^{113}Cd Shielding Tensors of Monomeric Cadmium Compounds Containing Nitrogen Donor Atoms. 3. CP/MAS Studies on Five-Coordinate Cadmium Complexes Having N_3X_2 (X = H, N, O, and S) Donor Atoms

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The principal elements of the ^{113}Cd shielding tensor for a set of five- coordinate compounds having mixed donor atoms coordinating to the cadmium were determined via CP/MAS NMR experiments. The first complex, $[HB(3,5\text{-}Me_2pz)_3]CdBH_4$ (where pz = pyrazolyl), has a CdN_3H_2 inner coordination sphere. The isotropic chemical shift in the solid state is 355.1 ppm, and its chemical shift anisotropy (CSA, $\Delta\sigma$**)** is −596 ppm with an asymmetry parameter (η) of 0.64. The second complex, $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$, has five nitrogen donor atoms bonded to the cadmium. This N_5 or N_3N_2 compound was the only material of this study to manifest dipolar splitting of the cadmium resonance from the quadrupolar ^{14}N. The isotropic chemical shift, CSA, and the value of η for this material were therefore determined at higher field where the dipolar splitting was less than the linewidth, yielding values of 226.6 ppm, −247 ppm, and 0.32, respectively. A second N_5 material, $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2\text{-}pz)_2]$, was also investigated and has an isotropic shift of 190.2 ppm, a CSA of 254 ppm, and an η of 0.86. Also studied was $[HB(3\text{-}Phpz)_3]Cd[(Bu^tCO)_2CH]$, which has an CdN_3O_2 inner core. The isotropic chemical shift of this complex is 173.6 ppm, and the values of $\Delta\sigma$ and η were determined to be −258 ppm and 0.38, respectively. The final compound, $[HB(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$, with N_3S_2 donor atoms, has an isotropic shift of 275.8 ppm, an η of 0.51, and a CSA of +375 ppm. Utilizing previous assignments, the most shielded tensor element was determined to be oriented normal to the plane of the tridentate ligand. The shielding tensor information is used to speculate on the coordination geometry of the CdN_3O_2 inner core complex.

Introduction

Cadmium-113 is an effective spin-spy used in NMR to probe the active site in metalloproteins where the native metals have poor spectroscopic properties (i.e., Ca^{+2}, Zn^{+2}, Cu^{+2}, Mn^{+2}, $Fe^{+2/+3}$, and Mg^{+2}). Due to the large chemical shift range of cadmium (in excess of 900 ppm) and the sensitivity of the chemical shift to coordination number, donor atom type, and ligand geometry, ^{113}Cd NMR has been widely used as a tool for elucidation of structural features in metal coordination chemistry.[1] In parts 1 and 2 of this series the magic angle spinning (MAS) spectra of a complex with an CdN_4 inner core and several CdN_6 inner core complexes were analyzed.[2] The N_4 compound allowed a comparison between the planar coordination of a porphyrin N_4 and the near-tetrahedral geometry of the poly(pyrazolyl)borates. The N_6 complexes show the effects of ligand geometry on the cadmium shielding tensors. The chemistry of the pyrazolylborate ligands allows for manipulations of both the coordination geometry and donor atom selection.

Most native metalloproteins and/or enzymes, however, have mixed donor atoms bound to the metal center. What is needed is a basis set of model compounds for facilitating interpretation of protein data. This study examines several five-coordinate species with donor atoms of N_3X_2 (where X is H, N, O, and S). The poly(pyrazolyl)borate family of ligands are used to form the N_3 donor set. The composition of the N_3 donor ligand is constant in three of the complexes with methyl substituents in the 3- and 5-positions of the pyrazolyl rings. For the remaining two compounds the pyrazolyl rings have a phenyl group in the 3-position. The other ligand (the bidentate chelate) is varied to determine the effects of the different donor atoms upon the chemical shift tensor.

The early studies of cadmium−oxo compounds have shown that ligated water oxygen atoms are the most deshielding oxygen ligands and that the most shielding contributions are determined by the longest cadmium donor atom bond.[1] There have been four empirical correlations deduced about the relationship between structure and shielding for cadmium complexes with oxygen donor atoms:[3−11] (1) Tensor elements of like magnitude have similar orthogonal environments. (2) The most deshielded element is aligned nearly orthogonal to planes containing water. (3) In the absence of water oxygens in the coordination sphere,

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Table 1. ^{113}Cd Shielding Tensors[a] Obtained from Magic Angle Spinning Experiments

complex	σ_{iso}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma^b$	η^c	ref
$[H_2B(pz)_2]_2Cd$	291.9	388.9(6)	381.6(7)	105.3(3)	−280.0	0.04	2a
$[HB(3,5\text{-}Me_2pz)_3]_2Cd$	175.2	250.2(5)	240.3(5)	35.1(2)	−210.2	0.07	2a
$[B(pz)_4]_2Cd$	217.7	369.9(2)	250.5(3)	32.8(4)	−277.3	0.65	2a
$[B(3\text{-}Mepz)_4]_2Cd$	188.1	296.0(2)	255.8(3)	12.5(3)	−263.4	0.23	2a
$[HB(3,5\text{-}Me_2pz)_3]CdBH_4$ (**1**)	355.1	681.5(4)	426.0(3)	−42.2(5)	−596.0	0.64	this work
$[HB(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$ (**2**)	275.8	85.9(3)	215.3(5)	525.5(4)	374.9	0.51	this work
$[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$ (**3**)	226.6	335.7(5)	282.3(4)	61.6(3)	−247.4	0.32	this work
$[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**4**)	190.2	33.1(3)	178.3(2)	359.3(2)	253.6	0.86	this work
$[HB(3\text{-}Phpz)_3]Cd[(Bu^tCO)_2CH]$ (**5**)	173.6	292.8(8)	226.6(7)	1.3(3)	−258.4	0.38	this work

