Table V. Heats of Formation of Reactant and Product Species

species	$\Delta H_f{}^\circ{}_{298}$, kcal mol^{-1}	ref	species	$\Delta H_f{}^\circ{}_{298}$, kcal mol^{-1}	ref
H$^+$	365.7 ± 0.1	22	HP$_2$$^+$	238 ± 4	this work
H$^-$	34.7 ± 0.1	22	HP$_2$$^-$	18 ± 5	this work
H$_2$	0	23a	FP$_2$$^-$	−59 ± 4	this work
F$^-$	−59.5 ± 0.5	22	HPPH	29 ± 7	this work
P$^+$	317.0 ± 0.2	22	FPPH	−48 ± 7	this work
PH$_2$$^+$	261.0 ± 0.6	22	C$_6$F$_5$$^-$	−190.5 ± 8.0	22
PH$_2$$^-$	6.5 ± 2.4	22	C$_6$F$_5$H	−192.6 ± 1.6	23b
PH$_3$	1.3 ± 0.4	29	C$_6$F$_6$	−228.3 ± 0.3	23b
P$_2$	34.3 ± 0.5	23a			

H$_2$P$^-$ and PH$_3$ to yield HP$_2$$^-$ (eq 2) is endothermic by 10 kcal mol^{-1}. The reaction shown in eq 2 is therefore likely to be an example of an "entropy-driven" reaction.[30] The typical gain in entropy for a reaction between two reactants resulting in the formation of three products is of the order of 20 cal K^{-1} mol^{-1}. Thus, $T\Delta S$ is generally about 6 kcal mol^{-1}. Considering the experimental uncertainty of the enthalpy of this reaction, it comes as no surprise that it occurs.

E. Comparisons between Phosphorus and Nitrogen Ions. DePuy and co-workers have compared the reactions of H$_2$P$^-$ and H$_2$N$^-$.[38] They found that the reactions of H$_2$P$^-$ are often qualitatively similar to those of H$_2$N$^-$. The observed differences were attributed to the weaker nucleophilicity of H$_2$P$^-$.

To date, there has been no experimental evidence for the existence of HN$_2$$^-$ in the gas phase. Bowie et al. have noted that the thiomethoxide ion does not hydride-transfer to N$_2$ in an ICR mass spectrometer.[39] This results in an upper limit of HA(N$_2$) < 25.4 kcal mol^{-1}.[24] Since high-level ab initio calculations have not been carried out on HN$_2$$^-$, we cannot turn to theory as a guide as to whether this species is stable or whether it spontaneously

loses an electron to form the radical species HN$_2$$^{\bullet}$[40] or a hydride ion to form N$_2$. Clearly, N$_2$ is much less willing than P$_2$ to accept the hydride at the expense of a π bond. N$_2$ (PA = 118.2 kcal mol^{-1})[27] is also a weaker gas-phase base than P$_2$ (PA = 162 kcal mol^{-1}), for similar reasons. An analogous situation arises for the pair CO (HA = 8 kcal mol^{-1},[24] PA = 141.9 kcal mol^{-1}[27]) and SiO (HA = 49 kcal mol^{-1},[18] PA = 189.3 kcal mol^{-1}[41]). Both of these examples indicate the weaker π bonding of third-row atoms relative to their second-row analogues.

Conclusions

In summary, we have shown that electron impact on phosphine in a FA-SIFT results in the condensation products P$_x$H$_y$$^{-/+}$ (where x = 1–3 and y = 0–6). FP$_2$$^-$ is formed in the first flow tube via an ion–molecule reaction between HP$_2$$^-$ and hexafluorobenzene. Using the mass selection capabilities of the FA-SIFT, we have studied the gas-phase ion–molecule chemistry of HP$_2$$^-$, FP$_2$$^-$, and HP$_2$$^+$. HP$_2$$^-$ reacts via a number of pathways, including hydride transfer and oxygen and sulfur atom abstraction. Using bracketing techniques, we have determined the hydride affinity, fluoride ion affinity, and proton affinity of P$_2$. They are 51 ± 5, 34 ± 3, and 162 ± 3 kcal mol^{-1}, respectively. In addition we have estimated the gas-phase acidities of HPPH ($\Delta G_{acid}{}^\circ$ = 348 ± 3 kcal mol^{-1}) and FPPH ($\Delta G_{acid}{}^\circ$ = 348 ± 4 kcal mol^{-1}). Using these values, we have estimated the heats of formation of HP$_2$$^-$, HP$_2$$^+$, HPPH, FP$_2$$^-$, and FPPH.

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^{113}Cd Shielding Tensors of Cadmium Compounds. 8. Solid-State ^{113}Cd NMR Studies of Poly(bis(glycine)cadmium chloride)

Edwin Rivera[†] and Paul D. Ellis*

The ^{113}Cd shielding tensor of the cadmium compound poly(bis(glycine)cadmium chloride) has been determined via powder and single-crystal solid-state NMR experiments. The isotropic chemical shift determined was 115 ppm, and the individual shielding tensor components obtained through single crystal methods are σ_{11} = 263.0 ± 0.4 ppm, σ_{22} = 196.0 ± 2.0 ppm, and σ_{33} = −111.0 ± 3.6 ppm. The spatial arrangement of the molecules in the crystal lattice generates two magnetically distinguishable tensors. The coordination about the cadmium metal ion is a distorted octahedron and can be described in terms of three molecular planes. By the use of these planes, the ligand contribution to the ^{113}Cd nuclear shielding could be predicted by the progression in the direction of lower shielding of the best least-squares planes of atoms: O–O–O–Cl > O–O–Cl–Cl > O–Cl–Cl–Cl. Here O represents a carboxylate oxygen from glycine and Cl a chloride ion. Generally, chlorides are more deshielding ligands of cadmium than are carboxylate oxygens. On the basis of this assessment and a collection of single-crystal experimental observations on cadmium compounds, an assignment of the ^{113}Cd shielding tensor to the appropriate lattice site was accomplished. The most shielded tensor element, σ_{33}, is oriented nearly perpendicular to the most shielding best least-squares plane defined by three oxygens and one chloride. The most deshielding tensor element is aligned mostly perpendicular to the most deshielding best least-square plane defined by three chlorides and one oxygen. The σ_{22} component is most perpendicular to the plane defined by two chlorides and two oxygens.

Introduction

Studies of NMR chemical-shifts by solid-state NMR provide more information about the electronic shielding of a nucleus than

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the corresponding liquid-state isotropic chemical shifts. The use of static or magic-angle-spinning (MAS) methods on powder samples yields the principal elements of the shielding tensor (i.e. σ_{xx}, σ_{yy}, and σ_{zz}). NMR experiments of oriented single crystals yield, in addition to the principal elements of the shielding tensor, the direction of the shielding tensor in the molecular frame. Because of fast molecular tumbling, most chemical shifts determined in the liquid state represent only an average of the shielding

tensor, i.e. the isotropic chemical shift, $\sigma_0 = {}^1/_3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$.[1] However, these liquid-state NMR chemical shifts are susceptible to experimental conditions such as temperature, solvent, pH, the presence of chemical equilibria and the lability the nucleus under investigation exhibits. If the NMR experiment is performed in the solid state, most of these variables can be avoided, and if a crystal structure is available, a direct correlation between the orientation and magnitude of the tensor elements and the crystal structure can be established. For these reasons solid-state NMR is becoming a better approach in the study of metal ion chemical shifts.

