Solid-State ^{113}Cd NMR Studies on Cadmium Complexes with Glycine, L-Alanine, and L-Cysteine

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Solid-state ^{113}Cd NMR spectra have been recorded for bis(glycinato)cadmium(II) hydrate, bis(L-alaninato)cadmium(II) trihydrate, and a 1:2 complex of cadmium and L-cysteine; the principal components of the ^{113}Cd shielding tensor have been determined. The spectra show useful additional fine structure due to dipolar coupling (both direct and indirect) between ^{113}Cd and ^{14}N, which allows the number of nitrogens bonded to the cadmium center to be determined directly. In the L-alaninate complex, two cadmium resonances are observed which are rationalized as being due to the presence of diastereoisomers within the powdered sample. The L-cysteine complex shows no ^{14}N coupling, indicating that any ^{113}Cd–^{14}N interactions are weaker than in the other two complexes. An improved X-ray single-crystal structure of the glycinate complex is also reported.

Introduction

^{113}Cd NMR spectroscopy is a sensitive probe of the number and type of coordinating groups around a cadmium atom and can be particularly useful in the study of proteins. Further, Cd^{2+} may often be exchanged for other divalent metals, such as Zn^{2+}, Ca^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, and Mg^{2+}, in proteins and ^{113}Cd NMR spectroscopy has developed into a useful probe of metal environments in metalloproteins.[1]

The chemical shift scale of ^{113}Cd covers about 900 ppm. Environments in which ^{113}Cd is completely ligated by oxygen usually give rise to resonances between −100 and +150 ppm, coordination to nitrogen results in a downfield shift and resonances between +200 and +380 ppm, and bonding to sulfur causes a further downfield shift to between +350 and +800 ppm.[1] However, within these regions there are relatively few useful correlations with coordination number, and so structural predictions from solution chemical shift data are difficult to make. There is the added difficulty that ^{113}Cd chemical shifts in solution are affected by changes in pH and concentration, and there may also be large anion dependences. Further, cadmium complexes in solution are often labile and the chemical exchange behavior of ligands can severely handicap spectral interpretation.[1] Some studies have used supercooled liquids in order to slow down such processes and overcome the problem of chemical exchange.[2]

Solid-state NMR spectroscopy of powders offers an alternative approach which can overcome many of these difficulties,[3] and it has the added advantage that it provides the three principal components of the shielding tensor,[4,5] rather than just the average value observed in solution NMR spectra. The chemical shift tensor is far more sensitive to local changes in geometry at the ^{113}Cd site than the isotropic shift seen in solution. Unlike solution chemical shifts, solid-state NMR results can be correlated directly with crystallographic structure determinations when available, and structural predictions can be made in the absence of crystallographic data.

In this paper we present high-quality solid-state ^{113}Cd NMR spectra of cadmium complexes with glycine, L-alanine, and L-cysteine, from which we have obtained the principal components of the shielding tensors. In the present work the glycinate and alaninate complexes show useful fine structure due to coupling to ^{14}N nuclei. The cadmium environment in these compounds is important as they provide models for more complicated species. We have also recorded ^{13}C NMR spectra of the complexes and a natural-abundance ^{15}N spectrum of the alaninate complex. X-ray single-crystal structures are known for the glycinate[6] and alaninate[7] complexes but not for the cysteinate. An improved crystal structure of bis(glycinato)cadmium(II) hydrate is also reported.

Experimental Section

Bis(glycinato)cadmium(II) Hydrate. Single crystals were obtained using the method of Low *et al.*[6] The X-ray single-crystal structure was redetermined and is reported.

Bis(L-alaninato)cadmium(II) Trihydrate. Crystals were obtained using the method as described by Démaret and Mercier.[8] The unit cell was determined and was found to be in good agreement with that previously published.[7]

Cadmium(II) Cysteinate (1:2). Cadmium(II) acetate (2.7 g, 0.01 M) was added to cysteine (2.4 g, 0.01 M) in water (20 cm^3) with stirring. The white amorphous precipitate was filtered off, washed with water, and dried under vacuum. Analysis by both DSC and infrared specroscopy showed the absence of water; the first change observable in the DSC was at 221.1 °C, at which temperature the sample decomposed. Chemical analysis was consistent with a 1:2 complex, $Cd(H_2NCH(CH_2SH)COO)_2$. Anal. Calcd for $CdC_6H_{12}N_2O_4S_2$: C, 20.42; H, 3.40; N, 7.94; Cd, 31.88. Found: C, 20.88; H, 3.96; N, 7.86; Cd, 29.6.