[a] Positive ^{113}Cd shifts denote lower shielding than external 0.1 M $Cd(ClO_4)_2$ at 0 ppm. [b] $\Delta\sigma = \sigma_{33} - {}^1/_2(\sigma_{11} + \sigma_{22})$. [c] $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\mathbf{iso}})$.

the least shielded tensor element is oriented to maximize the shortest Cd−O shielding contributions. (4) The most shielded tensor element is nearly perpendicular to the longest Cd−O bond.

Santos et al.[12] and others[2,13,14] have extended the rules to other atoms bonded to cadmium (i.e., selenium and/or sulfur). In each case, the applicable paradigms have proven to be generalized to these other ligand systems. In general for monodentate ligands, the deshielding of the ^{113}Cd increases in the order of O < N < S.[15] This ordering can be broken by geometrical constraints if for example a Cd−N bond is longer than a Cd−O bond in the same coordination sphere.[16]

The goal of the present investigation is to explore the cadmium shielding environments of mixed ligand coordination compounds. Reported here are the solid state ^{113}Cd NMR data for the compounds $[HB(3,5\text{-}Me_2pz)_3]CdBH_4$, $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$, $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$, $[HB(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$, and $[HB(3\text{-}Phpz)_3]Cd[(Bu^tCO)_2CH]$ (pz = pyrazolyl).

Experimental Section

Preparation. The syntheses of two of the compounds studied here, $[HB(3,5\text{-}Me_2pz)_3]CdBH_4$ and $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$, were accomplished as discussed by Reger et al.[17] Syntheses of $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$, $[HB(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$, and $[HB(3\text{-}Phpz)_3]Cd[(Bu^tCO)_2CH]$ are reported in a separate publication.[18]

^{113}Cd NMR Spectroscopy. The solid state ^{113}Cd NMR experiments were performed at 7.05 T (66.547 MHz Larmor frequency for ^{113}Cd) either on a Varian Associates XL-300 instrument in a narrow-bore Varian magnet or a Varian Unity$^+$ 300 with a wide-bore Oxford Instruments magnet. When a higher field was required, a Varian Associates XL-400 instrument (operating at 9.4 T) was used with a standard-bore Oxford Instruments magnet. The samples were ground and packed into 7 mm o.d. zirconia rotors with Kel-F end caps for use in a Doty Scientific, Inc., 7 mm standard speed MAS probe (7 mm Supersonic MAS probe with the Unity$^+$). All chemical shifts and shielding tensor elements are referenced to an external sample of 0.1 M $Cd(ClO_4)_2$ in a 1:1 H_2O/D_2O solution at 25 °C, with positive shifts denoting resonances to lower shielding. Since the chemical shift and shielding are referenced on a common scale, we are therefore defining the isotropic chemical shift and the isotropic shielding to be identical ($\delta \equiv \sigma_{iso}$). This common reference facilitates a direct comparison between not only the individual shielding tensor elements but the elements for each complex. The convention we are following is $|\sigma_{33} - \sigma_{iso}| \geq |\sigma_{11} - \sigma_{iso}| \geq |\sigma_{22} - \sigma_{iso}|$.

The cadmium resonances were observed under MAS conditions by utilizing a single contact cross-polarization (CP) sequence with proton decoupling.[19] The ^1H $\pi/2$ was 6 μs, the contact time used was 6 ms, and the recycle delay was 30 s for all samples except for the compound with the oxygen donor atoms which had a recycle delay of 5 s. Typical spinning speeds were 2−3 kHz for slow spinning and 5−7 kHz for fast spinning; at least two speeds were used to determine the isotropic peak.

The principal elements of the shielding tensor were determined by utilizing a program written in our laboratory which has an X11 interface (motif) and runs on both a VAXstation 3540 and a Silicon Graphics Onyx (R4400 series CPU).[20] Rather than relying upon accurate measurements of a few of the spinning side band intensities as with the Herzfeld−Berger approach,[21a] this code uses every point of the data. A nonlinear least squares analysis is performed on the overlap integral of the line shape calculated from a moment analysis (as described by Maricq and Waugh)[21b] and the experimental data. The asymmetry parameter and two of the three tensor values were optimized with either a SIMPLEX or Levenberg−Marquardt algorithm.[21c] The calculations assumed no couplings (neither dipolar nor scalar); however, Gaussian line broadening was added to simulate the line width resulting from these effects.