Cadmium-113 has proven to be an effective NMR probe of the metal site in metalloproteins[2] where the native metals have poor receptivities (i.e. $^{43}Ca^{2+}$, $^{67}Zn^{2+}$, and $^{25}Mg^{2+}$ with spin $> {}^1/_2$ and $^{57}Fe^{2+/3+}$ with spin $= {}^1/_2$).[3] Upon replacement of these native metals with ^{113}Cd (spin $= {}^1/_2$) in a metalloprotein an NMR-active probe sensitive to ligand coordination number and type is introduced at the metal site. In multidimensional NMR spectroscopy of metalloproteins,[4] ^{113}Cd provides additional heteronuclear coupling constants which aid in the unraveling of sequential assignment of protons. Although a chemical shift range of more than 1000 ppm is an indication of the sensitivity of the cadmium metal to changes in the type of ligand, geometry, and coordination number, a quantitative structure/cadmium chemical shift correlation in the liquid state is not simple and remains unclear. No definitive semiempirical structural/liquid shift correlation exists, although specific regions of the cadmium spectral window are dominated by ligands of a particular type. Overlapping of some of these regions gives rise to ambiguous structural correlations in the liquid state. In addition, the molecular structure in the liquid state may differ from that in the crystal. The concept of simple additivity relations for the isotropic chemical shift of ^{113}Cd is not followed in the same way as in ^{13}C and ^{1}H NMR spectroscopy. Part of this problem arises because individual tensor elements often do not respond to a substituent in the same way. The net change in the isotropic chemical shift could be small even when shifts in individual tensor elements are large,[3] for example, if tensor elements shift in opposite directions. A thorough understanding of the origin of the cadmium chemical shifts, compensating effects of the tensor elements, its relation to the crystal structure, and the possible applications to the study of the metal environment in metalloproteins are the prime objectives of this series of cadmium shielding tensor studies.

^{113}Cd NMR studies of structurally characterized model complexes can provide correlations between the structure and the cadmium chemical shifts.[6] Single-crystal NMR experiments on proteins are impractical with current NMR methods, and only the principal values of the shielding tensor are obtainable from protein powders or polycrystalline samples via MAS methods. However, by the determination of the orientation of the cadmium shielding tensor on corresponding model compounds, an indirect method to model the orientation of the tensor in the cadmium-substituted proteins could be established. Most correlations established to date involve cadmium model compounds where ni-
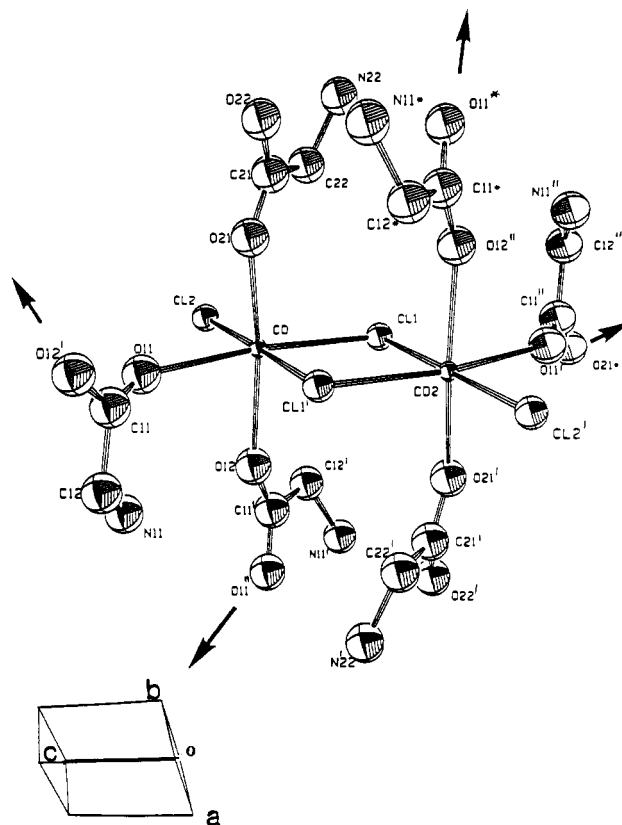

Figure 1. ORTEP diagram of the dimer of poly(bis(glycine)cadmium chloride). A perspective of the orientation of the unit cell is also included. An arrow indicates polymeric bonding to other dimeric units.

trogen, oxygen, and sulfur coordinations are part of the first coordination sphere. These model compounds are representative of the metal site of some classical proteins such as carp parvalbumin,[7] concanavalin,[7] pea lectin,[8] skeletal troponin-C,[9] whale myoglobin,[10] and, most recently, bovine carboxypeptidase-A.[11] A tensional analysis which combines powder and single-crystal solid-state NMR spectroscopy on selected model compounds will provide a more reliable and accurate analysis of the coordination number and the ligand identity, which may then be used to understand the nature of the ^{113}Cd chemical shift in cadmium-substituted metalloproteins.

Several cases[6] already exist where this indirect cadmium shielding tensor analysis has proven to be useful. For example, a moderately high resolution crystal structure (resolution = 1.93 Å)[12] of carp parvalbumin reported coordination numbers of 8 and 6 for the Ca^{2+} at the EF and the CD metal sites respectively. Liquid-state ^{113}Cd NMR spectroscopy showed similar environments based on similar chemical shifts. However, solely on the basis of the chemical shift values, a conclusion could not be drawn about the coordination number. If the coordination numbers is 8 and 6 for the EF and CD sites, respectively, this should have resulted in significant differences in the cadmium chemical shift of these two sites. An analysis of the powder chemical shifts of the EF and CD cadmium-substituted sites of carp parvalbumin and the data on single crystals for oxygen-ligand cadmium complexes suggests a coordination number different from those re-

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ported by X-ray crystallography.[7] The shielding tensors of cadmium-substituted carp parvalbumin when correlated with those for the model compounds were consistent with a coordination number of 7. Further, the fact that the two tensors could not be resolved demonstrated that the two sites were similar. The refinement of the native (resolution = 1.6,[13] 1.5[14]) and cadmium-substituted (resolution = 1.6[13]) carp parvalbumin was accomplished by two independent groups a few years after the solid-state NMR findings.[7] The new structure[13] demonstrated that the cadmium was occupying the same site as the native Ca^{2+} metal ion. Further, the metal sites have a coordination number of seven for both the EF and CD domains, in agreement with the solid-state NMR data. The above is a typical example of applications of [113]Cd solid-state NMR spectroscopy and of the relevance of obtaining the full [113]Cd shielding tensor information on representative cadmium compounds.

We report here the cadmium shielding tensor analysis of poly(bis(glycine)cadmium chloride). The crystallographic structure is displayed in Figure 1. The cadmium metal ion in poly(bis(glycine)cadmium chloride)[14] coordinates to three chlorides and three carboxylate oxygens in a distorted octahedral arrangement. Poly(bis(glycine)cadmium chloride) has a high degree of symmetry about its metal coordination sphere, which should facilitate the assignment of a given tensor element with a structural element in the molecule. The structure/chemical shift correlation was assigned by defining planes of ligands about the metal center of interest and relating the orientation of the principal components of the [113]Cd shielding tensor with these planes.