Crystallography. All measurements were made by using a CAD4 diffractometer operating in the $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation, as described previously.[9] The structure was solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods[10] with scattering factors calculated by using data from ref 11. Empirical absorption corrections were applied to the data;[12] minimum and maximum transmission factors were 70.03 and 99.25%. All non-hydrogen atoms were refined with anisotropic

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Table I. Crystallographic Data for $Cd(H_2NCH_2COO)_2 \cdot H_2O$

formula	$C_4H_{10}N_2O_5Cd$
MW	278.545
crystal system	monoclinic
space group	$I2/a$
crystal size, mm	0.25 × 0.25 × 0.02
octant data collection	$0 \le h \le 20$; $0 \le k \le 7$; $-14 \le l \le 14$
a, Å	14.818(5)
b, Å	5.297(2)
c, Å	9.990(1)
β, deg	90.40(2)
V, Å^3	784.11(0.40)
D_c, g cm^{-3}	2.359
Z	4
$F(000)$	544
radiation	Mo Kα
λ, Å	0.710 69
μ, cm^{-1}	27.614
2θ range, deg	$3 \le 2\theta \le 60$
tot. no. of reflns	1371
no. of unique reflns	1132
no. of obsd reflns $[F_o > 4\sigma(F_o)]$	965
no. of refined params	77
weighting scheme param, g, in $w = 1/[\sigma^2(F) + gF^2]$	0.000 33
final R^a	0.0258
final $R_G{}^b$	0.0358

^{a} $R = \sum|F_o - F_c|/\sum F_o$. ^{b} $R_G = [\sum w(|F_o - F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Fractional Atomic Coordinates (×10^4) for $C_4H_{10}N_2O_5Cd$

	x	y	z
Cd(1)	0[a]	0[a]	0[a]
O(1)	−367(1)	−2690(3)	1715(2)
O(2)	−1151(1)	−2995(4)	3590(2)
N(1)	−1087(2)	2055(4)	1144(2)
O(1W)	−2500[a]	5566(7)	0[a]
C(1)	−951(2)	−1898(4)	2510(2)
C(2)	−1493(2)	479(6)	2175(3)

[a] Invariant parameters.

Table III. Selected Bond Distances (Å) and Angles (deg) for $C_4H_{10}N_2O_5Cd$

		Distances	
O(1)–Cd(1)	2.297(4)	N(1)–Cd(1)	2.261(4)
C(1)–O(1)	1.251(4)	C(1)–O(2)	1.263(4)
C(2)–N(1)	1.459(5)	C(2)–C(1)	1.529(5)
O(2)–Cd(1)	2.447(4)[a]		
		Angles	
N(1)–Cd(1)–O(1)	75.4(2)	C(1)–O(1)–Cd(1)	115.7(2)
C(2)–N(1)–Cd(1)	112.3(3)	O(2)–C(1)–O(1)	123.8(3)
C(2)–C(1)–O(1)	120.1(3)	C(2)–C(1)–O(2)	116.1(3)
C(1)–C(2)–N(1)	114.1(3)		

[a] Intermolecular.

displacement factors; hydrogen atoms were identified in difference maps and included with isotropic displacement factors. Crystal data and details of the intensity measurements and refinement are given Table I, positional parameters are given in Table II, and selected bond distances and angles are given in Table III.

Solid-State NMR Spectroscopy. ^{13}C and ^{113}Cd solid-state NMR spectra were recorded on a Bruker MSL-300 spectrometer using cross-polarization (CP), magic-angle spinning (MAS), and dipolar decoupling. The relevant experimental parameters are spinning speeds of 4–5 kHz, contact time of 10 ms, proton decoupler power level of 55 kHz, and recycle delays of 2 s for the alaninate, 20 s for the cysteinate, and 60 s for the glycinate complex. The cross-polarization sequence used incorporated a 90° proton flip-back pulse immediately after the acquisition period in order to reduce the recycle delay needed between scans. Despite this, the glycinate complex needed the comparatively long recycle time of 60 s due to the exceptionally long T_1 relaxation time of the protons in this complex. A natural-abundance ^{15}N CP/MAS NMR spectrum was also recorded on the cadmium alaninate complex; the longer relaxation times of the protons in the other two compounds precluded the measurement of ^{15}N spectra for these (without isotopic enrichment being used). For the ^{15}N spectrum the proton power was 28 kHz during the mixing period, which was increased to 65 kHz during the decoupling period. All spectra were recorded at room temperature (296 K). Chemical shifts are reported relative to external TMS for ^{13}C, to 0.1 M $Cd(ClO_4)_2$ aqueous solution for ^{113}Cd, and to liquid nitromethane for ^{15}N. For the case of the ^{113}Cd spectra, the spinning sideband patterns were analyzed using the method of Herzfeld and Berger.[13]