Results

Summarized in Table 1 are the isotropic shieldings, the principal elements of the shielding tensors, the chemical shift anisotropies (CSA, $\Delta\sigma$) and the asymmetry parameters, η, of the five-coordinate compounds studied here. Also tabulated, for reference, are the results determined for the four- and six-coordinate nitrogen donor complexes of part 1 in this series.[2a]

The isotropic chemical shift of $[HB(3,5\text{-}Me_2pz)_3]CdBH_4$ (**1**) is 355.1 ppm in the solid state. The CSA and the value of η are −596.0 ppm and 0.64, respectively. Experimental and simulated spectra of **1** are compared in Figure 1a,b, respectively, and a difference spectrum is presented in Figure 1c. The broadening of the spinning side bands from 250 to 0 ppm in the experimental spectrum results from the presence of an impurity of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ which could not be completely removed.

Replacing the η^2-borohydride ligand with a sulfur donating ligand to give N_3S_2 coordination makes distinct changes in the shielding environment. The isotropic chemical shift of [HB-

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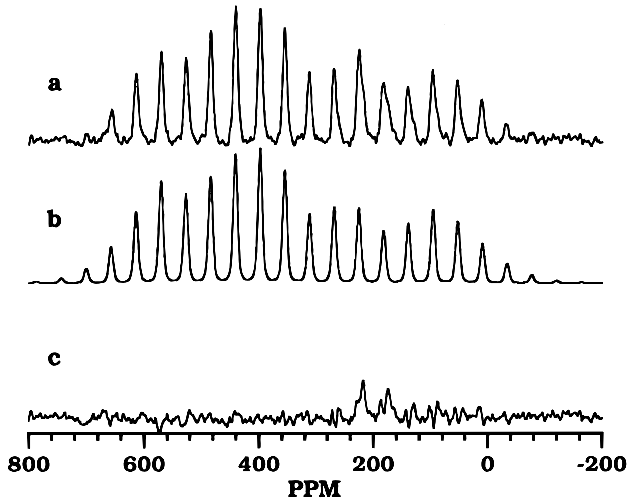

Figure 1. CP/MAS data of $[HB(3,5\text{-}Me_2pz)_3]CdBH_4$ (**1**) spinning at 2873 Hz without regulation: (a) experimental spectrum, (b) simulation using 200 Hz Lorentzian and 290 Hz Gaussian line broadening, and (c) the difference spectrum of a and b showing the impurity of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$.

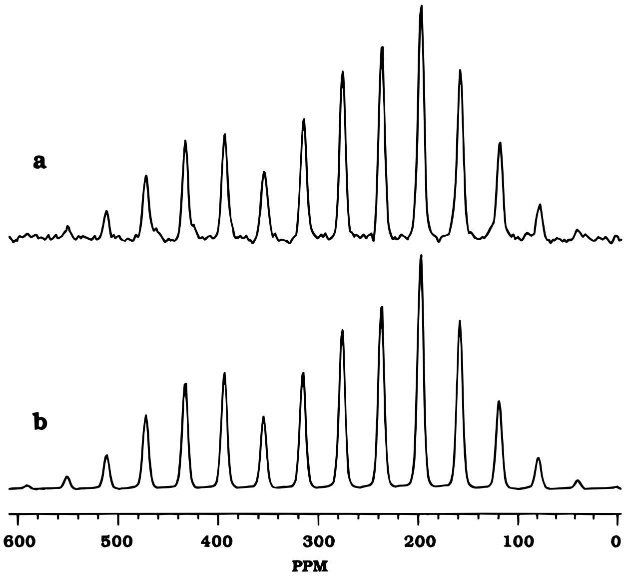

Figure 2. CP/MAS data of $[HB(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$ (**2**) with nonregulated spinning at 2630 Hz: (a) experimental spectrum and (b) simulation using 100 Hz Lorentzian and 275 Hz Gaussian line broadening.

$(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$ (**2**) is 275.8 ppm. The η value for the N_3S_2 is 0.51, and $\Delta\sigma$ is +374.9 ppm, which is opposite in sign to nearly all of the poly(pyrazolyl)borate cadmium complexes investigated thus far. The comparison of the experimental and simulated spectra is shown in Figure 2.

The first of the complexes combining different poly(pyrazolyl)borate ligands, $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$ (**3**) has five nitrogens coordinating to the cadmium and was the only sample in this study to manifest dipolar splittings from the ^{14}N in the ^{113}Cd MAS spectra. In order to determine the principal elements of the shielding tensor for this compound and to verify that the splitting was indeed the result of a dipolar interaction, the CP/MAS spectrum was acquired at a higher field, 9.4 T. The experimental spectra acquired at both fields and the simulation of the high-field spectrum are compared in Figure 3. The dipolar coupling is shown in an expanded region around the isotropic resonance of the spectrum acquired at 7.05 T. The simulated line shape was calculated by using an isotropic resonance of 226.6 ppm, a $\Delta\sigma$ of -247.4 ppm, and an η = 0.32.