Finally, the eigenvalues of the cadmium shielding tensor of poly(bis(glycine)cadmium chloride) reported herein were found to be identical to those obtained in an earlier study of cadmium glycine monohydrate.[6c] Cadmium glycine monohydrate[16] coordinates to two nitrogens and four carboxylate oxygens whereas poly(bis(glycine)cadmium chloride) coordinates to three chlorides and three carboxylate oxygens. The shielding tensor data did not reflect the expected differences in the shielding tensor components which should have originated from these two different coordination environments. Also, since the orientation of the [113]Cd shielding tensor of cadmium glycine monohydrate exhibited a trend opposite to those of other cadmium shielding tensor studies, a reevaluation of the [113]Cd shielding tensor of cadmium glycine monohydrate[6c] is proposed in the discussion.

Experimental Procedures

Preparation. Poly(bis(glycine)cadmium chloride), [$Cd_2C_6O_6N_3Cl_3$], was synthesized according to published procedures.[15] Glycine (0.2 mol) (Fisher Chemical Co.) was dissolved in 250 mL of aqueous solution containing 0.1 M $CdCl_2$ (J. T. Baker) (0.1 mol). The solution was heated ca. 100 °C for an hour. Crystals (>10 mm[3])[15] were grown from vapor diffusion at room temperature.

Cadmium glycine monohydrate was prepared according to published procedures.[16]

[113]Cd NMR Spectroscopy. All solid-state [113]Cd NMR experiments were performed on a Varian XL-300 instrument in a narrow-bore Varian magnet at 7.05 T with a Larmor frequency for the [113]Cd nucleus of 66.547 MHz. All chemical shifts and tensor elements are (δ scale, with negative numbers implying resonances to higher shielding) reported relative to 0.1 M $Cd(ClO_4)_2$ in a 1:1 H_2O-D_2O solution at 25 °C. A standard-single contact (i.e. 2.0 ms) Hartmann–Hahn match, cross-polarization pulse sequence[17] with a recycle delay of 2 s was employed. Typical 90° pulses were 8 and 4 μs for MAS and single-crystal probes, respectively. Clearly, with an 8 μs pulse, the spin lock condition was not uniform over the spectral pattern of 40 kHz. This lack of uniformity accounts for some of the differences observed between the MAS results and those obtained by single-crystal methods.

For MAS experiments, the sample was ground in a mortar and packed in a 7-mm-o.d. zirconia rotor, and spun at speeds of 1–4 kHz in a MAS

Table I. [113]Cd Shielding Tensors Obtained through MAS Spectra of Poly(bis(glycine)cadmium chloride)[a]

spinning speed, Hz	σ_{11}, ppm	σ_{22}, ppm	σ_{33}, ppm	σ_0, ppm	$\Delta\sigma$	η
1725	263.9	190.2	-109.1	115.0	-336.1	0.32
2059	282.6	192.2	-108.7	115.0	-346.1	0.39
av	273.2	191.2	-108.9	115.0	-341.1	0.36
std dev	±13.2	±1.4	±0.3		±7.1	±0.1

[a] All chemical shifts were referenced with respect to 0.1 M $Cd(ClO_4)\cdot6H_2O$ in 1:1 H_2O-D_2O at 25 °C.

probe purchased from Doty Scientific. The principal elements of the [113]Cd shielding tensor were determined by a SIMPLEX optimization of two parameters: the chemical shielding anisotropy, $\Delta\sigma$ ($\Delta\sigma = \sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy})$), and the asymmetry parameter, η ($\eta = (\sigma_{yy} - \sigma_{xx})/\delta$, where $\delta = \sigma_{zz} - \sigma_{iso}$.[18] The calculations, which were carried out on a Microvax II computer, yielded the best estimates of the principal elements of the chemical shielding tensor, assuming no dipolar or quadrupolar interaction.

Single-crystal experiments were performed by mounting a single crystal of poly(bis(glycine)cadmium chloride) on an open three-sided ceramic cube.[6a] The orientation of the crystal on the ceramic cube was accomplished by using X-ray photographic techniques. Rotational photographs were used in the alignment of the *b* and *c* axes of the unit cell. Rollett's[19,20] matrix convention requires only two axes to completely align a monoclinic crystal. The axes were properly aligned by adjustments of the angles of a conventional two-arc goniometer. These angles were found to be $\alpha = 5.0°$, $\beta = 88.0°$, and $\gamma = 2.5°$. The radiation source Cu Kα ($\lambda = 1.542$ Å) was used for diffraction work. The single crystal was rotated 182° about three axes mutually perpendicular to the static field. A spectrum was recorded at intervals of $\theta = 9.1°$ and the eigenvalues were extracted from a least-square analysis of eq 1. The eigen-

$$\sigma_{zz}^{LAB} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) + \frac{1}{2}(\sigma_{ii} - \sigma_{jj}) \cos 2\theta + (-\sigma_{ij}) \sin 2\theta \quad (1)$$

vectors for the shielding tensor are the result of diagonalizing the tensor in the crystal reference frame.[20] The best least-squares plane [BLSP] analysis was performed on the atoms of the first coordination sphere of cadmium by using the crystallographic package SDP (Structure Determination Package) from Enraf-Nonius.

Results

Poly(bis(glycine)cadmium chloride) crystallizes as a polymeric dimer in the monoclinic crystal system. The structure was solved[15] using the nonstandard space group $P2_1/n$ and the monoclinic unit cell constants for poly(bis(glycine)cadmium chloride) are $a = 8.17$ Å, $b = 8.91$ Å, $c = 13.62$ Å, and $\beta = 107°$.

The monomer structure of poly(bis(glycine)cadmium chloride) is shown in Figure 1 (arrows indicate polymer expansion). Although it was not indicated in the previous report,[15] this dimer polymerizes through two of the axial glycines and the two equatorial glycines. The two remaining axial glycines do not bridge. The cadmiums (inversion related), sit on a general e Wyckoff position and are chemically and magnetically equivalent. Thus, the discussion will concentrate on just one cadmium. The cadmium metal ion has an octahedral arrangement and coordinates to three chloride ions and three carboxylate oxygens. Two of the glycine carboxylate oxygens (the axial oxygens) are bridging with other dimeric units. This metal center is intersected by three planes formed by the atoms of the first coordination sphere (Figure 2). The number of shielding or deshielding atoms present in the planes defines the shielding tensor environment of the cadmium nucleus. Since chlorides are known to be generally more deshielding than carboxylate oxygens,[2] the following shielding interaction is expected for the molecular planes present in the poly(bis(glycine)cadmium chloride): O–Cl–Cl–Cl < O–O–Cl–Cl < O–O–O–Cl. This order results from empirical observations of the shielding contribution of oxo ligands and chlorides from liquid[2] and solid-state chemical shifts.[6f]

