

^{113}Cd Shielding Tensors of Monomeric Cadmium Compounds Containing Nitrogen Donor Atoms. 1. CP/MAS Studies on Cadmium Poly(pyrazolyl)borate Complexes Having N_4 and N_6 Coordination Environments

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Abstract: The principal elements of the ^{113}Cd shielding tensor for a series of complexes containing nitrogen donor atoms were determined via cross polarization/magic angle spinning (CP/MAS) nuclear magnetic resonance experiments. The N_4 coordination compound $[\text{H}_2\text{B}(\text{pz})_2\text{Cd}]$ has an isotropic chemical shift of 291.9 ppm (all ^{113}Cd chemical shifts are referenced to an external sample of 0.1 M $\text{Cd}(\text{ClO}_4)_2$ in 1:1 H_2O) in the solid state. The chemical shift anisotropy and asymmetry parameter of $[\text{H}_2\text{B}(\text{pz})_2\text{Cd}]$ are 280.0 ppm and 0.04 for $\Delta\sigma$ and η , respectively. The three N_6 coordination compounds $[\text{HB}(3,5\text{-Me}_2\text{pz})_3\text{Cd}]$, $[\text{B}(\text{pz})_4\text{Cd}]$, and $[\text{B}(3\text{-Mepz})_4\text{Cd}]$ have the isotropic chemical shifts of 175.4, 217.7, and 187.9 ppm, respectively, in the solid state. The chemical shift anisotropies and asymmetry parameters for these N_6 complexes are -210.2 , -277.3 , and -263.4 ppm and 0.07, 0.65, and 0.23, respectively. Using available X-ray crystallography data and previous shielding/symmetry relations, the ^{113}Cd shielding tensors are described with respect to the molecular axis system.

Introduction

The past 15 years or so have seen the development of a surrogate probe strategy, involving the substitution of Cd^{+2} for Zn^{+2} and/or Ca^{+2} (and more recently for Fe, Mg, Mn, and Cu sites), in the nuclear magnetic resonance (NMR) investigations of metalloproteins.¹⁻⁵ The excellent NMR spectroscopic properties of the cadmium in substituted proteins have allowed valuable information to be extracted from many systems. In this paper, we present a new class of cadmium model compounds that should allow for the easy manipulation of the ligand donor atoms around the metal center to better match the ligand environment of the protein of interest.

The family of ligands used are the poly(pyrazolyl)borates, whose chemistry with cadmium is only now being fully explored. Other model compounds such as cadmium diimidazole diacetate, which has been the only model employed in the interpretation of ^{113}Cd -substituted carboxypeptidase A (CPA), tend to polymerize.⁶ This polymerization makes the structure significantly different from that of the CPA, making the interpretation of the ^{113}Cd shielding tensor data of CPA difficult. In order to correlate the structural changes associated with inhibitor binding to CPA, intelligently crafted model compounds are necessary.

One source of nitrogen coordination model compounds has been the porphyrin family of ligands.⁷⁻⁹ These studies were aimed at understanding such molecules as hemoglobin, that is, sickled systems or other protoporphyrin dependent systems, such as chlorophyll. However, the coordination geometry is not at all similar to that of CPA. The porphyrins have planar coordination, while the models desired are distorted octahedrons and/or tetrahedrons.

The basic structure of the poly(pyrazolyl)borate ligands coordinated to cadmium is depicted in Figure 1. These ligands are extremely versatile because the number of donor atoms can be varied in going from the dihydrobis-, hydrotris-, to tetrakis-(pyrazolyl)borate. The 3- and/or 5-positions of the pyrazolyl rings can also be substituted. By altering the poly(pyrazolyl)borate ligand, we can control the core atoms to range from N_4 to N_6 and to several mixed-ligand donor atom combinations (i.e., N_5 , N_3S_2 , N_3O_2 , N_3H_2 , N_3C , and N_3H).¹⁰

Using these ligands, we can determine the effects of several core atom models of nitrogen ligation on the solution and solid state NMR parameters. By fixing the atoms coordinating to the cadmium and changing substituents on the ligand, the sensitivity of the shielding of the cadmium with respect to subtle changes in its environment can be determined. This critical aspect of ligand design can now be accomplished without the complications introduced by polymerization.