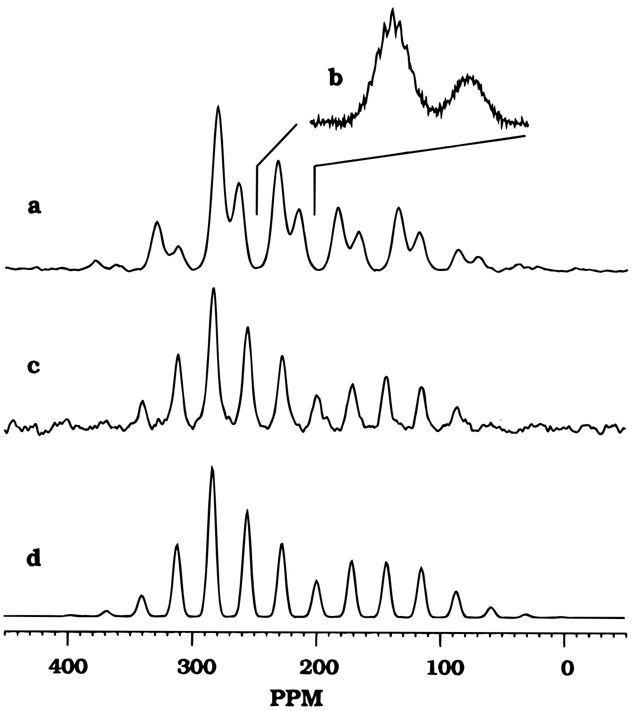

Figure 3. CP/MAS data of $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$ (**3**): (a) experimental spectrum at 7.05 T with nonregulated spinning at 3200 Hz, (b) 50 ppm expansion of the region surrounding the isotropic resonance of a, (c) experimental spectrum at 9.4 T with nonregulated spinning at 2504 Hz, and (d) simulation using 200 Hz Lorentzian and 378 Hz Gaussian line broadening of the data in c.

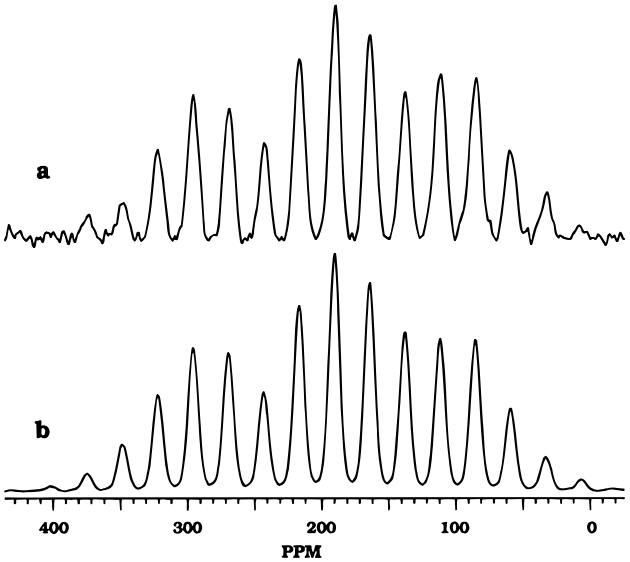

Figure 4. CP/MAS data of $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**4**) with regulated spinning at 1750 Hz: (a) experimental spectrum and (b) simulation using 100 Hz Lorentzian and 325.8 Hz Gaussian line broadening.

In contrast to **3**, $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**4**) is a second N_5 central core complex which does not manifest any visible dipolar or scalar couplings. The tridentate nitrogen donor ligand of this second mixed poly(pyrazolyl)borate complex comes from a slightly different nitrogen donor chelate, the tris-3-phenyl-substituted poly(pyrazolyl)borate ligand rather than the tris-3,5-dimethyl substituted one. The bidentate ligand is also different, now a dihydrobis(3,5-dimethylpyrazolyl)borate ligand versus a nonsubstituted dihydrodipyrazolylborate.

Figure 4 depicts the experimental and simulated spectra for this complex. A slight impurity of the six-coordinate, homoleptic compound (in this case $[HB(3\text{-}Phpz)_3]_2Cd$) can be seen in the broadening of the side bands from 0 to 125 ppm. The

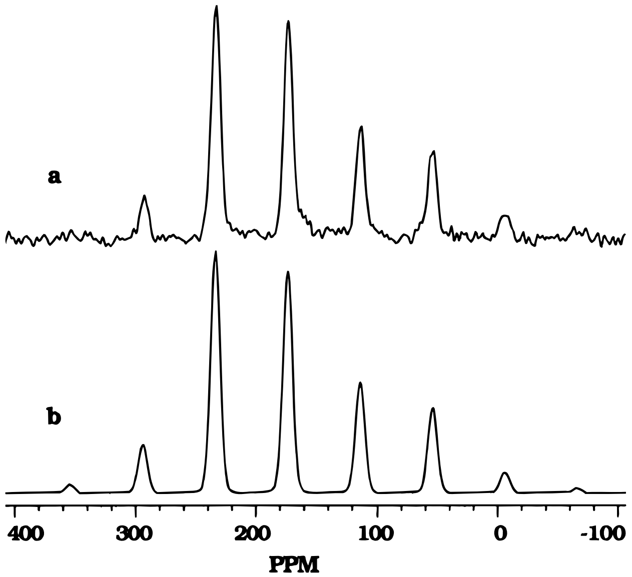

Figure 5. CP/MAS data of [HB(3-Phpz)$_3$]Cd[(Bu^{t}CO)$_2$CH] (**5**) with regulated spinning at 4000 Hz: (a) experimental spectrum and (b) simulation using 50 Hz Lorentzian and 250 Hz Gaussian line broadening.

value of $\Delta\sigma$ for this second N_5 complex, **4**, is 253.6 ppm, with an η of 0.86 and an isotropic chemical shift of 190.2 ppm. An important difference between the two N_5 coordination complexes is the opposite sign of the shielding anisotropy.