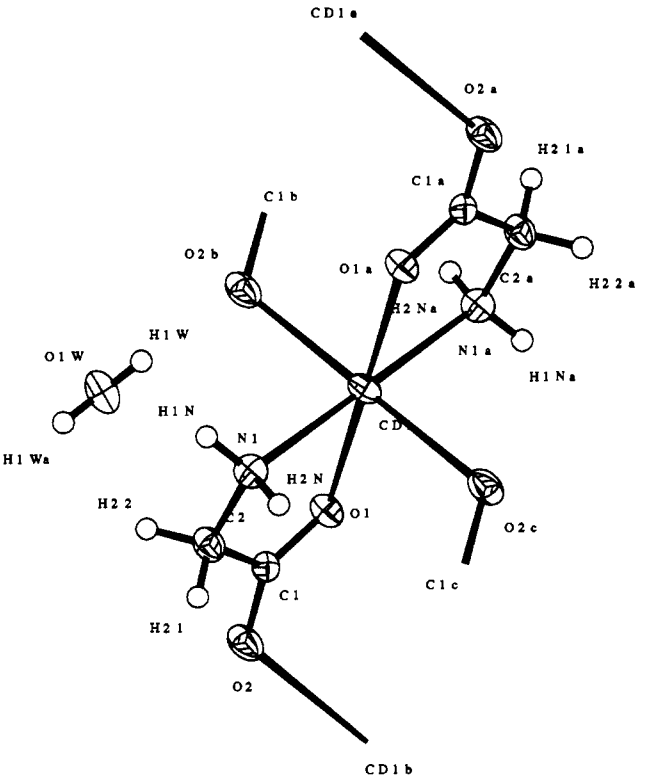

Figure 1. X-ray crystal structure of bis(glycinato)cadmium(II) hydrate, $Cd(H_2NCH_2COO)_2 \cdot H_2O$.

Results and Discussion

Bis(glycinato)cadmium(II) Hydrate, $Cd(H_2NCH_2COO)_2 \cdot H_2O$. The structure of this complex is known from the X-ray determination of Low *et al.*[6] in 1959 and consists of a distorted octahedral cadmium coordination with two glycine ligands chelating the metal through the nitrogen and oxygen atoms in a *trans* square planar configuration; the two other coordination sites are occupied by oxygens of neighboring glycine ligands, leading to a polymeric structure. The accuracy of the structure determination was limited (mainly due to the photographic method used to collect the data), and at present, data for bis(glycinato)cadmium(II) hydrate, $Cd(H_2NCH_2COO)_2 \cdot H_2O$, are not available from the major X-ray structure databases. Consequently, we have redetermined the X-ray structure. The results are largely in agreement with the work of Low *et al.*,[6] but much more precise atomic coordinates have been obtained. The complex is monoclinic, and the cadmium is in a distorted octahedral environment with 2N,2O + 2O coordination (see Figure 1).

The ^{13}C CP/MAS NMR spectrum of the glycinate complex shows a single narrow carboxylate peak at 182.4 ppm, while the signal from the α-carbon is split into an asymmetric doublet due to direct dipolar coupling to ^{14}N. Such coupling between ^{13}C and ^{14}N has been extensively documented in the solid state and is due to the quadrupole interaction on the ^{14}N nucleus.[14-16] It is

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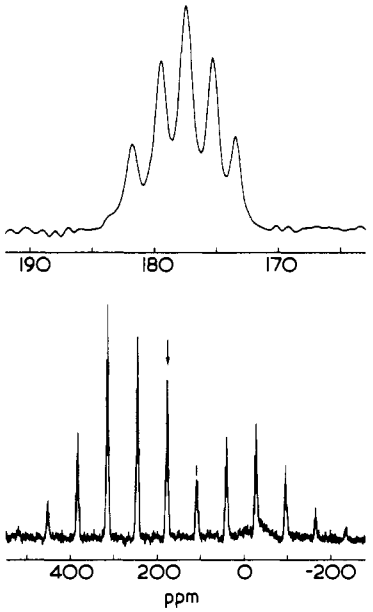

Figure 2. ^{113}Cd CP/MAS NMR spectrum of bis(glycinato)cadmium(II) monohydrate: (top) expansion of isotropic peak; (bottom) whole spectrum. The arrow denotes the isotropic peak.

appropriate here to discuss this splitting in slightly more detail as it is relevant to the interpretation of the ^{113}Cd spectra of the glycinate and alaninate complexes discussed below.