There has also been a long series of studies performed in this laboratory on ^{113}Cd shielding tensors of cadmium-oxo compounds.¹¹⁻¹⁹ From these investigations there have been four

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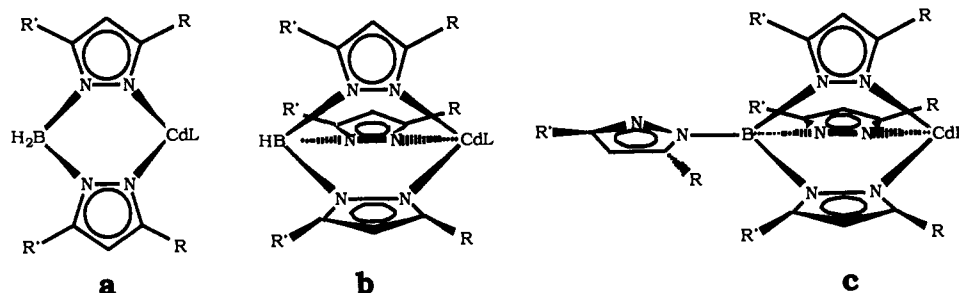


Figure 1. General structures of some poly(pyrazolyl)borate ligands bound to a cadmium: (a) dihydrobis(pyrazolyl)borate, (b) hydrotris(pyrazolyl)borate, and (c) tetrakis(pyrazolyl)borate. The R groups are in the 3-position, and the R' groups are in the 5-position of the pyrazolyl rings, where R and/or R' is H or Me.

empirical correlations deduced between tensor elements (and their relative orientation) and structure: (1) Tensor elements of like magnitude have similar orthogonal environments. (2) The most deshielded element is aligned nearly orthogonal to planes containing water. (3) If water oxygen atoms are not present in the coordination sphere, the least shielded 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. These empirical rules have been extended to other atoms bonded to cadmium, such as cadmium–sulfur or cadmium–selenium coordination systems, by Santos et al.²⁰ and others.^{21,22} In each case, the applicable paradigms have proven to be generalized to these other ligand systems.

These systems however do not give any information about nitrogen coordination. Barrie et al.²³ have explored some nitrogen and oxygen mixed coordinations to cadmium using bis(glycinato)cadmium(II) monohydrate and bis(L-alaninato)cadmium(II) trihydrate. These compounds are both nearly octahedral with N₂O₄ coordination about the cadmium. The solid state spectra of these compounds exhibit fine structure due to a dipolar coupling between ¹¹³Cd and ¹⁴N, which Barrie has utilized to determine the number of nitrogen atoms coupled to the cadmium. Also, in that paper, Barrie and co-workers use the four empirical rules stated above to propose tensor element orientations, although more information (such as a single crystal experiment) is needed to fully determine the relative orientations. To correctly apply the four rules, one must be sure that they are applicable for each coordination; that is, we must confirm that compounds with nitrogen donor atoms follow the patterns laid out by the oxygen coordination compounds.

From the four rules, one can see there is a sensitivity of the shielding tensor to changes in geometry (internuclear distances and orientations within the crystallite) as opposed to the insensitivity of the isotropic shift obtained from solution state NMR. One such case is illustrated by the ¹¹³Cd NMR spectra of ligated Cd²⁺ in protoporphyrin IX dimethyl ester (PPIXDME) and myoglobin. Kennedy and Ellis⁸ measured the solution and solid state chemical shifts for Cd–PPIXDME, Cd–PPIXDME–

pyridine (4- and 5-coordinate, respectively), and Cd–myoglobin and determined the isotropic shifts to be nearly identical for all three. Hence, one might conclude that these systems had common ligands. However, the principal elements of the shielding tensors told another story, as all three compounds had very different chemical shielding parameters. Likewise, the ¹¹³Cd isotropic chemical shifts of bis(glycinato)cadmium(II) monohydrate and bis(L-alaninato)cadmium(II) trihydrate determined by Barrie and co-workers²³ were identical, yet the principal components of the shielding tensor were very different. This illustrates the power of multiphase NMR investigations with so-called “heavy” nuclides such as ¹¹³Cd.

The goal of the present investigation is to explore nitrogen coordination compounds to test the applicability of, and possibly extend, these “rules” with regard to nitrogen coordination chemistry. Reported here are the solid state ¹¹³Cd NMR data for the compounds [H₂B(pz)₂]₂Cd, [HB(3,5-Me₂pz)₃]₂Cd, [B(pz)₄]₂Cd, and [B(3-Me₂pz)₄]₂Cd (pz = pyrazolyl ring).