The final complex investigated in this study is a mixed nitrogen and oxygen donor compound, [HB(3-Phpz)$_3$]Cd[(Bu^{t}CO)$_2$CH] (**5**). The CP/MAS data of the N_3O_2 donor atom complex are depicted in Figure 5 with the simulated spectrum. The isotropic shift of **5** was 173.6 ppm in the solid state with a $\Delta\sigma$ of -258.4 ppm and an η of 0.38.

Discussion

A graphical representation of the principal elements of the shielding tensors of the five complexes discussed here are included in Figure 6. Also incorporated in the plot, for comparison, are the tensor elements for the six- coordinate compounds from part 1 of this series[2a] and an alkyl derivative which has three nitrogen donor atoms and a methyl group bound to the metal (from unpublished results). The similarity of the most shielded element of the CdN_6 complexes allows for the orientation of that tensor element. From the symmetry of [HB(3,5-Me$_2$pz)$_3$]$_2$Cd, this component was assigned to be orthogonal to the plane defined by the coordinating nitrogens of the tridentate ligand.[2] A model of the tridentate ligand coordination and the most shielded tensor element is depicted in Figure 7.

Figure 8 shows the structure of **2** determined from X-ray crystallography[18] and highlights the least squares plane that contains $N_1{-}N_3{-}N_5$. A second plane is defined by $S_1{-}Cd{-}S_2$, which makes an angle of 94.2° with the first plane. It is this second plane that directs the most deshielded tensor element, σ_{33}. That is, σ_{33} is normal to the plane containing S_1, Cd, and S_2. The $S_1{-}Cd{-}S_2$ plane also contains a nitrogen donor atom of one of the pyrazolyl rings. This nitrogen adds extra shielding (or deshielding) that has to be considered when the different donor atoms are ranked.

From the X-ray structure of **1**,[17a] the average cadmium−nitrogen bond distance of the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand is 2.255 Å, which can be contrasted with the average of 2.348 Å from [HB(3,5-Me$_2$pz)$_3$]$_2$Cd.[17b] The BH_4^- coordination of **1** also forces an asymmetry of the poly(pyrazolyl)borate ligand, which has one short and two longer Cd−N bonds. The borohydride is tilted away from the short Cd−N bond, making an angle of 165.4° between the two borons through the cadmium center.

The orientation of σ_{33}, the most shielded tensor element for this complex, is tilted to reflect the asymmetry of the Cd−N coordination; favoring the longer bonds. This trend was also seen in the first part of this series with the six-coordinate complexes. Similarly, the N_3S_2 compound has one long and two short Cd−N bonds, which is reflected in the shielding difference of the most shielded tensor element for **1** and **2**. The relationship between this tensor element and the average Cd−N bond length or the root mean square distance of the cadmium to the plane defined by the coordinating nitrogens has been investigated.[2,22]

As with the bidentate sulfur ligand, the orientation of the most deshielded tensor element is directed to maximize the effect of the two bridging hydrogens. However, it should also be considered that each bridging hydride system is a three center/two electron bond, making the Cd(μ-H)$_2$B coordination a four center/four electron bond. The large CSA observed for this complex, $\Delta\sigma$ of -601 ppm, resembles that of the N_3X coordination (where X is an alkyl group) which can have anisotropies on the order of 1000 ppm (see the methyl example in Figure 6).

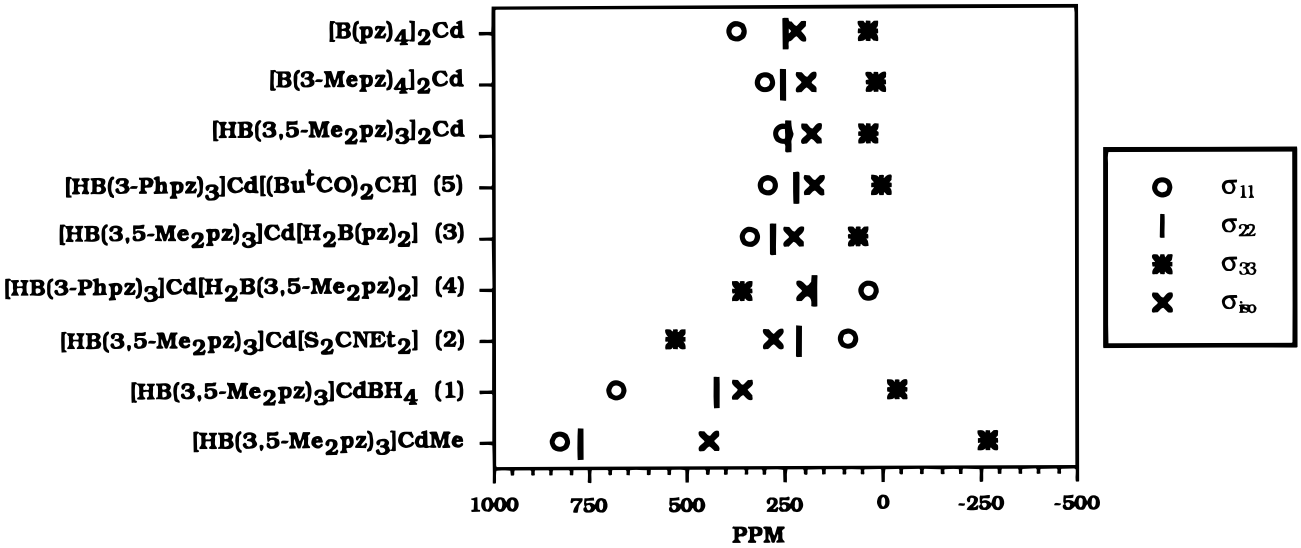

Figure 6. Pictorial representation of the individual elements of the shielding tensor of the six-coordinate complexes of ref 2a, the compounds studied here, and an alkyl derivative.