The quadrupolar interaction shifts the axis of quantization on the ^{14}N away from the direction of the applied magnetic field, and thus the dipolar coupling is not completely removed by magic-angle spinning. The usual appearance of the line resulting from ^{13}C coupled to ^{14}N with MAS is as a doublet (with intensity 2:1) with a splitting of[16]

$$S_1 = \frac{9\chi D}{20Z}(3\cos^2\beta_{CN} - 1 + \eta\sin^2\beta_{CN}\cos 2\alpha_{CN}) \quad (1)$$

where D is the dipolar coupling between ^{13}C and ^{14}N ($D = \gamma_C\gamma_N h/4\pi^2 r^3$, where r is the internuclear C–N distance), Z is the Zeeman energy of ^{14}N, χ is the quadrupole coupling constant, η is the asymmetry in the quadrupole coupling tensor, and β_{CN} and α_{CN} are the polar and azimuthal angles defining the orientation of the C–N vector in the principal axis system of the electric field gradient tensor. It should be noted that this effect is strongly dependent on the internuclear distance and inversely proportional to the applied magnetic field (through the Zeeman energy of ^{14}N). Simulation of the observed line shape, or measurement of the peak splitting, allows any of the parameters in the expression above to be calculated, provided that the other quantities are known (or can be estimated) from other techniques. In our case, the ^{13}C–^{14}N splitting is observed to be 47 Hz in the 7.05-T magnetic field used. While the parameters D and Z in the above expression are known, the quadrupole coupling parameters (χ and η) are not known in this case (although they are in principle measurable by NQR spectroscopy), and neither is the orientation of the electric field gradient tensor (unless an assumption about the symmetry is made).

The ^{113}Cd CP/MAS NMR spectrum of the glycinate complex is shown in Figure 2 and reveals a spinning sideband pattern covering over 600 ppm. The peaks show significant fine structure, the expansion of which shows a quintet in approximate intensity ratio of 1:2:3:2:1. This is explicable on the basis of indirect coupling (J-coupling) between ^{113}Cd and two equivalent ^{14}N nuclei. In the solid state, J-coupling patterns between spin I = $^1/_2$ and quadrupolar spins when observed are usually affected additionally by direct dipolar coupling (as discussed above for the coupling between ^{13}C and ^{14}N) and there can also be a contribution from the anisotropy of the **J** tensor. Olivieri has recently obtained an expression by first-order perturbation theory to model such cases.[17] In the event that the z direction of the **J** tensor and the internuclear direction are coincident, for coupling to identical spin I = 1 nuclei the lines are shifted by[17,18]

$$\nu_m = -J_{iso}\sum m_i + \frac{3\chi}{20Z}(2 - 3\sum m_i^2)(D - \Delta J/3) \times (3\cos^2\beta_{CdN} - 1 + \eta\sin^2\beta_{CdN}\cos 2\alpha_{CdN}) \quad (2)$$

where m_i are the ^{14}N magnetic spin quantum numbers, J_{iso} is the isotropic J-coupling, ΔJ is the anisotropy in the **J** tensor, and all other terms are defined as in eq 1. Note that it is impossible to distinguish the effects of the contributions from direct dipolar couplings, D, from the anisotropic indirect coupling, ΔJ.

In the case of coupling to two equivalent ^{14}N nuclei, eq 2 predicts six lines of relative intensity 1:2:2:1:2:1 with separations $J + S$, $J - S$, $2S$, $J - S$, and $J - S$, where S is related to S_1 in eq 1 but with an additional ΔJ term:

$$S = \frac{9\chi(D - \Delta J/3)}{20Z}(3\cos^2\beta_{CdN} - 1 + \eta\sin^2\beta_{CdN}\cos 2\alpha_{CdN}) \quad (3)$$

If we allow for the fact that the two peaks with separation $2S$ are not resolved but are a weighted average of the two components, this predicts a multiplet of relative intensities 1:2:3:2:1, with line separations of $J + S$, $J - S/3$, $J + S/3$, and J – S, respectively. This is exactly what is observed in this case. The observed peak separations are 149, 133, 144, and 126 Hz (all ±4 Hz). This gives a value for $J(^{113}Cd–^{14}N)$ of 138 Hz (calculated from the separation of the highest and lowest field lines) and a value for S of *ca.* 12 Hz.

The magnitude of the direct dipolar contribution, D, to the observed value of S can be estimated from the splitting, S_1, seen in the ^{13}C spectrum of the same compound. Using bond lengths of r(C–N) = 1.459 Å and r(Cd–N) = 2.261 Å gives a ratio of $D(^{13}C)/D(^{113}Cd)$ = 4.2. However, the orientation terms in eqs 1 and 3 are not identical as α_{CdN} and β_{CdN} are not necessarily equal to α_{CN} and β_{CN}. In the event that the orientation terms are comparable, such as would be the case if the z axis of the electric field gradient tensor was perpendicular to the Cd–N–C plane and η was close to zero, then this would predict an S value of *ca.* 11 Hz for ^{113}Cd–^{14}N coupling from direct dipolar effects alone. This value is close to the experimentally determined figure, and this suggests that the contribution from the ΔJ term in eq 3 is probably negligible in this case.