Experimental Section

Preparation. The compounds studied here, [H₂B(pz)₂]₂Cd, [HB(3,5-Me₂pz)₃]₂Cd, [B(pz)₄]₂Cd, and [B(3-Me₂pz)₄]₂Cd, were prepared as discussed by Reger et al.^{10a}

¹¹³Cd NMR Spectroscopy. The solid state ¹¹³Cd NMR experiments were performed on a Varian Associates XL-300 instrument in a narrow-bore Varian magnet operating at 7.05 T (66.547 MHz Larmor frequency for ¹¹³Cd). 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. All chemical shifts and tensors elements are referenced to an external sample of 0.1 M Cd(ClO₃)₂ in a 1:1 H₂O/D₂O solution at 25 °C, with positive shifts denoting movement of resonances to lower shielding.

The pulse sequence used was a single contact cross polarization (CP) sequence with proton decoupling.²⁴ The ¹H π/2 was 6 μs, the contact time used was 6 ms, and the recycle delay was 30 s for all samples. Typical spinning speeds were 1.8–4.5 kHz; at least two speeds per sample were used to determine the isotropic peak.

The principal elements of the shielding tensor were determined using a SIMPLEX algorithm to optimize the asymmetry parameter and two of the three tensor values with a program run on a VAXstation 3540.²⁵ The calculations assumed no couplings (neither dipolar nor scalar).

Results

The chemical shift information obtained in both the solution and solid state is summarized in Table 1. The principal values of the shielding tensors, the chemical shift anisotropy (CSA, Δσ), and the asymmetry parameter, η, are also tabulated.

The isotropic chemical shift for [H₂B(pz)₂]₂Cd (1) is 291.9 ppm, and the asymmetry parameter is almost zero (0.04). In this complex, the four nitrogen donor atoms from the two bidentate dihydrobis(pyrazolyl)borate ligands are arranged in a distorted

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Table 1. ^{113}Cd Chemical Shifts^a Obtained from Both Solution and Solid State Experiments

compd	δ^b	σ_{iso}^c	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma^d$	η^e
1	298.7	291.9	388.9(6)	381.6(7)	105.3(3)	-280.0	0.04
2	201.9	175.2	250.2(5)	240.3(5)	35.1(2)	-210.2	0.07
3	221.1	217.7	369.9(2)	250.5(3)	32.8(4)	-277.3	0.65
4	202.5	188.1	296.0(2)	255.8(3)	12.5(3)	-263.4	0.23

^a Positive ^{113}Cd chemical shifts denote lower shielding than that of external 0.1 M $\text{Cd}(\text{ClO}_4)_2$ at 0 ppm. ^b Solution state ^{113}Cd chemical shifts from ref 10a. ^c Solid state ^{113}Cd isotropic chemical shifts from this work. ^d $\Delta\sigma = \sigma_{33} - 1/2(\sigma_{11} + \sigma_{22})$. ^e $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\text{iso}})$.

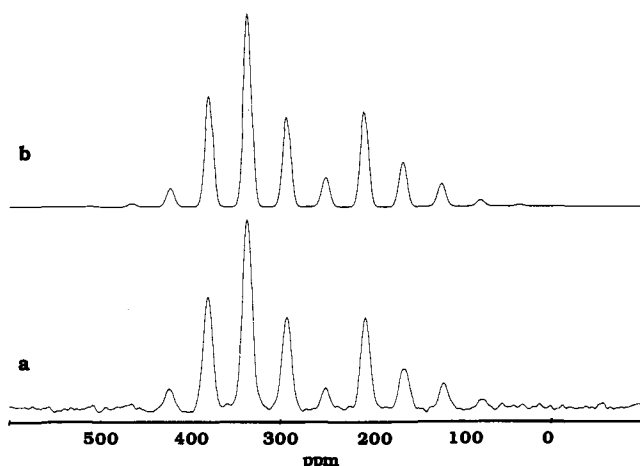


Figure 2. CP/MAS spectrum of $[\text{H}_2\text{B}(\text{pz})_2]_2\text{Cd}$ (1) compared with a simulated result: (a) the experimental data acquired with a spinning speed of 2890 Hz and (b) simulated spectrum of 1 with 200 Hz Lorentzian and 413 Hz Gaussian line broadening.

tetrahedral arrangement about the cadmium atom. This would seemingly account for the low value of η ; however, from the recently obtained X-ray crystal structure, it was determined that a 3-fold axis is absent in the unit cell.²⁶ The space group of 1 is *Pbca*, and the coordination about the cadmium is a distorted tetrahedron. The chelate rings restrict the intraligand N–Cd–N bond angles to an average of 93°. Three of the four interligand angles are fairly similar, averaging 113°, but the fourth is much larger at 132°. The two intraligand N–Cd–N planes are at an angle of 89.7°.