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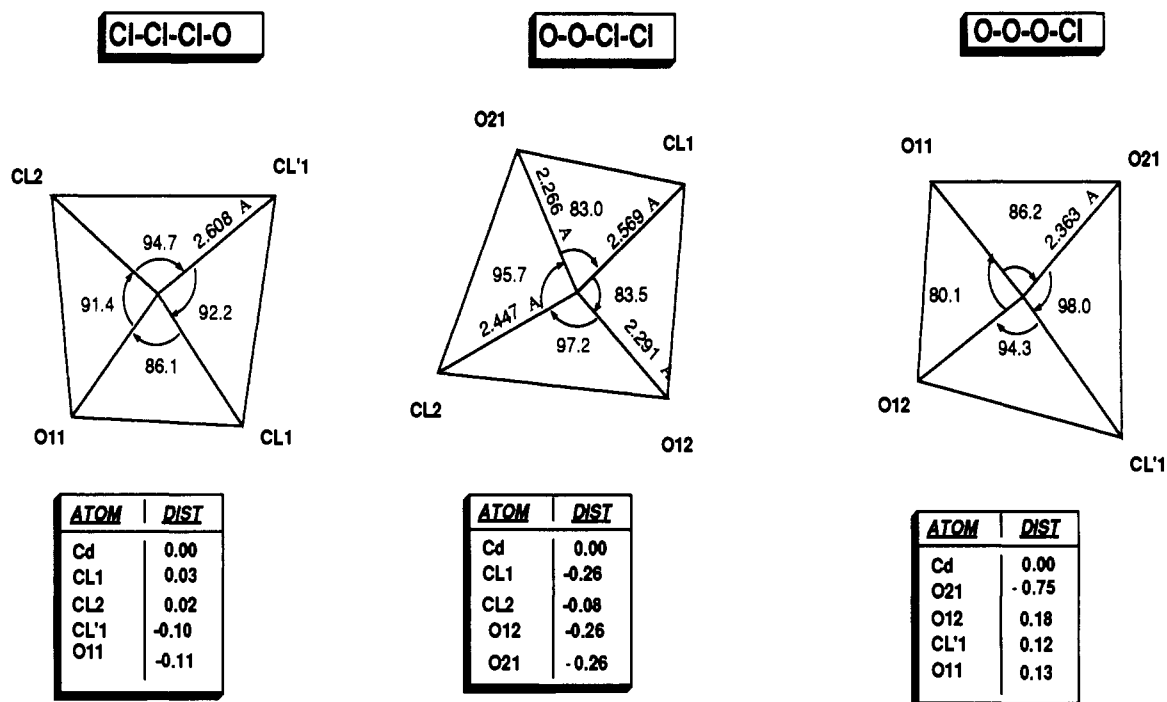
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Figure 2. View of the molecular planes formed by atoms of the first coordination sphere of poly(bis(glycine)cadmium chloride). The block area indicates the distances of each atom from the best-least-square plane. In the plane the bond angles are given in degrees. Key: (a) Cl–Cl–Cl–O plane, the most deshielding plane formed by three chlorides and glycine oxygen; (b) O–O–Cl–Cl plane, plane formed by two chlorides and two glycine oxygens; (c) O–O–O–Cl plane, the most shielding plane formed by three glycine oxygens and one chloride.
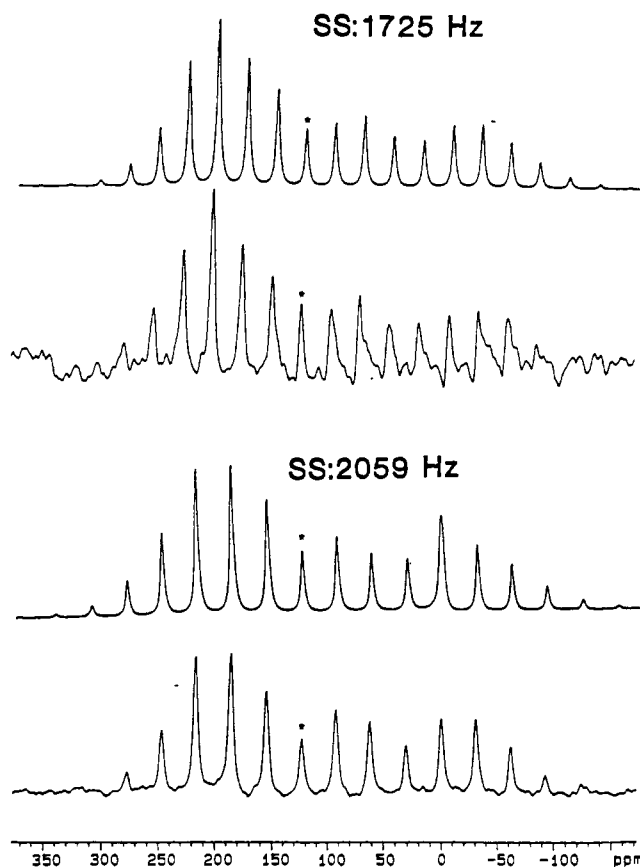
Table II. Direction Cosine[a] of the Principal Elements of the ^{113}Cd Shielding Tensor on the Molecular Frame of Poly(bis(glycine)cadmium chloride)

tensor[b] elements	chem shift,[c] ppm	direction cosine			angles, deg		
		a'	b'	c'	a'	b'	c'
		Tensor 1					
σ_{11}	263.9	−0.5596	0.6238	−0.5456	124	51	123
σ_{22}	194.8	0.2363	0.7512	0.6164	76	41	52
σ_{33}	−113.7	0.7934	0.2160	−0.5678	37	78	124
σ_0	115.8						
		Tensor 2					
σ_{11}	263.4	0.4548	0.8721	0.1804	63	29	80
σ_{22}	197.8	−0.3136	0.3464	−0.8840	108	70	152
σ_{33}	−108.6	0.8335	−0.3455	−0.4311	34	110	115
σ_{iso}	117.5						

[a] All eigenvectors reported in orthogonal Cartesian coordinates. [b] The convention used for labeling the shielding tensor elements is after Haeberlen's *High Resolution NMR in Solids*, which ascribes $\sigma_{33} - \sigma_0 > \sigma_{iso} > \sigma_{11} - \sigma_0$. [c] The ^{113}Cd chemical shifts are reported with negative values to higher shielding with respect to 0.1 M Cd(ClO$_4$)$_2$·6H$_2$O.