The observation of coupling between ^{113}Cd and ^{14}N is useful as it gives an immediate determination of the number of bonded nitrogens, which is not usually possible from chemical shift positions alone. The isotropic peak, which is the only resonance whose position does not alter upon changing the spinning speed, comes at 177.6 ppm. This may be compared with results for a cadmium/^{15}N-labeled glycine system in a supercooled solution at 233 K, which was reported to give a triplet for $Cd(gly)_2$ species at δ = 153.9 ppm with $J(^{113}Cd–^{15}N)$ = 165 Hz.[19] The similarity in chemical shift suggests that the solution species, most likely to be $Cd(gly)_2(OH)_2$, probably has a structure similar to that of the solid complex (i.e. 2N,4O ligation).[20] The similarity between $J(^{113}Cd–^{15}N)$ in solution and the value of $J(^{113}Cd–^{14}N)$ obtained for the solid is also encouraging. It should be emphasized that

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Table IV. Summary of ^{113}Cd Solid-State NMR results[a]

compd	δ_{iso}/ ppm	σ_{11}/ ppm	σ_{22}/ ppm	σ_{33}/ ppm	$\Delta\sigma$/ ppm	η_{csa}
cadmium glycinate[b]	177.6	−445	−277	+189	550	0.46
cadmium alaninate[b,c]	177.1	−321	−266	+56	349	0.23
cadmium cysteinate	402.5	−170	−380	−657	−382	0.82

[a] The σ values have been given as shieldings, rather than chemical shifts which have the opposite sign, using the convention $|\sigma_{33}-\sigma_{iso}| > |\sigma_{11}-\sigma_{iso}| > |\sigma_{22}-\sigma_{iso}|$. The anisotropy $\Delta\sigma$ is defined as $\sigma_{33}-0.5(\sigma_{11}+\sigma_{22})$, and the asymmetry parameter, η_{csa}, by $(\sigma_{22}-\sigma_{11})/(\sigma_{33}-\sigma_{iso})$, where $\sigma_{iso} = -\delta_{iso} = (\sigma_{11}+\sigma_{22}+\sigma_{33})/3$. [b] Spectrum includes additional coupling to ^{14}N. [c] The fine structure of the alaninate spectrum indicates two distinct ^{113}Cd sites are present—the values in this table are calculated for the average position.

the isotropic chemical shift alone (i.e. ignoring the ^{14}N coupling) does not unambiguously confirm that two nitrogen atoms are bound to the metal center as a Cd(2N,4O) environment occurs at 103.4 ppm in solid poly(bis(acetato)bis(imidazole)cadmium(II))[21] and a Cd(3N,3O) environment in a cadmium insulin complex in solution comes at 165 ppm.[22]

The intensities of the spinning sidebands give important structural information, as they enable the principal components of the shielding tensor to be determined; these are given in Table IV. The original measurement of the shielding tensor of bis(glycinato)cadmium(II) hydrate, using single-crystal methods,[23] is incorrect as the authors were inadvertently using a completely different compound.[24] A later measurement from powder data is of poor spectral quality, probably due to an inappropriate choice of recycle time.[24]

It has been suggested that the anisotropy of the ^{113}Cd shielding tensor can be correlated with the differences in bond length around the metal center.[25] In our case, the observed anisotropy ($\Delta\sigma$ = 550 ppm, η_{csa} = 0.46) is fairly high and reflects the presence of the two long Cd–O bonds to the neighboring (nonchelating) glycine molecules. These have bond lengths of 2.447 Å, compared to 2.297 Å for the chelating Cd–O bonds and 2.261 Å for the Cd–N bonds.

The orientation of the shielding tensor is also important. Ellis and co-workers have obtained ^{113}Cd shielding tensors using single-crystal methods for a number of compounds and suggested guidelines for assigning the principal components to specific directions within the crystal.[24] It should be borne in mind that a tensor element reflects the electronic environment of its orthogonal environment. It is usually found that the most deshielded tensor element is nearly normal to the most deshielded plane in the molecule.[24] This allows us to suggest that the σ_{11} component in this case is probably in the axial direction, while the other two components are roughly in the plane of the chelating ring.

Bis(L-alaninato)cadmium(II) Trihydrate, $Cd(H_2NCH(CH_3)COO)_2 \cdot 3H_2O$. The crystal structure of the alaninate complex consists of an octahedral cadmium coordination with two alanine ligands chelating the metal through the nitrogen and oxygen atoms. However, unlike those in the glycinate structure discussed above, the oxygen atoms have a *cis* rather than *trans* relationship (see Figure 3). The remaining two coordination sites of the alaninate are occupied by the oxygens of water molecules.[7]

The ^{113}Cd CP/MAS NMR spectrum of bis(L-alaninato)cadmium(II) trihydrate is shown in Figure 4. The isotropic peak comes at a chemical shift position identical to that of the glycinate complex, but the anisotropy, as manifested in the range of the spinning sideband pattern, is significantly less than that for the glycinate sample. This suggests that 2N,4O ligation exists for both the bis(glycinato)- and bis(L-alaninato)cadmium(II) complexes, while the differences in symmetry and local geometry between them are revealed by the differing chemical shift anisotropies. This is a good example of a case where solid-state NMR spectroscopy distinguishes between different environments even though they have the same isotropic chemical shift. The principal components of the shielding tensor (ignoring the fine structure initially) calculated from the spectrum are given in Table IV.