The experimental and simulated spectra for 1 are compared in Figure 2. This compound is interesting in that the only previous data for four nitrogens coordinated to a cadmium have been with porphyrin ligands.^{8,9} A cadmium bound to four nitrogen atoms from a porphyrin ligand has chemical shifts that are more deshielded (480 ppm for Cd–PPIXDME) than those of 1 and a different CSA, +432 ppm for Cd–PPIXDME compared with that determined for 1, –280 ppm.

In distinction to the low symmetry of 1 is $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]_2\text{Cd}$ (2), which has a C_3 axis with six nitrogen atoms coordinating to the cadmium, in contrast with 1, which has four. Rather than the distorted tetrahedral geometry of 1, the structure of 2 now approaches a distorted octahedron. Although the crystal structure shows axial symmetry (space group $R\bar{3}$), η is not zero, which reflects errors in the NMR experiment. The principal source of this error is the lack of “active” spinning speed control utilized in the present experiment. As a result of the spinning speed error of $\Delta\nu$, the n th sideband is broadened by $n\Delta\nu$. This artificial broadening thus adds an uncertainty to the extracted anisotropy and its asymmetry parameter. The asymmetry parameter extracted from the CP/MAS spectra is 0.07. There could also be slight distortions due to a dipolar interaction between the nitrogens and the cadmium.

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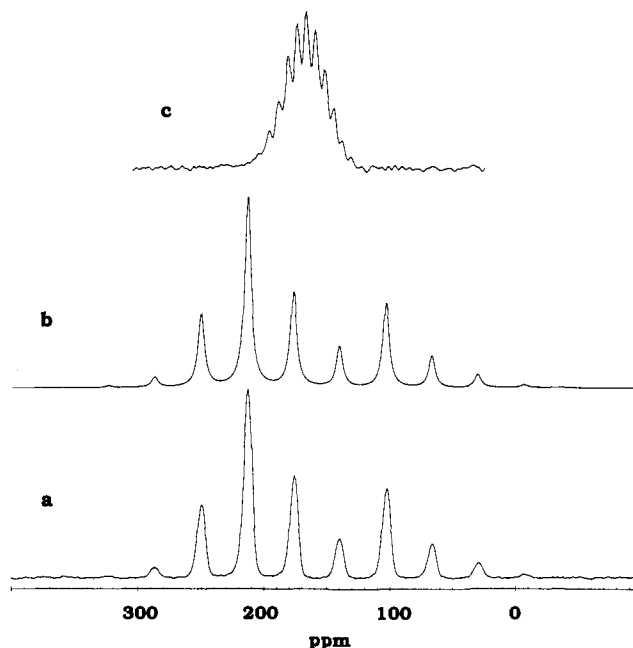


Figure 3. Experimental and simulated spectra of $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]_2\text{Cd}$ (2): (a) experimental spectrum at a spinning speed of 2442 Hz, (b) simulated spectrum using 200 Hz Lorentzian and 231 Hz Gaussian line broadening, and (c) 50 ppm zoom region of the experimental isotropic line with 10 Hz Lorentzian line broadening added.

Compound 2 is the only one in the series that exhibits couplings between the ^{113}Cd and the ^{14}N donor atoms. Figure 3 shows the experimental and simulated spectra and an expanded plot of the isotropic peak of the experimental spectrum, which clearly shows the coupling. Although the simulated data in Figure 3 do not take this coupling into account, the overall effect on the extracted parameters should be minimal.

For comparison, we have studied two other compounds with an N_6 coordination sphere, $[\text{B}(\text{pz})_4]_2\text{Cd}$ (3) and $[\text{B}(3\text{-Mepz})_4]_2\text{Cd}$ (4). These three complexes, 2, 3, and 4, with N_6 coordination provide a perspective of ligand geometry effects on the chemical shielding of the cadmium. Both 3 and 4 have four pyrazolyl rings on each ligand, removing the 3-fold symmetry axis of the ligands present in 2. The effect of substituting the 3-position of the pyrazolyl ring is also explored as the only difference between 3 and 4 is the methylation of that position in 4. This means that for each of the N_6 coordination compounds we have a different number of substituents on the pyrazolyl rings; they range from zero, one, and two methyl groups for 3, 4, and 2, respectively. The solid state structures of these complexes have been determined by X-ray crystallography, and ORTEP plots representing the different N_6 -coordinated compounds can be seen in Figure 4.

Figures 5 and 6 show the respective experimental data and the simulations for compounds 3 and 4 using the tensors extracted from the spinning sideband pattern. Neither of these compounds manifests any visible J or dipolar coupling to the cadmium from the quadrupolar nitrogen atoms. As expected, the asymmetry parameters reflect the addition of the fourth pyrazolyl ring, $\eta = 0.65$ and 0.23 for 3 and 4, respectively, versus the 0.07 value for 2. The remaining tensor information is summarized in Table 1.

