bridging acetate group that links two different cadmium atoms. This has been taken into consideration while performing our calculations. Figure 2a shows the discrete central coordination sphere. In Figure 2b, one more cadmium moiety was added to see the effect of bridging cadmium on the chemical shielding tensors of the first cadmium. The same procedure was followed to extend it to one more molecule (Figure 2c). In the final structure (Figure 2d), one more water molecule was added to see the effect of water molecules on the CSA values. Increasing the number of molecules led to slowing down of calculations as a result of high dependence of ab initio methods on the number of atoms. Calculated values for all the structures are listed in Table 7. In Cd1Ac, the magnitudes of σ_{33} and σ_{11} principal elements differed from the experimental value by a few ppm but the σ_{22} value of −50.6 ppm was 19 ppm greater than the experimental value. To rationalize this difference, we increased the network and the values were calculated again for this new molecule. In this case (Cd2Ac), the σ_{33} value increased by 23 ppm, whereas σ_{22} and σ_{11} changed only by 2 ppm. Further addition of another moiety to the central cadmium sphere improved the σ_{22} value from −48.6 ppm to −68.3 ppm ,whereas the other two shielding elements changed by 4 ppm. In the final case, replacing the DZVP basis set by the Sadlej set on the neighboring atoms and addition of one more water molecules did not affect the values much but slowed the calculations due to an increase in the number of basis functions. On the basis of this calculation, we can conclude that the DZVP basis set is sufficient for the cadmium atoms surrounding the central one. The exact reason for the worsening effect of additional cadmiums on the σ_{33} is not known. Perhaps, this may be attributed to the addition of cadmium moieties along the bridging acetate−Cd bond, which orients in the same direction as the σ_{33} principal shielding element.

TABLE 7: A Comparison between Theoretical and Experimental Chemical Shift Tensor Values of Cadmium Acetate Dihydrate[a]

	σ_{iso} (ppm)	σ_{33} (ppm)	σ_{22} (ppm)	σ_{11} (ppm)
Cd1Ac	−42.7	36.5	−50.6	−114.1
Cd2Ac	−33.7	59.2	−48.6	−111.6
Cd3Ac	−40.7	62.3	−68.3	−116.0
Cd3Ac + H_2O	−39.5	59.3	−63.9	−113.7
experiment	−51.6	33.5	−69.5	−118.7

[a] Cd1Ac: $Cd(OAc)_3(H_2O)_2$; Cd2Ac: $Cd_2(OAc)_4{\cdot}4H_2O{\cdot}AcOH$; Cd3Ac: $Cd_3(OAc)_6{\cdot}AcOH{\cdot}6H_2O$; Cd3Ac+$H_2O$: $Cd_3(OAc)_6{\cdot}AcOH{\cdot}7H_2O$.

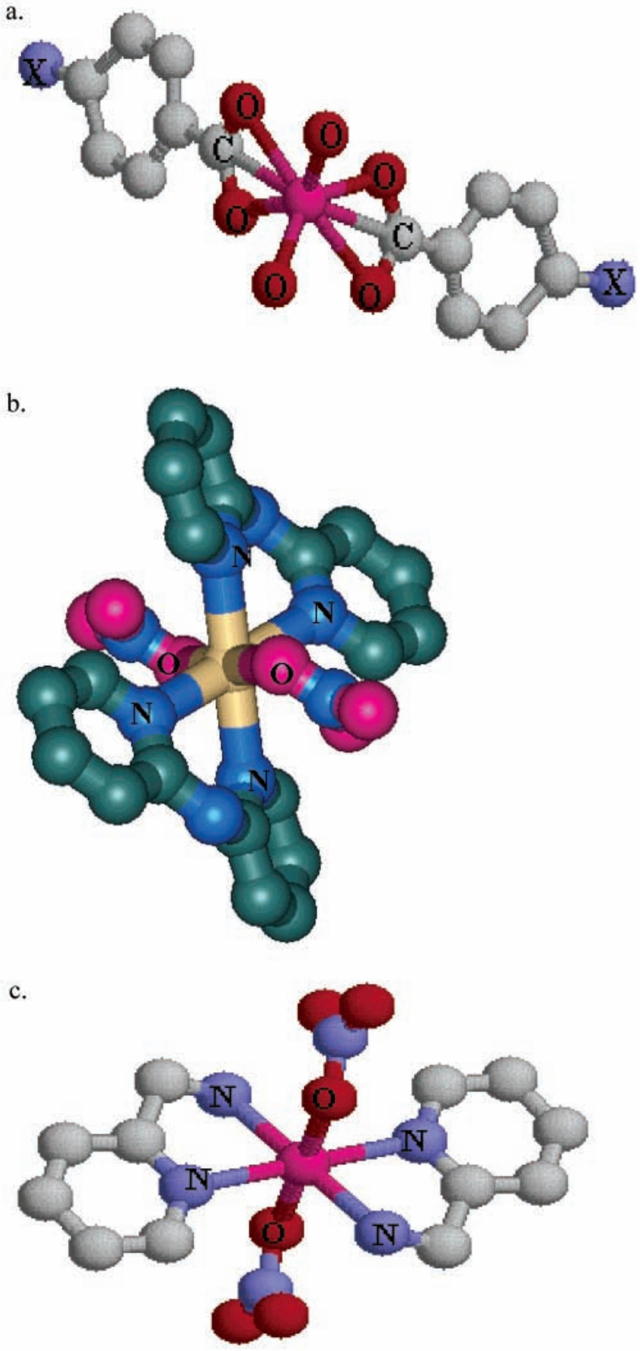

Figure 3. Structure of cadmium complexes considered in the ab initio calculation of the isotropic chemical shift of ^{113}Cd nuclei. (a) Cadmium benzoate;[33] (b) bis(2,2′dipyridylamine)dinitratocadmium;[34] (c) bis(2-aminomethylpyridine) dinitratocadmium.[34]

This study of cadmium nitrate and cadmium acetate does not give us concrete evidence of secondary effects on chemical shifts but clearly shows the influence of hydrogen bonding and additional cadmium atoms on the shielding values.