The reduction in shielding anisotropy relative to the glycinate complex indicates that the bond lengths surrounding the cadmium are likely to be similar. This is indeed the case as the Cd–O distances to alanine and water molecules are 2.326 and 2.296 Å, respectively, and the Cd–N distance is 2.334 Å.[7]

Figure 4 also shows the expansion of the isotropic ^{113}Cd peak, showing the fine structure due to coupling to ^{14}N nuclei. As in the case of the glycinate complex discussed above, the resulting multiplet is a combination of direct and indirect dipolar coupling

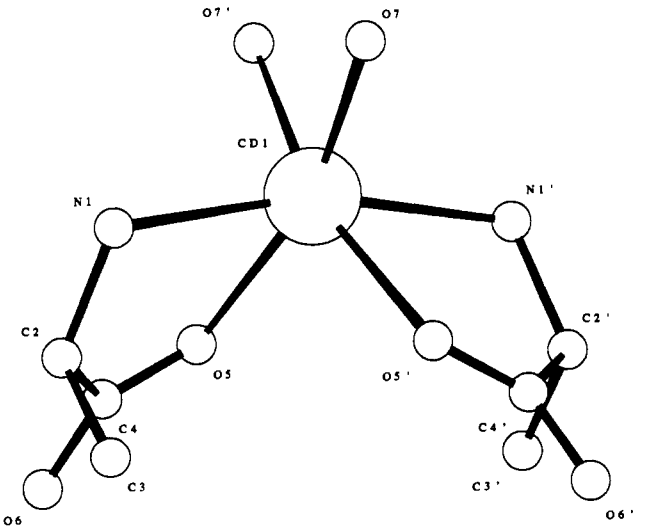

Figure 3. X-ray crystal structure of bis(L-alaninato)cadmium(II) trihydrate, $Cd(H_2NCH(CH_3)COO)_2 \cdot 3H_2O$ (coordinates taken from ref 7).

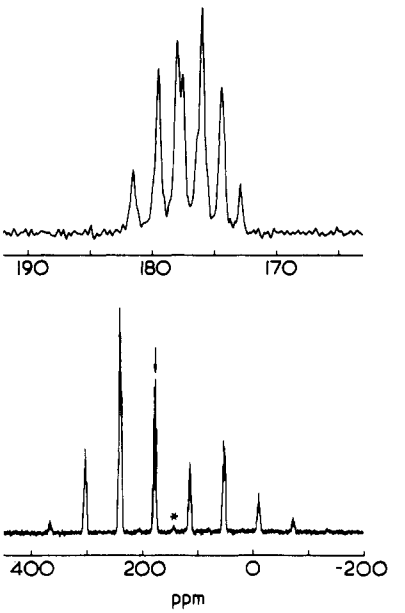

Figure 4. ^{113}Cd CP/MAS NMR spectrum of bis(L-alaninato)cadmium(II) trihydrate: (top) expansion of isotropic peak; (bottom) whole spectrum. The arrow denotes the isotropic peak. A minor amount of impurity is marked by an asterisk.

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Table V. Comparison of Observed and Simulated Intensities for the Fine Structure in the Centerband of the ^{113}Cd Spectrum of Bis(L-alaninato)cadmium(II) Trihydrate[a]

experimental		simulated	
position (δ/ppm)	intensity (approx)	position (δ/ppm)	intensity
181.57	1	181.57	1
		180.04	1
179.53	3	179.62	2
178.01	3	178.05	4
177.55	2	177.57	1
176.43 (sh)	1	176.49	2
176.01	4	176.03	3
174.45	3	174.48	3
172.95	1	172.95	1

[a] The simulation is for two ^{113}Cd sites, at 177.87 and 176.34 ppm, both coupled to two identical ^{14}N nuclei with J = 118 Hz and S = 15 Hz.

effects. In the ^{13}C spectrum of the alaninate complex (not shown) the peak splitting of the α-carbon due to direct coupling is 52 Hz, which is similar to that observed for the glycinate complex (47 Hz); this suggests that the effects of direct dipolar coupling in the ^{113}Cd spectrum (the S term in eq 3) will also be similar. However, the pattern cannot be simulated on the basis of a single ^{113}Cd site coupled to two identical ^{14}N nuclei. Coupling to two identical ^{14}N atoms could produce at most a multiplet of six peaks (as discussed above for the glycinate complex), which approximate to a 1:2:3:2:1 quintet if the S term in eq 3 is much less than the isotropic J-coupling. Coupling to three identical ^{14}N atoms is another possibility, and this would give a multiplet of 10 peaks which would approximate to a 1:2:3:3:3:2:1 septet if $S \ll J$. This also does not agree with the observed spectrum. The most likely explanation is that the spectrum results from *two* distinct ^{113}Cd sites which both couple to two identical ^{14}N nuclei. If the chemical shift separation of the two ^{113}Cd sites is similar to the J-coupling, then this would predict a sextet of an approximate intensity ratio of 1:3:5:5:3:1, with the central peaks capable of showing additional fine structure. This corresponds fairly well with the observed spectrum.