Shown in Figure 3 is the ^{113}Cd MAS spectrum of poly(bis-(glycine)cadmium chloride and the corresponding MAS simulation. Table I summarizes the parameters of the cadmium shielding tensor obtained from the simulation at two different spinning speeds. The isotropic chemical shift from MAS (Table I), and single-crystal analysis (Table II) is 115 ppm and falls in the range expected for other oxo/chloride–cadmium compounds.[21] The shielding tensor obtained from MAS at low spinning speeds correlates with the single-crystal results. At higher spinning speeds however, the correlation with the single-crystal data is less than at lower spinning speeds. If the sideband intensities are low near the edges of the sideband pattern, the error in the measurement introduces a larger discrepancy into the measurement of the shielding tensor (in this case σ_{11} has the largest discrepancy with the single-crystal tensor data). As noted, in the Experimental
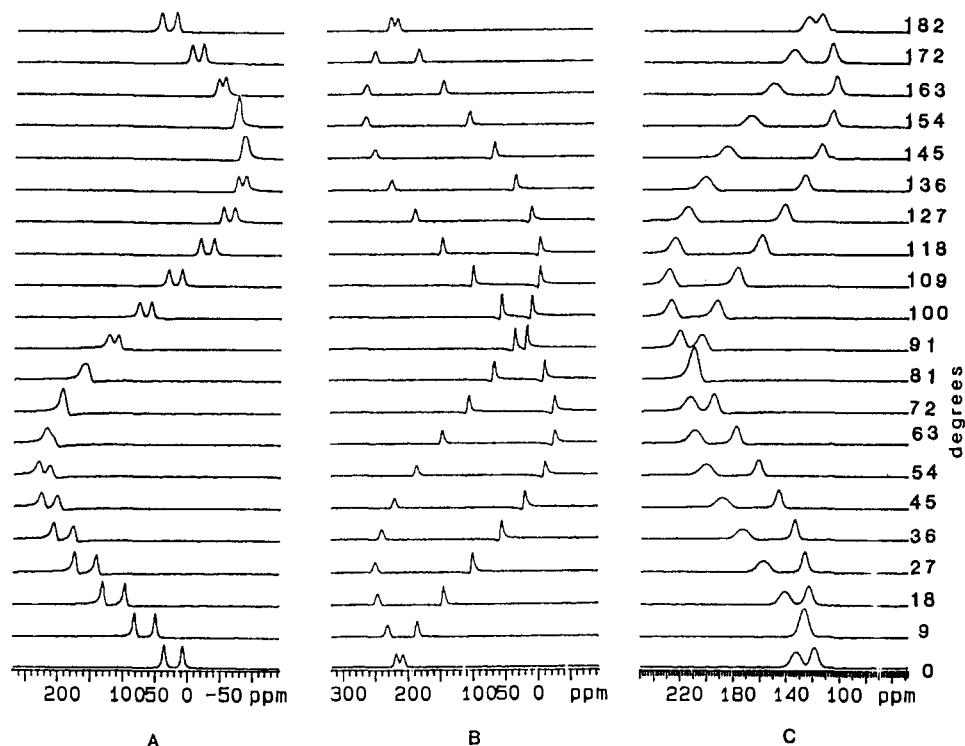
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SS:1725 Hz

SS:2059 Hz

Figure 3. 66.547-MHz ^{113}Cd MAS NMR spectra of poly(bis(glycine)-cadmium chloride) with cross polarization at spinning speeds of (a) 1725 and (b) 2059 Hz. The simulated spectra are included. The star indicates the isotropic chemical shift.

Section, most of the error can be traced to insufficient pulse power.

Single-crystal-rotation plots (Figure 4) exhibit two distinguishable resonances. Table II summarizes the results of the single-crystal analysis. The two sets of eigenvectors associated

Figure 4. 66.547-MHz ^{113}Cd single-crystal NMR rotation plots for poly(bis(glycine)cadmium chloride). Two distinguishable tensors are observed in agreement with the crystallographic analysis. Notice that in rotation plot A, the two tensors are almost degenerate. This is the consequence of rotating the crystal about a symmetry point group of either the crystal or the molecule. An example of the effect of rotating a crystal along a crystallographic symmetry elements is provided in ref 5f for $Cd(OAc)_2(Im)_2$.

with each resonance are related by the crystallographic point-group symmetry operator[22] (2c, 2-fold about the c axis) resulting in two choices of orientation. Since the symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal,[23] we can estimate the uncertainty involved in the experimental single-crystal NMR data. An estimate of the uncertainty in the orientation of the tensor was obtained by operating the point-group element on one set of experimentally determined eigenvectors. The result of this operation is a set of eigenvectors equivalent to the second experimental set. A maximum angle deviation of 8° is observed between the two symmetry-related tensors and is representative of the experimental uncertainty that is introduced by successively mounting and dismounting the cube holder on to the goniometer.

ORTEPs of poly(bis(glycine)cadmium chloride) (Figure 5), show the orientation of the three principal tensor components corresponding to the two magnetically distinguishable lattice sites. Referring to the orientation depicted from tensor **1** shown in Figure 5a, the following spatial arrangement was observed. The most shielded tensor element σ_{33} (-114 ppm), makes an angle of 73.5° with respect to the most shielded BLSP O21–O11–O12–Cl1, whereas σ_{11} (264 ppm) and σ_{22} (195 ppm) are practically *in* the most shielded BLSP of the molecule, 8.9 and -13.7°, respectively. σ_{11}, the most deshielding tensor element, is the most perpendicular, 78.0°, with respect to the most deshielding BLSP (Cl1–Cl1'–Cl2–O11 plane), whereas σ_{33} and σ_{22} are *in* the most deshielding BLSP of the molecule, 3.6 and 11.6°, respectively. σ_{22} is most perpendicular to the BLSP O21–O12–Cl2–Cl1' (-71.2°), whereas the tensor elements σ_{11} and σ_{33} are 9.8° and -15.2°, respectively.

With tensor **2** depicted in Figure 5b, the following features are relevant. σ_{22} and σ_{33} (the most shielding tensor elements), make angles of 49.6 and -33.7°, with respect to BLSP O21–O11–O12–Cl1. σ_{11} (the most deshielding element) makes an angle of 19.5°, with respect to the BLSP O21–O11–O12–Cl1. σ_{11} and σ_{33} are oriented -42.1 and 32.2°, respectively, to the BLSP

Cl1'–Cl1–Cl2–O11 (the most deshielding plane), whereas σ_{22} is the most perpendicular element to the most deshielding BLSP (Cl1'–Cl1–Cl2–O11 plane), 81.0°. Finally, σ_{11} makes an angle of -66.1° with respect to the BLSP O21–O12–Cl1–Cl1' (the mixed plane), whereas σ_{33} and σ_{22} are 23.8 and 1.0°, respectively, from BLSP O21–O12–Cl2–Cl1'.

**Discussion**

The single-crystal NMR spectrum of poly(bis(glycine)cadmium chloride) (Figure 4), yields two magnetically-distinguishable tensors. From the rotation plot depicted in Figure 4a, the two lines or resonances are distinguishable but almost superimpose on each other, indicating that a crystallographic-symmetry element is present along the axis of rotation of the crystal. This was confirmed upon alignment of the crystal using X-ray diffraction techniques. From the crystal alignment, the rotation leading to almost degenerate lines reveals that the b axis of the unit cell is almost collinear (approximate alignment angles were 5 and 2.5°) about the crystal rotation axis. A two-arc goniometer was employed to determine the alignment of the crystal. Perpendicular to the b axis is a mirror that accounts for the almost-degenerate rotation plot observed in Figure 4a. The remaining two unit cell axes do not coincide with any of the rotational axes to the crystal nor any of the other possible symmetry elements. Therefore, two distinguishable and nondegenerate resonances in the single-crystal NMR spectrum are produced, Figure 4b,c.