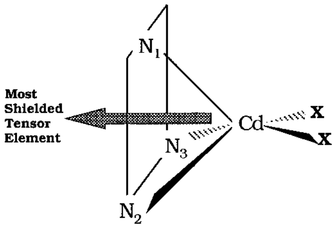

Figure 7. Simple depiction of the nitrogen donor atoms of the tridentate poly(pyrazolyl)borate ligand coordinating to a cadmium center and the orientation of the most shielded tensor element. Where "X" can represent either a monodentate, bidentate, or tridentate ligand.

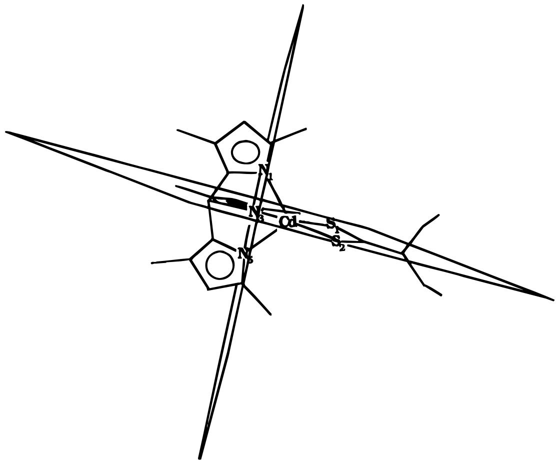

Figure 8. Illustration of the least squares planes of 2 defined by the donor nitrogen atoms of the tridentate chelate and S_1−Cd−S_2.

The remaining structural information pertains to the mixed poly(pyrazolyl)borate complex, [HB(3-Phpz)$_3$]Cd[H$_2$B(3,5-Me$_2$-pz)$_2$] (**4**).[18] The orientational assignment of the principal components of the shielding tensor are similar to the other complexes. The most shielded tensor element is aligned toward the plane of coordinating nitrogens of the η^3-[HB(3-Phpz)$_3$]$^-$ ligand. The deshielded tensor element is orthogonal to the plane defined by the bidentate [H$_2$B(3,5-Me$_2$pz)$_2$]$^-$ nitrogen donors. These planes are illustrated in Figure 9a and have a 103.4° plane angle.

In contrast to the coordination geometry depicted in Figure 8, we see in Figure 9a that the plane defined by the bidentate ligand no longer contains a donor atom from the tridentate chelate. However, for another perspective, we can rotate the plane to contain four of the coordinating nitrogens (two from each ligand), as pictured in Figure 9b. The metal now sits 0.3 Å above the new plane, and the third nitrogen of the tridentate ligand sits above the metal. This "axial" donor is 15.5° from the normal of the plane. The coordination scheme described here strongly resembles that of a porphyrin system with an axial ligand bound to the metal, which has been lifted out of the plane of the porphyrin. In other words, we can think about this coordination scheme as N_4N rather than N_3N_2 (or N_5).

Although the structure of [HB(3,5-Me$_2$pz)$_3$]Cd[H$_2$B(pz)$_2$] (**3**) is unknown, we can speculate that it resembles the square pyramidal arrangement of **4**. This follows from the variable temperature ^{1}H NMR data of Reger et al.,[17b] which show the two rings of the [H$_2$B(pz)$_2$]$^-$ ligand to be equivalent even at temperatures down to −89 °C. The proton resonances of the three pyrazolyl rings from the tridentate ligand also support this as they are equivalent at room temperature and split into the ratio 2:1 at −89 °C.

If we now assume that the two N_5 structures are similar, why then do they have shielding anisotropies of opposite sign? This question has been asked regularly when attempts are made to interpret the solid state NMR data of Cd^{+2} substituted myoglobin.[23] Figure 10 contrasts the shielding tensor information for some porphyrin systems[23−25] (and texaphyrin)[26] and the poly(pyrazolyl)borates. In all three five-coordinate, model porphyrin systems, Cd−TPP−pyridine, Cd−TPP−piperidine, and Cd−PPIXDME−pyridine, the sign of the anisotropy was positive; however, for the myoglobin sample it was negative. Kennedy et al. attributed this to the histidine pulling the metal out of the plane of the porphyrin.[23] In a subsequent crystallographic investigation it was revealed that the metal is already out of the porphyrin plane of the model compounds before binding an axial ligand (i.e., in Cd−TPP the metal is 0.58 Å out of the plane).[27] Therefore, another explanation is required to rationalize the changes in the shielding environment.