Discussion

The present study examines several different cadmium model compounds with varying nitrogen coordination to the cadmium center. The influences of the ligand geometry and coordination number are examined by systematic variation of substituents on the pyrazolyl rings and the number of pyrazolyl rings on the ligand. The relationship between the shielding effects and structural changes will be explored in the following section.

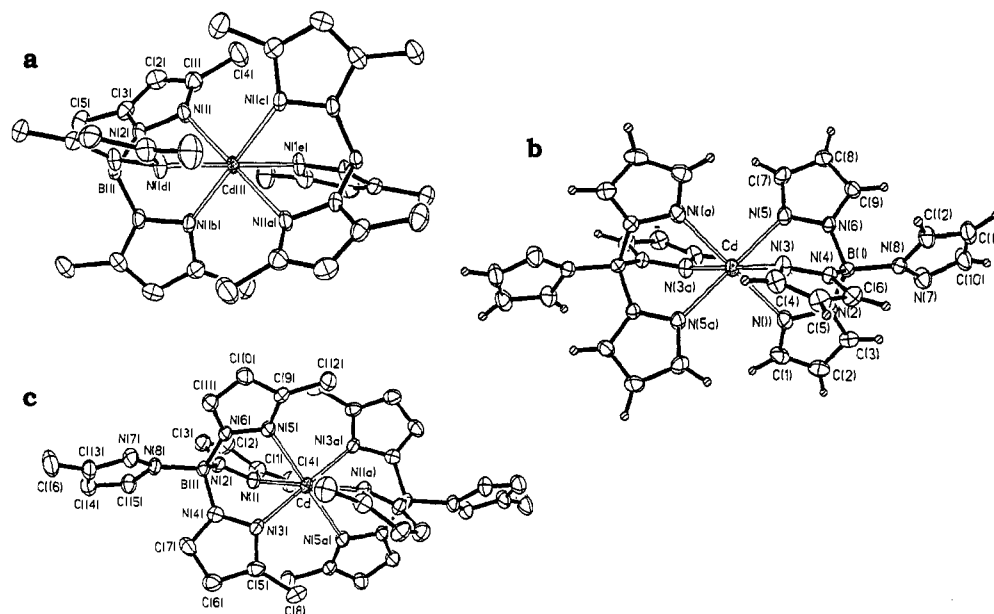


Figure 4. ORTEP drawings of the three N_6 coordination compounds: (a) $[\text{HB}(3,5\text{-Me}_2\text{pz})_3]_2\text{Cd}$ (2), (b) $[\text{B}(\text{pz})_4]_2\text{Cd}$ (3), and (c) $[\text{B}(3\text{-Mepz})_4]_2\text{Cd}$ (4). All three were generated from the X-ray crystallographic data of ref 10a.

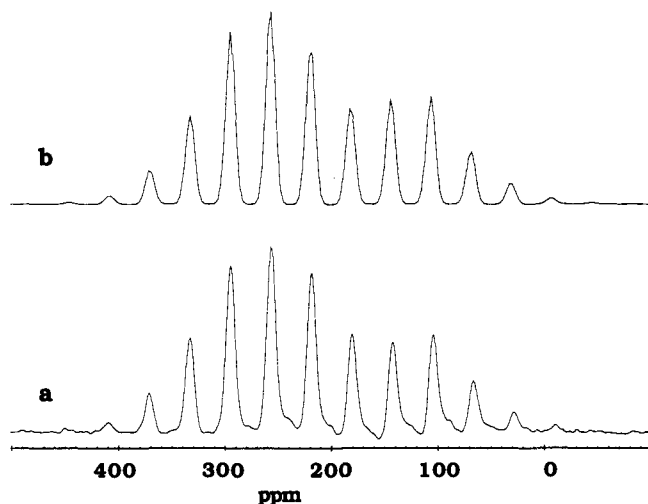


Figure 5. Experimental and simulated data of $[\text{B}(\text{pz})_4]_2\text{Cd}$ (3): (a) experimental spectrum spinning at 2523 Hz and (b) simulated spectrum using 200 Hz Lorentzian and 398 Hz Gaussian line broadening.