However, we have, as yet, been unable to simulate the fine structure observed in this spectrum exactly. Our best simulation (using eq 2) is for two ^{113}Cd peaks to be present which are separated by 102 Hz (1.53 ppm); these are coupled to two identical ^{14}N nuclei with an isotropic J-coupling of 118 Hz and an S value of *ca.* 15 Hz. This gives the results shown in Table V. The failure to simulate the observed spectrum exactly may be due to the breakdown in some of the assumptions made in the derivation of eq 2.

The existence of a second cadmium site might also be expected to be revealed through differences in the fine structure of the spinning sideband peaks as the sites would probably have different anisotropies. However, the fine structure of the sidebands is also affected by any variation in spinning speed during the course of the experiment, and this could account for the differences in the fine structure that are observed. It does appear, however, that the two sites have similar anisotropies as well as isotropic chemical shifts. It is worth emphasizing that the shielding anisotropy values given for the alaninate in Table IV are calculated on the basis of a single site at the average position, which, as discussed here, is probably an oversimplification.

The X-ray single-crystal structure of bis(L-alaninato)cadmium(II) trihydrate shows, however, only one cadmium site.[7] It is possible that our sample has a structure different from that on which the X-ray crystal structure determination was performed, but the unit cell parameters determined for a single crystal from our sample were found to be identical to those of the published structure solution ($a = b$ = 6.375 Å; c = 25.52 Å; $\alpha = \beta = 90°$; $\gamma = 120°$; trigonal). We also note that there is no evidence for more than one cadmium site from our ^{13}C CP/MAS NMR results.

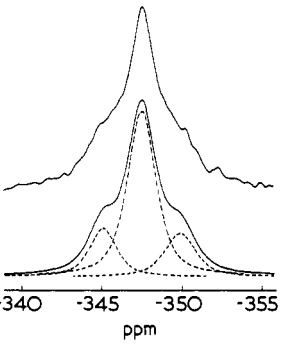

Figure 5. ^{15}N CP/MAS NMR spectrum of bis(L-alaninato)cadmium(II) trihydrate: (top) experimental; (bottom) simulation with an average $J(^{15}N–^{111/113}Cd)$ = 146 Hz.

One possible explanation of these observations is that the powdered sample (on which the NMR measurements were made) might consist of two diastereoisomers. There are two chiral centers: in the optically active alanine molecule and the cadmium center. The X-ray structure was for a single crystal in the Δ-L form (and so has one specific cadmium site), while the powder may contain a mixture of the Δ-L and Λ-L forms. The latter would imply the presence of two distinct cadmium sites in nearly equivalent chemical environments in the powder, which agrees with our analysis of the NMR results. The two diastereoisomers are expected to have very similar powder diffraction patterns, and so possibly not be distinguishable on this basis.

In an attempt to clarify the situation further, a natural-abundance ^{15}N CP/MAS NMR spectrum was recorded for the same sample of bis(L-alaninato)cadmium(II) trihydrate. This shows the presence of a single ^{15}N environment, with the peak shape being affected by J-coupling to both ^{111}Cd (12.8% natural abundance) and ^{113}Cd (12.3% natural abundance), both of which are of spin $I = {}^1/_2$. Coupling to ^{111}Cd is expected to be similar, but not identical, to coupling to ^{113}Cd.[1] A least-squares fit of the observed spectrum (Figure 5) gives a value for the average $J(^{15}N–^{111/113}Cd)$ coupling to be 146 (±15) Hz, which is comparable to the value of 165 Hz measured for $J(^{15}N–^{113}Cd)$ of $Cd(gly)_2$ species in a supercooled solution.[19] There are few other values of J-couplings between ^{15}N and $^{111}Cd/^{113}Cd$ available in the literature.[26]

Cadmium Cysteinate (1:2), $Cd(H_2NCH(CH_2SH)COO)_2$. The structure of cadmium cysteinate is unknown, mainly because it is obtained as an extremely insoluble amorphous material. The insolubility probably indicates a polymeric structure. The low solubility, amorphous nature, and the consequent lack of X-ray single-crystal information makes any information available from solid-state NMR spectroscopy particularly valuable. There has been a preliminary report of the structure of a 1:1 cadmium–β,β-dimethylcysteine complex[27] which might be expected to have a similar structure; however, the stoichiometry of the cadmium cysteinate reported here is 1:2, and so a significantly different coordination must exist.