The magnitudes of the most shielded and most deshielded tensor elements for **3** and **4** are similar, as one would expect for similar environments; however, the sign of the anisotropy is reversed. The main difference arises in the σ_{22} element, which is responsible for the sign of the CSA. In the simple porphyrin models, Cd−TPP and/or Cd−PPIXDME, the shielding tensor is axially symmetric. Simply pulling the metal out of the plane of the porphyrin is not enough to disturb the symmetry, nor is adding an axial ligand which has high mobility. If the axial ligand can freely rotate about the axis of symmetry, then the shielding tensor is likely to remain near $\eta = 0$. An example of this is the comparison between pyridine and piperidine as axial ligands for Cd−TPP. The pyridine has virtually no barrier to rotation;[28] however the piperidine requires greater than 30 kcal/mol to rotate about the Cd−N axis.[25] In this case, the σ_{22} element moves away from the σ_{11} element and η is consequently closer to one.

With the coordination geometries of **3** and **4** and the subsequent assignment of the tensor element orientations, we now have some clues as to the shielding environment of the porphyrin models. As before, the most shielded element samples the current density of the tridentate chelate, and the most deshielded element is aligned orthogonal to the porphyrin (-like) plane. This forces σ_{22} to fall under the influence of the axial bond, whose changing bond distance can result in large changes in the shielding of this element. The tilt angle of the ligand also influences the shielding to some degree. The effects of both axial bond distance and tilt angle in a five-coordinate model for myoglobin are the subject of an ***ab initio*** chemical shift investigation.[29]

Although there is no crystal structure for the Cd^{+2} substituted myoglobin, we can now speculate as to what is happening in the shielding environment. Working from a previously reported structure of the deoxy form of myoglobin, we can see that the metal does indeed sit above the plane, as Kennedy et al. surmised, and the Cd−N bond of the proximal histidine residue is tilted from the normal of the heme plane.[30] One can now

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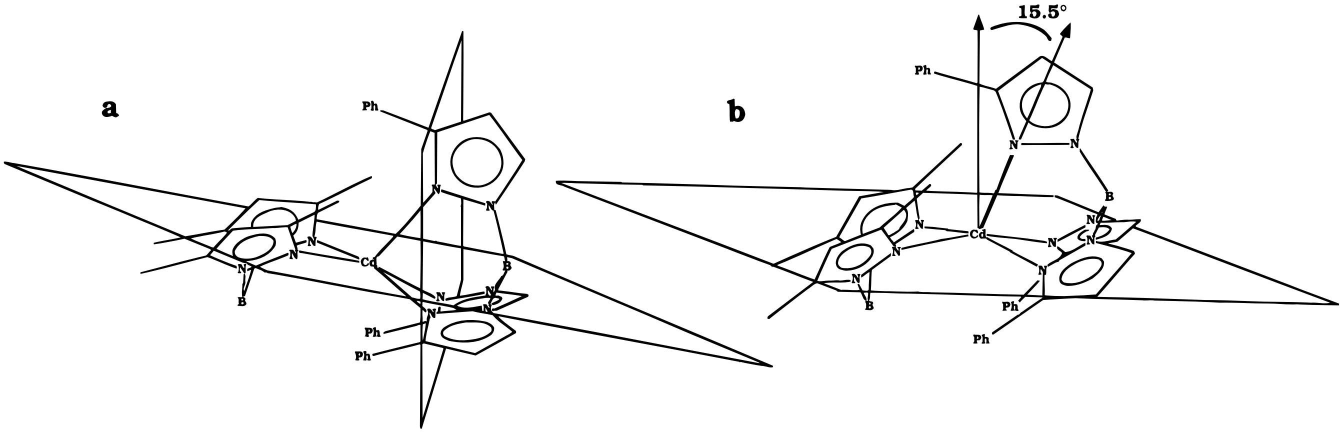


Figure 9. Representation of the different orientations of the least squares planes of 4 where the definitions are (a) the coordinating nitrogens of the tridentate ligand as one plane and the donor nitrogens of the bidentate ligand and the metal included in the other or (b) two of the donor nitrogens from the tridentate ligand and both the donor atoms of the bidentate chelate, making a plane with the metal ≈0.3 Å above it, and the remaining donor nitrogen of the tridentate ligand being 15.5° from the normal of the plane.

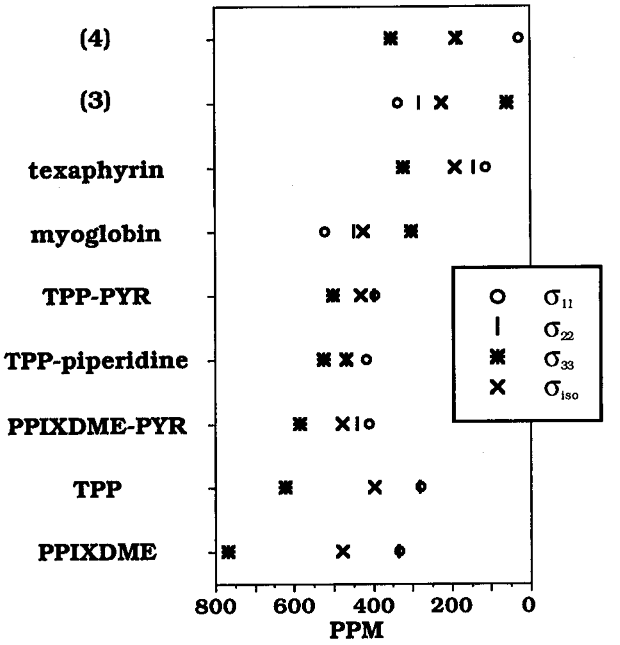


Figure 10. Depiction of the individual elements of the shielding tensor of several porphyrin (or porphyrin-like) cadmium compounds.