Structure and Shielding in N_6 Environments. Using the correlations between known structure and chemical shielding one can work backward from the existing correlations (rules 1–4) and the shielding data to speculate about the orientations of the ^{113}Cd shielding tensors. The crystal structures of 2, 3, and 4 ($[\text{HB}(3,5\text{-Me}_2\text{pz})_3]_2\text{Cd}$, $[\text{B}(\text{pz})_4]_2\text{Cd}$, and $[\text{B}(3\text{-Mepz})_4]_2\text{Cd}$, respectively) are available,^{10a} thereby allowing us to make direct comparisons between the three structures and our interpretation of the NMR data. A summary of the Cd–N bond distances of the three N_6 compounds, 2, 3, and 4, is in Table 2.

The trend of the isotropic chemical shifts in order of decreasing shielding goes $2 > 4 > 3$. This trend is also in decreasing order of the number of methyl substituents on the pyrazolyl rings, 2, 1, and 0, respectively. The σ_{iso} 's of 2 and 4 are within 13 ppm; however, 3 is 30 ppm to lower shielding than 4. This illustrates the sensitivity of the ^{113}Cd chemical shift to the methyl substituents. The influence of the methyl groups is indirect; due more to changes in the geometry of the coordination sphere about the cadmium than a direct influence on the shielding of the cadmium. The pyrazolylborate ligand of 3 has an average Cd–N bond distance of 2.328 Å, while the average Cd–N bond distances in 2 and 4 are fairly similar (2.348 and 2.344 Å, respectively).

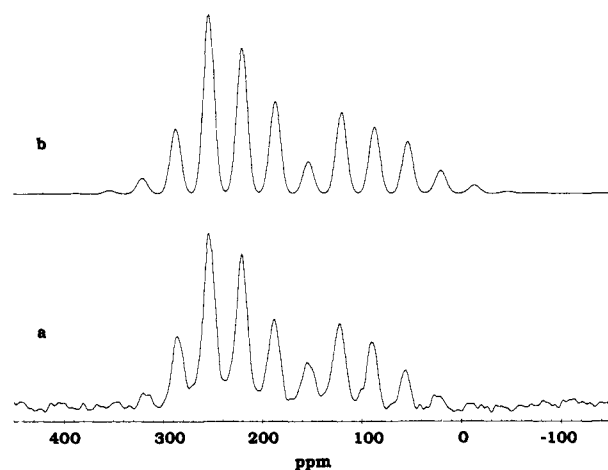


Figure 6. Experimental and simulated data for $[\text{B}(3\text{-Mepz})_4]_2\text{Cd}$ (4): a is the experimental spectrum acquired at a spin rate of 2200 Hz, and b is the simulated spectrum using 200 Hz Lorentzian and 471 Hz Gaussian line broadening.

Table 2. ^{113}Cd – ^{14}N Bond Distances Obtained from X-ray Crystallography^{10a}

compd	Cd–N ₁ (Å)	Cd–N ₂ (Å)	Cd–N ₃ (Å)	av (Å)
2	2.348(5)	2.348(5)	2.348(5)	2.348
3	2.314(3)	2.387(3)	2.284(3)	2.328
4	2.362(8)	2.308(8)	2.365(8)	2.344

The trends illustrated by the asymmetry parameters lead one to believe that 3 is the most distorted of the three compounds. The crystal structures concur with the NMR data. The crystal structure of 2 shows all the Cd–N bond distances to be equal and to verify that the unit cell contains at least a C_3 axis of symmetry. By replacing the proton on the boron with a pyrazolyl ring, both the local symmetry of the ligand and the symmetry axis of the unit cell for 3 and 4 are broken. The lack of 3-fold symmetry makes each of the nitrogen atoms on the ligand inequivalent, which in turn probably masks any J and/or D coupling by making the resulting splitting pattern too complicated to resolve.

To begin to postulate orientations of the shielding tensor elements, we need to utilize the symmetry of 2. In the case of axial symmetry, the three tensor elements, σ_{11} , σ_{22} , and σ_{33} , are reduced to only two, σ_{\perp} and σ_{\parallel} , where σ_{\parallel} is the unique element

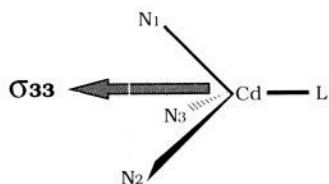


Figure 7. Simple representation of the nitrogen donor atoms of one tridentate poly(pyrazolyl)borate ligand coordinating to a cadmium center.