The two lines of the single-crystal NMR spectrum results from molecules positioned on symmetry-related sites within the unit cell. In the MAS spectrum the two orientations are averaged to one resonance because of the natural random distribution of microcrystals in the powder sample. Symmetry-related tensors differ only in their space group symmetry; that is, these tensors have indistinguishable eigenvalues but distinguishable eigenvectors and can only be resolved via single-crystal NMR spectroscopy. Symmetry-related tensors with the exception of translation and inversion operations may result in the presence of additional lines in the single-crystal spectrum[22] leading to ambiguities in the assignment of the eigenvectors of the tensor. There are no symmetry arguments allowing for an assignment of a given set of symmetry-related resonances to the corresponding crystallo-

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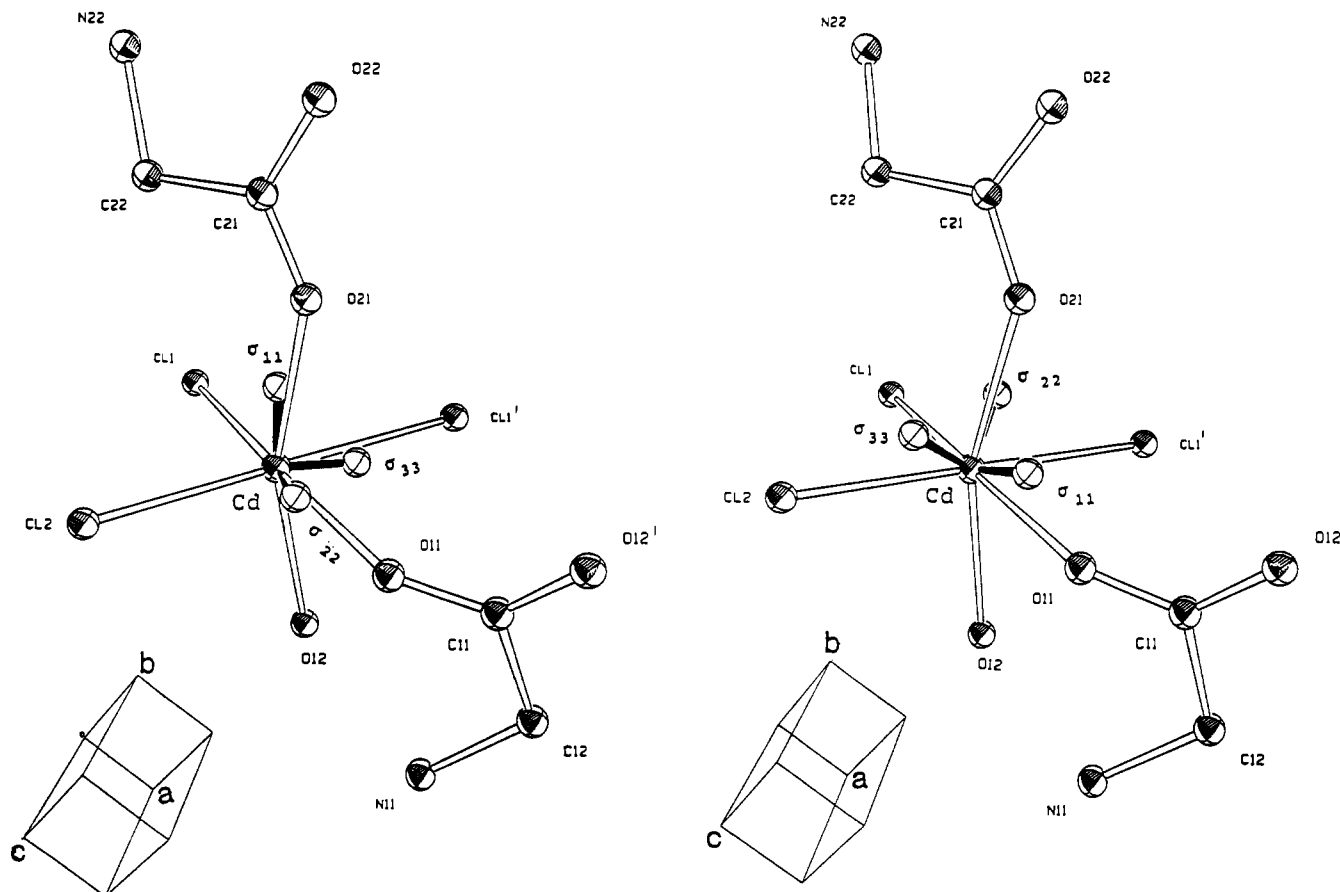
Figure 5. ORTEP diagram of poly(bis(glycine)cadmium chloride), displaying the two tensors from single-crystal analysis on a single lattice site of the unit cell: (a, left) tensor 1 [*xyz*] site; (b, right) tensor 2 on [*xyz*] site. Hydrogen atoms are used to represent the direction of the individual shielding tensor elements. The nuclear thermal ellipsoids are not representative of 50% probability distribution. Instead, the size of the hydrogen atoms has been chosen for clarity of the display. A perspective of the orientation of the unit cell is also included in the figures for reference.

graphically equivalent sites. In spite of this ambiguity, a series of single-crystal NMR studies revealed that the orientation of the cadmium shielding tensor follows a pattern[6] which is apparently dictated by the spatial arrangement of the ligands in the cadmium coordination sphere. These semi-empirical observations follows after a series of cadmium compounds were studied by single-crystal NMR.[6] The coordination sphere for the cadmium models included ligands containing oxygen,[6a,b,d] mixed nitrogen–oxygen[6c,e–g] and mixed oxygen–sulfur[6c,11] atoms. These general semiempirical observations are briefly summarized below:

(1) Tensors with similar eigenvalues have similar molecular environments. This observation follows from examples[6a,b,f] of axially-symmetric shielding tensors.

(2) A tensor element is a reflection of its orthogonal environment. The induced field has its origin in current densities which circulate in a plane perpendicular to an induced field.[6b] Several examples[6e–g] with cadmium environments containing a mixture of shielding and deshielding ligands seem to always follow with this trend.

(3) The first mixed oxygen–chloride single-crystal NMR study (i.e. $CdCl_2$·18-crown-6[6f]) seems to reflect a higher [113]Cd^{2+} deshielding interaction toward chlorides relative to the ester oxygens.

In this study we have examined whether or not these general patterns continue to exist in at least one of the two possible orientations of the [113]Cd tensor of poly(bis(glycine)cadmium chloride). This will represent only the second example of a single-crystal study of a cadmium coordination containing a mixture of chlorides and carboxylate oxygens.

Knowing the direction of the tensor elements and keeping in mind the above precepts, we can initiate the analysis of each tensor. Referring to Figure 5a, the orientation depicted by tensor 1 displays each element of the tensor in a position mostly orthogonal to one of the planes defined previously in Figure 2. Each tensor element, σ_{33}, σ_{22}, and σ_{11}, is normal to one of the molecular planes

containing one, two, and three chlorides, respectively. This observation is consistent with the semiempirical observation that a shielding tensor is a reflection of its orthogonal environment. In this case the most deshielding plane would be the one with the greatest number of chlorides. The σ_{33} (most shielded element) makes an angle of 73.5°, with the most shielding BLSP (O11–O21–O12–Cl1). σ_{11} (the most deshielded element) makes an angle of 78.0° with the most deshielding BLSP (Cl1'–Cl2–Cl1–O11). Finally, σ_{22} makes an angle of −71.2°, with the BLSP (O21–O12–Cl1–Cl2). An asymmetry parameter of 0.32 suggests that the three principal elements of the shielding tensor are in direct environments. In contrast, a different interpretation is obtainable from the orientation depicted in tensor 2 (Figure 5b). The angles that each tensor element makes with the same molecular planes do not reflect orthogonality with the planes. On the basis of the acute angle between the tensor element and the molecular planes, the symmetry of the tensor could be predicted. For instance, σ_{22} and σ_{33} appear to be in the same molecular environment, making the same acute angle (49 and −33°, respectively) with the BLSP (O11–O21–O12–Cl1) of the molecule. Furthermore, σ_{11} and σ_{33} make about the same acute angle with the (Cl1–Cl1'–Cl2–O11) BLSP of the molecule. These angles are −42 and 32°, respectively. We must emphasize that the error in the tensor orientation could be as much as 8°. On the basis of this information alone, the symmetry of a tensor corresponding to the above geometric arrangement would most likely exhibit some axial symmetry. From the above data the orientation depicted in tensor 1 (Figure 5a) instead of the orientation depicted in tensor 2 (Figure 5b) follows more closely those semiempirical precepts observed in other cadmium shielding tensor compounds. This finding provides the first evidence of support between the two choices of eigenvectors available for this compound.