Cadmium Chemical Shifts in Hexacoordinated Molecules. The structure (Figure 3) and coordination geometry of the hexacoordinated complexes are listed in Table 8. Two kinds of molecules containing a N_4O_2 and O_6 coordinating environment were considered in this calculation. All the molecules in this list have chemical shifts between 24 and 52 ppm. The only exception is bis(2-aminomethylpyridine)dinitratocadmium (CdPyr2), which has a chemical shift of 218 ppm.[33] We determined all the values relative to the isotropic chemical shift value of −102.2 ppm for cadmium nitrate and used the Sadlej basis set on the cadmium atom and 6-311+G on the other atoms. Substituted cadmium benzoates[34] employed in the present study are isostructural with two bidendate carboxylates and two water molecules around the central cadmium atom. Changing the para substitutents has minimal effect on the cadmium chemical shift values.

TABLE 8: Comparison between Theoretical and Experimental Chemical Shifts of Hexacoordinated Cadmium Molecules[a]

molecule	geometry	theoretical (ppm)	experimental (ppm)
cadmium benzoate	6O	46	
p-chloro cadmium benzoate	6O	43	24
p-nitro cadmium benzoate	6O	37	24
CdPyr1	4N, 2O	5	51
CdPyr2	4N, 2O	177	218

[a] δ(CdPyr2 − CdPyr1) is 172 ppm (theoretical) and 167 ppm (experimental).

Our calculations resulted in an isotropic chemical shift value of 46 ppm for cadmium benzoate, 43 ppm for *p*-chloro cadmium benzoate, and 37 ppm for *p*-nitro cadmium benzoate. Careful examination of these values clearly shows a good matching in the chemical shift values among the hexacoordinated molecules as shown in Table 8. Similarly, in the case of pyridine molecules, theoretical values were found to be 5 ppm for CdPyr1 and 177 ppm for CdPyr2 compared to experimental values of 51.4 and 218 ppm. Again, there is a better match between these two hexacoordinated molecules. Setting the theoretical value of CdPyr1 to 51.4 ppm leads to an isotropic chemical shift value of 223.4 ppm for CdPyr2. Unlike quantum chemical calculation studies on model peptides to determine the CSA tensors of ^{13}C and ^{15}N nuclei,[8] ^{113}Cd chemical shift studies are more complicated due to the presence of d-orbitals and higher coordination geometry. Although it is difficult to get the exact chemical shift values of cadmium molecules, the Sadlej basis set can be used for studying cadmium with different coordination numbers. There was a distinct difference in the theoretically calculated chemical shifts for the different coordination numbers such as 2, 6, 7, and 8.

Summary and Conclusions

Even though cadmium chemical shifts are valuable in understanding the role of metals, such as zinc or calcium, in the function of chemical and biological complexes, chemical principles underlying the variation of ^{113}Cd chemical shifts are not well characterized. Availability of ultrahigh magnetic fields (ca. 900 MHz) and a plethora of higher resolution multidimensional solid-state NMR techniques would enable experimental analysis of ^{113}Cd CSA tensors from a variety of biological systems such as metalloproteins and metal-bound RNA. In addition, recovery of CSA tensors under fast magic-angle spinning conditions provides ^{113}Cd CSA tensors from multiple sites of a complex. Therefore, ab initio studies are inevitable to understand the experimentally determined ^{113}Cd CSA tensors.

All of the previous studies determined the influence of various basis sets on cadmium chemical shifts in two dialkylcadmium compounds, namely, dimethylcadmium and diethylcadmium using the Hartree−Fock method. In this paper, we have reported the influence of three basis sets, 3-21G, DZVP, and Sadlej on cadmium chemical shifts. In addition, we were also able to compare GIAO/DFT method with HF.

Comparison of calculated and experimental ^{113}Cd chemical shift values suggests that the density functional method is more accurate than the Hartree−Fock method. As reported earlier, the nature of the cadmium basis set used in the calculation affects the chemical shift value. The basis set 3-21G is the least significant, and both DZVP and Sadlej basis sets resulted in reasonable values for dialkylcadmium compounds.

Further studies on cadmium nitrate and cadmium acetate suggest that the use of the Sadlej basis set is important not only in finding ^{113}Cd chemical shift values but also in accurately determining the magnitude of the principal elements of the CSA tensor. Despite the 30 ppm difference in the theoretical and experimental chemical shift values, the use of the DFT/Sadlej method resulted in completely different theoretical chemical shift values for various coordination numbers. Implementation of this method should surely be valuable in identifying coordination numbers in discrete moieties such as Cd−porphyrin complexes. To understand the effect of secondary interactions, we are currently working on bioinorganic cadmium complexes for which the CSA tensors are being characterized using solid-state NMR experiments. One of the drawbacks of this method is the computational time. Increasing the number of atoms from 25 in Cd1Ac to 74 in Cd2Ac slowed the computation time from 1 day to 14 days. However, with the availability of faster computers and parallel computing facilities, performing calculations on larger networks should be feasible soon.

Though this study is restricted to a few molecules, it can be applied on model complexes mimicking discrete active binding sites in cadmium-containing proteins. Finally, it may be pointed out that a difference of 30 ppm between theoretical and experimental chemical shift values can be considered reasonably good as this would amount to 3% of the ^{113}Cd CSA span (about 1000 ppm) for various cadmium molecules.

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