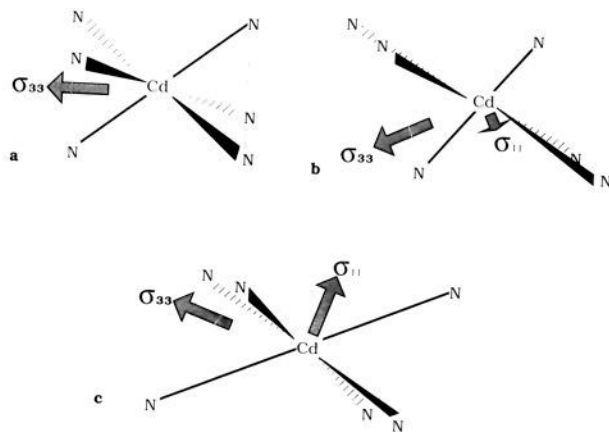


Figure 8. Depiction of the hypothetical orientation of the principal elements of the cadmium shielding tensor for a distorted octahedron: (a) an axially symmetric compound, with the unique tensor element aligned along the axis of symmetry, (b) an example of four long and two short Cd–N bonds, with σ_{11} coming out of the page, and (c) an illustration of a model with four short and two long Cd–N bonds.

aligned parallel to the symmetry axis. Therefore, the σ_{11} element (σ_{33}) of **2** must be along the 3-fold symmetry axis or the B–Cd–B' axis. As each tensor element samples the current density in the plane orthogonal to it, the most shielded element must be orthogonal to the plane of highest shielding. In these molecules, that element is σ_{33} , which is perpendicular to the plane of the nitrogen donor atoms of each ligand. A model of one of the tridentate ligands coordinating to a cadmium is depicted in Figure 7.

From the fourth rule obtained for the cadmium–oxo compounds, “the most shielded tensor element is nearly perpendicular to the longest Cd–O bond”, we can surmise that a longer Cd–N bond is associated with greater shielding. From the near axially symmetric case of **2**, we have assigned the most shielded tensor element, σ_{33} along the 3-fold axis of the ligand. Note that this is not perpendicular to the bonds, rather the bonds define a cone about the σ_{33} element. The environment that is orthogonal to σ_{33} is the base of that cone which is defined by the nitrogen donor atoms of each ligand.

The most shielded tensor elements for all three N_6 compounds are comparable, 35, 33, and 12 ppm for **2**, **3**, and **4**, respectively. As mentioned earlier, the first structure/shielding correlation states that “tensor elements of like magnitude have similar orthogonal environments.” Therefore, if σ_{33} for **2** is orthogonal to the plane of the donor nitrogens, it must be similarly oriented in **3** and **4**.

An explanation for the greater shielding of this element for **4** is that, although the average Cd–N bond length is about the same as that in **2**, there are actually two long bonds and one short one per ligand. This results in a tilting in the plane of the donor nitrogens away from the cadmium. The tensor elements must now adjust to reflect the new shielding environment. Figure 8 contrasts the axially symmetric case with the tilted planes expected for **3** and **4**.

There are now two competing environments for the shielding, one being the triangular arrangement of the donor atoms of each ligand and the second being an interligand effect created by the

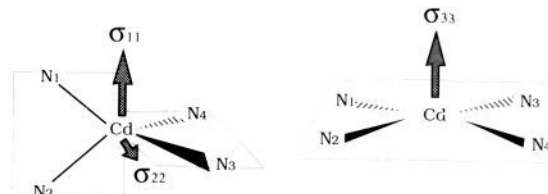


Figure 9. Representation of the nitrogen coordination around the cadmium center in a tetrahedral N_4 poly(pyrazolyl)borate and a planar N_4 porphyrin.

rectangular plane containing the four long Cd–N bonds. Bear in mind that the most shielded element should be orthogonal to the longest bonds. If these compounds had octahedral geometries (i.e., all adjacent N–Cd–N angles of 90°), then the σ_{33} element would now be parallel to the two short Cd–N bonds, i.e. on a C_4 axis. In our distorted geometry, the σ_{33} orientation is only influenced by the interligand effect; as depicted in Figure 8b, the σ_{33} element is not expected to be perpendicular to the interligand plane.

The small difference in the σ_{33} element between **2** and **3** implies that the same arguments made for the tensor element orientation in **4** cannot be made for **3**. One long Cd–N bond per ligand is not enough to dominate the shielding orientations. However, the deshielding effects are prominent for **3**. The most deshielded tensor element for the N_6 complexes is σ_{11} , and due to the absence of water ligands, the third rule applies. This means that σ_{11} is aligned to maximize the effects from the shortest Cd–N bonds. As seen in Figure 8c, we assign this tensor element to be nearly orthogonal to the interligand plane defined by the four short Cd–N bonds. Analogously, the σ_{11} element of **4** is oriented to maximize the effect of the two short Cd–N bonds (one from each ligand); most likely it is in the interligand plane of the four long bonds.