An additivity scheme for cadmium shielding tensors introduced earlier[6b] has also been applied to this poly((glycine)cadmium

chloride) study, in order to try to differentiate between the two choices of eigenvectors for the tensor. The additivity model calculates the bonding and nonbonding shielding contributions defined in eq 2, where $\sigma_{ii}{}^{Cd}$ are the principal elements of the ^{113}Cd

$$\sigma_{ii}{}^{Cd} = \Sigma_j \frac{\theta_j}{R_{Cd-j}{}^3} \cos \phi_j \qquad (2)$$

shielding tensor, R_{Cd-j} is the bond distance from the ligands to the cadmium, ϕ_j is the acute angle between the vector Cd–j and the plane perpendicular to the principal elements of the shielding tensor σ_{ii}, and θ is the estimated shielding contribution constant that atom j makes to the cadmium nucleus. The sum in eq 2 can extend over all atoms in the molecule. However, because of the cubic dependence on the bond distance R, the contributions from atoms in the first coordination sphere are expected to be larger than the contributions[6b] from nonbonded atoms.

For poly(bis(glycine)cadmium chloride) the θ or the shielding tensor contributions have been partitioned in the following manner: $\theta_{non-bond}$, which contains all atoms that are outside the coordination sphere; θ_{O1}, which contains the longest carboxylate oxygen–cadmium bonds with distances of 2.363 and 2.291 Å; θ_{O2}, which contains the shortest carboxylate oxygen–cadmium bond distance of 2.266 Å; and finally θ_{Cl}, which contains all the chloride contribution bond distances from 2.447 to 2.608 Å. The nonbonded contributions or secondary contributions can be handled in two different ways: (1) On the basis of the atomic position of the contributing atom (this assumes that the major part of the electron density is at the nucleus); (2) by the atom dipole method of Flygare et al.[24] (which assumes that the major part of the electron density is along a vector defined by two bonded atoms). The general method (that is, nonbonding atoms are treated as centers of high electron density) yields reasonable estimates ($\theta_{non-bond}$ < $\theta_{primary-coordination}$). Once again, this could be expected from the R^3 dependence of eq 3. The following represents a summary of the θ values obtained from the calculations on poly(bis(glycine)cadmium chloride).

	tensor **1**	tensor **2**
θ_{Cl}	3007	−5596
θ_{O1}	−3405	−24844
θ_{O2}	−974	−12093
$\theta_{non-bond}$	−4.61	19.629

As previously stated, by Honkonen and Ellis,[6b] the sign on θ discriminates between the two possible tensor assignments. In this case a positive sign indicates deshielding while a negative sign indicates shielding. The magnitude θ_{Cl} is larger than that predicted for the oxygen of a water molecule θ_{H_2O} (750 ± 250 ppm Å³)[6b] indicating a large deshielding interaction with the cadmium nucleus. Also an increase in θ_{O1} for nonbridging glycine oxygens is observed. The magnitude on θ_{O2} is in the range prescribed by other oxygen systems −800 ± 250 ppm Å³ and $\theta_{non-bonding}$ is less than $\theta_{bonding}$. The values for tensor **2** obtained under the same set of conditions are unreasonable and out of the range expected, once again supporting the orientation depicted in tensor **1**.

The preferred orientation (tensor **1**) of the ^{113}Cd shielding tensor of poly(bis(glycine)cadmium chloride) correlates with the orientation observed in CdCl$_2$·18-crown-6.[6f] Although the oxygen in CdCl$_2$·18-crown-6 is donated by an ether and the oxygen of poly(bis(glycine)cadmium chloride) from a carboxylate, certain qualitative features are discernible about the shielding tensor. First, since there is only one magnetically distinguishable tensor per unit cell, no symmetry ambiguity arises unlike in poly(bis-(glycine)cadmium chloride). Second, the plane that comprises six oxygen atoms (the crown ring) forms the most shielding molecular plane; corresponding to the O–O–O–Cl BLSP, which represents the most shielding feature in poly(bis(glycine)cadmium chloride). The two axial chlorides or perhaps any of three possible O–Cl–O–Cl BLSP of the CdCl$_2$·18-crown-6 ring form the most

deshielding structural feature of the molecule. These planes correspond to the most deshielding Cl–Cl–Cl–O and the Cl–O–Cl–O BLSP in poly(bis(glycine)cadmium chloride). The most shielded tensor element in CdCl$_2$·18-crown-6, σ_{zz}, is perpendicular to the most shielding plane of the molecule (ca. 90°). The most deshielded tensor elements σ_{xx} and σ_{yy} are normal to two of the Cl–O–Cl–O BLSPs in CdCl$_2$·18-crown-6. Symmetry dictates that σ_{11} and σ_{22} be equal.[25] CdCl$_2$·18-crown-6 follows once again the trend described above. That is, a tensor element will reflect its orthogonal environment. A correspondence between the O–O–Cl–Cl BLSP in CdCl$_2$·18-crown-6 and the O–O–Cl–Cl BLSP in poly(bis(glycine)cadmium chloride) indicate that differences in the bond distances and angles between these two BLSPs should be reflected in the σ_{11} and σ_{22} components of CdCl$_2$·18-crown-6 and the σ_{22} component in poly(bis(glycine)cadmium chloride).

The most remarkable tensor/structure correlation between poly(bis(glycine)cadmium chloride) and CdCl$_2$·18-crown-6 is revealed by the most deshielding BLSP of both molecules. A decrease in the Cd–Cl bond distance shifts the most deshielding tensor elements in the direction of lower shielding (i.e. from 2.508 Å (σ_{22} = 197.8 ppm) in poly(bis(glycine)cadmium chloride) to 2.361 Å (σ_{11} = σ_{22} = 399 ppm) in the CdCl$_2$·18-crown-6. The Cd–Cl bond distance seems to be the dominating feature in this plane since the geometric perturbation in the angles and the deviations from the BLSP are insignificant (Figure 2).

A rationale of the mechanism of shielding of the cadmium nucleus can be obtained from studies using ab initio calculations. Natkasutji and co-workers[26] initiated the approach from a series of ab initio finite perturbation SCF (self-consistent field) calculations (gauge dependent, with the gauge origin taken at the metal), to understand the nature of cadmium chemical shift of a series of cadmium–ligand complexes. By calculation of the paramagnetic and diamagnetic contribution to the nuclear shielding constant on a number of complexes,[26] the following conclusions were made: (1) valence electrons contribute the most to the paramagnetic term, (2) core electrons, mainly those from the metal, contribute largely to the diamagnetic term, (3) the paramagnetic term dominates the shielding contribution (ca. 100 times) of the nucleus, and (4) the p orbitals and not the d orbitals in their respective contributions to the shielding are mostly responsible for the shielding tensor of the cadmium nucleus. In the p mechanism, electrons from p ligand orbitals donate electrons to an empty valence 5p orbitals in the cadmium metal. In the d mechanism, back-donation of electrons to either an empty p, π, or a d orbital of a ligand occurs. As shown by perturbation theory,[27] a closed-shell d or p orbital in metals contributes little to the paramagnetic term.