The ^{113}Cd CP/MAS NMR spectrum is shown in Figure 6. The spectrum has a spinning sideband pattern with an anisotropy intermediate between those of the glycinate and alaninate complexes. The principal components of the shielding tensor are given in Table IV. The first point of significance is that there is no evidence for any coupling to ^{14}N nuclei, which suggests that, unlike the cases of the glycinate and alaninate complexes discussed above, that there is no direct bonding between cadmium and nitrogen. There are, however, examples in the literature of Cd–N environments that do not show noticeable coupling between ^{113}Cd

(26) Witanowski, M; Stefaniak, L.; Webb, G. A. *Annu. Rep. NMR Spectrosc.* **1986**, *18*, 1.
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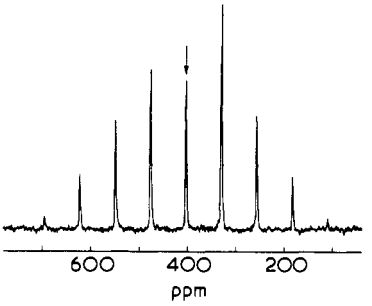

Figure 6. ^{113}Cd CP/MAS NMR spectrum of cadmium cysteinate (1:2). The arrow denotes the isotropic peak.

and ^{14}N,[28-30]although the observed line widths in these cases may have been greater than the coupling. In our case, the observed line width at half peak height is 170 Hz, indicating that the *J*-coupling, if any, between ^{113}Cd and ^{14}N must be less than 60 Hz. The isotropic chemical shift position is 402.5 ppm, which is in the region that signifies that sulfur must be bonded to cadmium. In a study of various (solid) salts of $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$, the Cd(3S,3O) environment was observed between 392 and 409 ppm, while the Cd(4S,1O) and Cd(4S) environments resonated at *ca.* 495 and *ca.* 660 ppm respectively.[31] Thus the observed chemical shift is compatible with coordination dominated by the charged oxygen and sulfur ligands. The NMR results do not completely preclude long-range bonding between cadmium and nitrogen, as any *J*-coupling between ^{113}Cd and ^{14}N might be significantly less than that in the glycinate and alaninate complexes.

It is interesting to note that there is a high degree of local order at the cadmium site (as it gives a narrow ^{113}Cd NMR peak), but the overall structure is amorphous, presumably due to extensive branching and cross-linking of polymeric chains. These observations can be explained by chain structures (Figure 7) and related chains involving *cis* bridges or other chiralities at the metal center. The infrared spectrum for the cadmium cysteinate complex shows the N–H stretching frequencies at 3404 and 3010 cm^{-1} to be much broader than those for the cadmium glycinate complex. This is indicative of the presence of NH_3^+ groups, as in the proposed structure, rather than NH_2 species.

Unfortunately, there is thus far insufficient data on similar cadmium environments to be able to draw any firm conclusions from either the precise value of the isotropic chemical shift or the magnitude of the shielding anisotropy.

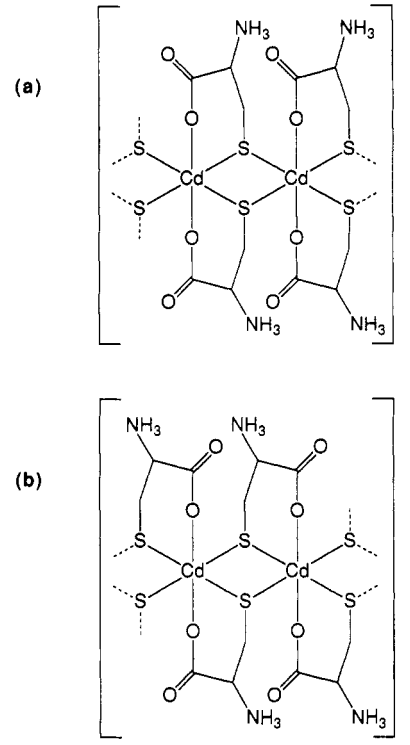

Figure 7. Possible structures for cadmium cysteinate (1:2): (a) Simple structure; (b) stepped chain structure.

Conclusions

Solid-state ^{113}Cd NMR spectroscopy is shown to be a very sensitive probe of the cadmium environment in cadmium–amino acid complexes. Not only does it provide the isotropic chemical shift (as observed in solution NMR), but it also gives information on the chemical shift anisotropy. Coupling to ^{14}N may also be observed, and this gives more highly useful information on the cadmium environment. On the basis of the ^{113}Cd NMR results in this paper, the presence of two diastereoisomers in a powder sample of bis(L-alaninato)cadmium(II) trihydrate has been inferred and a model proposed for the (unknown) structure of cadmium cysteinate.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, and bond lengths and angles involving hydrogen (2 pages). Ordering information is given on any current masthead page.

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