These tensor element orientations agree well with the trends extracted from the simulated data. The magnitude of σ_{11} for each of the N_6 complexes reflects the number of short Cd–N bonds, which in turn is an indication of the substitution of the pyrazolyl ring. In the axially symmetric case of **2**, the value of σ_{11} is 250.2 ppm, while in **4**, where a fourth pyrazolyl ring has been added to break the symmetry of the ligand, σ_{11} is 296.0 ppm. The length of the shortest Cd–N bond has changed by 0.04 Å between **2** and **4**. In the case of **3**, where there is no methyl substitution on the pyrazolyl rings, there are two short bonds per ligand and the value of σ_{11} is 369.9 ppm. We can therefore correlate the methylation of the 3-position of the pyrazolyl rings and the resulting structural changes with the value of the most deshielded tensor element, σ_{11} for these molecules.

Poly(pyrazolyl)borate vs Porphyrin N_4 . Extrapolating the structure/shielding correlations of the four oxygen rules to the N_4 environment of **1** is straight forward. The low η value of 0.04 leads one to believe that the unit cell of this molecule must have near axial symmetry. Unlike the N_4 coordination geometry of a porphyrin, this compound is a distorted tetrahedron. There are two planes of nitrogens in the tetrahedral case made up of donor atoms from two ligands, N_1 and N_2 from one and N_3 and N_4 from the other. Figure 9 contains pictorial representations of the planes of deshielding for **1** and a 4-coordinate porphyrin.

The tensor orientations depicted in Figure 9 show the most deshielded elements. For the porphyrin compounds, this element is σ_{33} ; however, for compound **1**, it is both σ_{11} and σ_{22} . The magnitudes of σ_{11} and σ_{22} for **1** are about one-half that of σ_{33} of the porphyrins, which is understandable when one considers that there are now two nearly orthogonal planes instead of one plane for metal–ligand interactions. From the crystal structure of **1**, it has been shown that there is *no* symmetry axis to account for the low η value. This can be explained by the proposed orientation of the tensor elements. If both of these ligands generate the same environment about the cadmium, but orthogonal to each other,

Table 3. ¹¹³Cd Shielding Tensor Data of Compounds Having Four Nitrogens Coordinated to a Cadmium

compd	σ_{100}	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$	η	ref
[H ₂ B(pz) ₂] ₂ Cd	291.9	388.9	381.6	105.3	-279.97	0.04	this work
Cd-PPIXDME	480	336	338	770	432	0.01	8
Cd-TTP	399	285	285	626	341	0.00	9

then the tensor elements must also reflect that. Therefore, σ_{11} and σ_{22} are equal, giving the appearance of an axis of symmetry by forcing η to near zero. In future research, proposed tensor element orientations will be verified via single crystal experiments.

It is interesting to note the changes of the anisotropy for these two models of N₄ coordination. Table 3 compares the principal elements of the shielding tensors for the N₄ coordination compound studied here and two porphyrin samples also of N₄ coordination. The Cd-PPIXDME has an anisotropy of +432 ppm, which Kennedy et al. attributed to exceptionally strong in-plane covalent interactions.⁸ Kennedy et al. noted that by adding an axial ligand the magnitude of the anisotropy decreased as the metal was pulled out of the plane of the nitrogens. In the case of **1**, not only is the magnitude of the CSA nearly one-half that of Cd-PPIXDME but it has the opposite sign. The balance between symmetry and electronic effects will be the subject of future research.

Conclusions

The poly(pyrazolyl)borate ligands are indeed well suited for studying cadmium coordination chemistry and chemical shielding

effects. Minor changes, such as methylation of the pyrazolyl rings of the ligand, can lead to large variations in the elements of the shielding tensor, while leaving differences in the isotropic shifts relatively small. These minor changes in similar ligands can be utilized to tailor the model compounds to more closely approximate the metal environment of a protein.

The potential problems of large, complicated, second-order quadrupole effects and complex dipolar line shapes (associated with the nitrogen donor atoms) do not seem to apply to the N₄ and N₆ complexes. However, more experiments are needed to fully understand when such dipolar effects will be manifested. This study does demonstrate that shielding tensor orientations for nitrogen coordination compounds are qualitatively consistent with the guidelines introduced for cadmium-oxo compounds.²⁷ However, single crystal experiments are needed to confirm these qualitative deductions. Now variations of the cadmium coordination sphere with mixed donor atoms can be explored (i.e., N₃O₂, N₂O₂, N₃S₂, etc.). Systems such as these will allow for the interpretation of the solid state NMR spectra for ¹¹³Cd²⁺-substituted protein systems (i.e., carboxypeptidase A).

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