These observations can only suggest that these mechanisms are conceivable in our model compound. For instance, chlorides will be expected to promote the p mechanism via electron donation from their 3p orbitals to virtual d orbitals on the cadmium. The monodentate carboxylates of the glycine may only promote the p or π mechanism since no low-lying empty vacant molecular orbitals are accessible. However, from a detailed examination of the calculations mentioned above, one has to conclude that the dominance of the "p-type" mechanism may be a product of the basis set used in these calculations. That is, no d-orbital polarization functions were used. Hence, the lack of d-orbital participation may be simply related to the lack of availability in the calculation of a set of d orbitals. This point is being reexamined and will be discussed elsewhere.[28]

Comments on the Shielding Tensor of Cadmium Glycine Monohydrate. Although the semiempirical postulates for the cadmium shielding tensor discussed in this and other studies[6] have modeled

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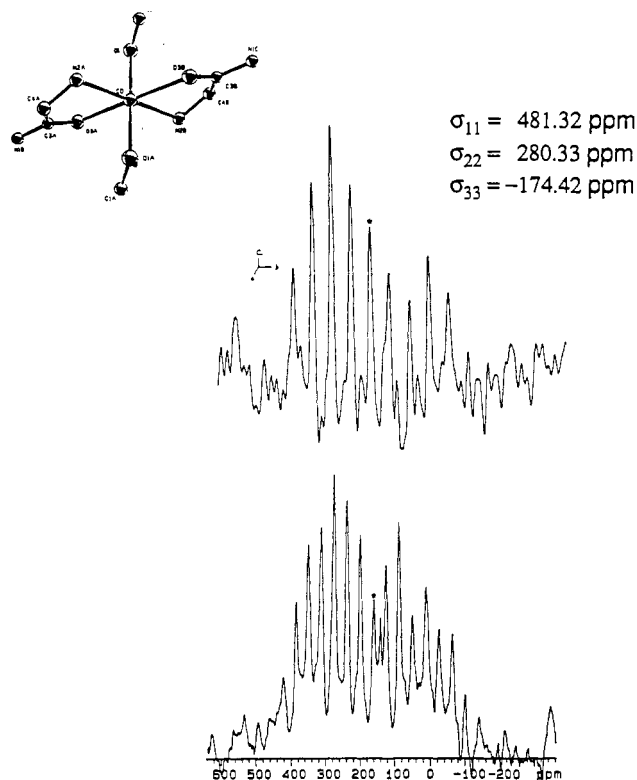(25) Richardson, M. F. *Inorg. Chem.* **1990**, *29*, 3620–3621.
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$\sigma_{11} = 481.32$ ppm

$\sigma_{22} = 280.33$ ppm

$\sigma_{33} = -174.42$ ppm

Figure 6. 66.547-MHz [113]Cd MAS spectra obtained from a stoichiometric mixture of cadmium oxide and glycine in aqueous solution: (a) spinning speed, 4000 Hz; (b) spinning speed, 2600 Hz.

most of the shielding tensor data obtained by single-crystal NMR, one exception deviated from these studies: cadmium glycine monohydrate.[6c] We wish to report here that this exception is due to an error in the choice of preparation. That is, crystals thought to be cadmium glycine monohydrate were in fact poly(bis(glycine)cadmium chloride).

The correspondence of the cadmium shielding tensor of poly-(bis(glycine)cadmium chloride) with cadmium glycine monohydrate obtained from single-crystal NMR experiments is good (i.e. $\sigma_{11} = 263 \pm 2$ (256 $\pm$ 1), $\sigma_{22} = 196 \pm 1$ (200 $\pm$ 1), and $\sigma_{33} = -111 \pm 5$ (-117 $\pm$ 1) ppm). This similarity is not however coincidental but accidental as the authors mistakenly prepared poly(bis(glycine)cadmium chloride) instead of the desired cadmium glycine monohydrate. The main difference in the method of preparation between the single-crystal paper[6c] and the crystallography paper[15] lies in the absence of the highly reactive chlorides in the reaction mixture containing cadmium oxide and glycine. Our findings were supported when an attempt at synthesizing cadmium glycine monohydrate by following the procedures in the crystallographic paper[16] of cadmium glycine monohydrate yielded a different MAS NMR spectrum from that of poly(bis(glycine)cadmium chloride), Figure 6. A complete analysis of the tensor of the compound whose MAS spectrum is shown in Figure 6 by single-crystal NMR has been hampered by the lack of suitable single crystals and the inherent slow solubility of cadmium oxide in water. The following shielding tensor parameters were recovered from the high spinning speed spectrum

of Figure 6 ($\sigma_{11} = 481$ ppm; $\sigma_{22} = 280$ ppm; $\sigma_{33} = -174$ ppm).

An ORTEP diagram of cadmium glycine monohydrate is included in Figure 6. On the basis of the above semiempirical treatment, the most deshielded tensor element should be nearly normal to the most deshielded plane in the molecule. The most deshielded plane in the molecule comprises the chelate ring formed by an amine nitrogen and the carboxylate oxygen. Nitrogens are generally most deshielding than oxygens; therefore, the most deshielded tensor elements should be normal to the most deshielding plane and not in the plane. This orientation has been confirmed by single-crystal NMR on an analogous cadmium compound of very similar coordination environment, cadmium glycylglycinate monohydrate.[6h]

Conclusions

The orientation of [113]Cd shielding tensor of poly(bis(glycine)cadmium chloride) has been investigated using single-crystal NMR. The well-defined electronic surrounding of the cadmium nucleus helps in the interpretation of the structural properties responsible for the orientation of the elements of the shielding tensor in poly(bis(glycine)cadmium chloride). The assignment of the shielding tensor to a lattice site was accomplished by following the semiempirical trend observed in other cadmium compounds studied by single-crystal NMR including the chloride–oxygen complexes $CdCl_2 \cdot 18$-crown-6.[6f] The preferred tensor orientation selected in this study correlates with the cadmium shielding orientation observed in the $CdCl_2 \cdot 18$-crown-6 complex. The most shielded tensor element is perpendicular to the most shielding plane of the molecule, while the most deshielded element of the tensor is perpendicular to the most deshielding BLSP.

A closer examination at the synthetic pathway employed[6c] in the single-crystal study of cadmium glycine monohydrate reveals that the compound synthesized was instead poly(bis(cadmium)-glycine chloride). This is evidenced from the similarity between the individual shielding tensor components. Further work to complete the full analysis of the tensor is in progress.

Finally, this study is part of the ongoing investigation in the elucidation of the rules governing the cadmium shift by employing single-crystal NMR. Chlorides are important ions present in many biological systems. These shielding tensor studies can provide a better understanding of how chloride ions could affect the [113]Cd chemical-shift interpretation obtained for cadmium-substituted proteins when a metal–ion interaction occurs in buffers with high salt concentrations. The study suggest that a decrease in the Cd–Cl bond distance results in a shift toward lower shielding in the tensor component normal to this bond. This information is not obtainable from the most simplistic approach of cadmium liquid-state NMR.