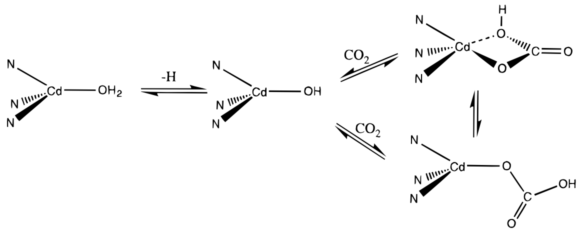
theorize that the length of the Cd−N bond from the axial histidine is small enough at that tilt angle to account for the crossover of $\Delta\sigma$.

If the structure of **5** were similar to the porphyrin-like structure of the all nitrogen coordination compounds, one would expect the shielding tensor elements to be aligned in the same orientations. The most shielded element would be normal to the plane of the coordinating nitrogens of the tridentate chelate, and the least shielded element is orthogonal to the plane defined by the donor atoms of the bidentate ligand and two of the nitrogens from the pyrazolylborate. This second plane allows for a direct comparison of the deshielding ability of the bidentate ligand in the deshielded tensor element, σ_{11}. As oxygen ligands are known to cause greater shielding than nitrogen donors, it is surprising that the σ_{11} element is similar for both donor atom combinations.

This implies that **5** has a similar structure to the N_3S_2 coordination complex, **2**. In that configuration, the plane sampled by the most deshielded tensor element is defined by the two donor atoms of the diketonate ligand and the metal. Remember that one of the coordinating nitrogens of the tridentate ligand also falls into this plane, adding its deshielding effects. As the metal is included in this plane, the electronic environment around the cadmium should be more affected in this configuration. Another piece of supporting information is the steric consideration of the side chains on each ligand. The butyl groups of the oxygen donor ligand would be oriented directly at the phenyl rings of the tridentate chelate if the structure of **5** resembled that of **4**.

What we have seen is basically two forms of five-coordinate geometries for cadmium. The first has three donor atoms and the metal in a plane with the remaining two donor atoms sitting above and below the plane. This arrangement describes the coordination of **2** and probably **5** as well. The second form is the porphyrin-like geometry of **3** and **4**, where four donor atoms make a plane below the metal with the fifth donor atom binding "axially". Complex **1** also seems to take this form, but the four center/four electron bond causes further changes in the shielding environment than what one might expect considering only the geometry of the first coordination sphere. Although it is unclear at this point what factors determine the form of the coordination, interpretation of the solid state NMR line shape can give confidence in one geometry over the other.

This technique for structure differentiation can be important as it has been suggested that the activity of metal substituted enzymes can be influenced by coordination mode. The question of coordination mode can be the number of ligands, the geometry of binding, or both. An example is the hypothetical bicarbonate intermediate of the carbonic anhydrase catalytic cycle (i.e., unidentate vs bidentate coordination) depicted in eq 1. Armitage and co-workers demonstrated a dependence upon counterion and pH in the ^{113}Cd NMR spectra of the cadmium substituted enzyme.[31] They determined that the enzyme was in rapid exchange between at least two species, such as in the first step of eq 1. This was followed up by a study of Sudmeier and co-workers who observed both a high- and a low-pH form



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of various ^{113}Cd substituted carbonic anhydrases.[32] They also reported a shift to higher shielding for the carbonate ligand, 216 ppm for the high-activity HCAC and 164 ppm for the low-activity HCAB.[32b] This 52 ppm difference is a measure of the different coordination environments; however, without more information, such as the individual shielding tensor elements, one cannot make a precise judgment about the type of coordination. The possibilities include uni- versus bidentate coordination of the bicarbonate ligand or the presence of bound water. Either example or a combination of both are plausible explanations for this difference in the isotropic chemical shifts.

A recent structure has been reported of a bicarbonate complex of a mutant of carbonic anhydrase which indicated asymmetric, but bidentate, coordination to the zinc.[33] This supports the hypothesis that a pentacoordinate species (of the native zinc) is involved in the catalytic cycle. In addition to our own work, Parkin and co-workers have generated several models in an attempt to understand the coordination preferences of each of the metals, Zn and Cd.[34] A solid state NMR comparison of the Cd(II) enzyme (with and without added CO_2 or HCO_3^-), the N_3O_2 complex, and an N_3O model compound would be of some utility in answering some of the coordination questions. From the methyl derivative shown in Figure 6, one would expect a four-coordinate species to have a dramatically different CSA than the five-coordinate complex shown here. This set of experiments is currently under way in our laboratory.

Conclusions

In summary, we have determined the principal elements of the shielding tensors of a series of five-coordinate cadmium compounds. The apparent order of the deshielding of the bidentate ligand follows the trend $H \gg S \gg N > O$. However, ligand geometry also seems to play an important role as shielding planes may be modified to include (or exclude) donor atoms, thus complicating any interpretation. The all nitrogen coordination compounds have also given new insight into the shielding environments of the cadmium substituted porphyrin systems, in particular cadmium(II) myoglobin.

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