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The Crystal and Molecular Structure of Bis(2,2′-dipyridylamine-*N*,*N*′)di(nitrato-*O*)-cadmium(II); Solid State ^{113}Cd NMR, Components and Orientation of the Chemical Shift Tensor Relative to the Donor Ligands

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Abstract

The structure of the titled compound has been determined and refined. The structure consists of isolated molecules separated by ordinary Van der Waals' distances. The Cd atom is on a crystallographic center of symmetry. The coordination polyhedron of the Cd atom is distorted octahedral with four pyridine nitrogen donors in the equatorial plane and with axial oxygen atoms from the nitrate groups. The Cd–O distance is 2.599(4) Å, the Cd–N distances are 2.310(4) and 2.316(3) Å, and the N–Cd–N bite angle is 79.0(1)°. The solid state magic angle spinning/cross polarization ^{113}Cd NMR isotropic chemical shift is +51.4 ppm and the components of the chemical shift tensor are: $S_{11} = -92$ ppm, $S_{33} = +208$ ppm and $S_{22} = +39$ ppm and their directions are: in the CdN_4 plane and bisecting the N–Cd–N bite angle, perpendicular to the CdN_4 plane and the third perpendicular to the other two, respectively. This permits the assignment of contributions to the chemical shift tensor of 50 ppm from pyridine nitrogen and of −50 ppm from nitrate oxygen. From the tensor components, aromatic nitrogen can be distinguished from aliphatic nitrogen donors. Crystal data: $C_{20}H_{18}O_6N_8Cd$; $M_r = 578.8$, $F(000) = 580$, monoclinic, $P2_1/c$, $a = 8.591(1)$, $b = 16.496(2)$, $c = 7.878(1)$ Å, $\beta = 95.97°$, $\lambda = 0.71073$ Å, Mo Kα, $V = 1110(1)$ Å^3, $Z = 2$, $D_m = 1.73(2)$, $D_x = 1.73$ g/cm^3, $\mu = 10.3$ cm^{-1}, $R_f = 0.039$, 1834 reflections, 160 parameters, $T \sim 298$ K. Refinement was by full matrix least-squares with anisotropic temperature factors.

Introduction

Ca and Zn are spectroscopically inert and probes of these metal sites are in general difficult to find. In addition, the Ca and Zn nuclei of reasonable abundance are quadrupole nuclei and the detection and interpretation of their NMR is still difficult. Therefore, ^{113}Cd NMR continues to develop as a probe of Ca and Zn sites in biological molecules. A number of reviews now cover the biological significance and applications of ^{113}Cd NMR [1–3] and the ^{113}Cd NMR literature has been referenced [4, 5]. Ideally, one would like to develop correlations between the ^{113}Cd NMR chemical shift and the coordination environment and in this way assess the relative contributions from different electron donor ligands to the chemical shift. Such correlations between chemical shift positions and the coordination environment of cadmium(II) compounds with known structure are absolutely essential to the rational application of ^{113}Cd NMR to biological systems. This is especially relevant since recent results indicate that relying on isotropic chemical shift positions to predict atom types and/or environments can be very misleading [6, 7]. Therefore, solution ^{113}Cd NMR will also be misleading without care and other information.

As part of a long-standing commitment toward establishment of such correlations with the end view of making ^{113}Cd NMR a more powerful investigative tool, we have synthesized a number of compounds with varying donor atoms and different coordination polyhedra, determined their crystal structures and measured their solution and solid state ^{113}Cd NMR spectra. At times these results have been disappointing in that the isotropic chemical shift has not differentiated between atom types and coordination polyhedra as hoped. However, recently it has become possible to extract from the spinning side-bands of the MAS/CP (magic angle spinning/cross polarization) solid state ^{113}Cd NMR, the components of the chemical shift tensor [8, 9]. The components of the chemical shift tensor in turn indicate that the desired chemical information is contained therein and gives us new hope to obtain our desired goal. This report shows how structural information coupled with the ^{113}Cd NMR gives the orientation and magnitude of the components of the chemical shift tensor and how this information can be related to donor atom type. To illustrate the sensitivity of this new tool, a compar-

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ison with the structure and recently calculated chemical shift tensor components of bis(2-aminomethylpyridine)dinitratocadmium(II) shows differences between two very similar chemical environments [10]. Furthermore, we have shown very recently that although the isotropic chemical shift may be the same for two different compounds, the components of the chemical shift tensor are sufficiently different to distinguish between the two [7]. The present structure and ^{113}Cd NMR data further develop this project.

Experimental

A methanol solution (250 ml) containing 1.71 g (0.01 mol) 2,2′-dipyridylamine (Aldrich) and 1.54 g (0.005 mol) $Cd(NO_3)_2 \cdot 4H_2O$ (Baker) was warmed gently with stirring and then was allowed to evaporate at ambient temperature until diffraction quality crystals appeared (3–5 days). They were collected by gravity filtration and either sealed in thin-walled capillaries for X-ray diffraction studies or stored for NMR measurements.

X-ray Data

X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer interfaced to PDP-11/60; crystal aligned and intensity data were collected by standard techniques [11]. Bis(2,2′-dipyridylamine)-dinitratocadmium(II), $C_{20}H_{18}O_6N_8Cd$, $D_x = 1.73$ g/cm^3; $D_m = 1.73(2)$ g/cm^3 by flotation in $CHBr_3$/$CHCl_3$ solution; $h0l$, $l = 2n + 1$; $0k0$, $h = 2n + 1$ absent; crystal 0.41 X 0.18 X 0.11 mm; faces: (010), (0 – 10), (001), (00 – 1), (101), (10 – 1), (–100); numerical absorption correction (based on Gaussian integration formula) max., min. transmission factors 0.897–0.834; $\mu = 10.3$ cm^{-1}; graphite monochromator, $\theta = 6.1°$; $P = 0.030$ in $\sigma(F_o{}^2) = [\sigma(I_{raw})^2 + (PI_{raw})^2]^{1/2}/Lp$; data considered non-zero if F^2 greater than 4 $\sigma(F^2)$, 4181 independent hkl values measured in ω–2θ mode to 2θ max = 60°, $\sin\theta/\lambda = 0.766$; hkl range –12 to 12, –23 to 0, 0 to 11; 1834 reflections used; structure solved by standard heavy atom methods; variable scan speed of 0.7–3.3°/min with preliminary scan speed of 3.3°/min 2θ; scan parameter 'DOMA' = 0.65°; 25 general reflections used to determine orientation matrix (checked fully every 24 h) and used for all parameter measurements; intensity and orientation of three standard reflections (–3 –2 4, –2 –8 2, 2 8 –4) monitored every 2 h with overall decay of less than 1% I, structure refined by full matrix least-squares, anisotropic temperature factors for all non-hydrogen atoms and anomalous dispersion corrections with weights based upon intensity statistics; function minimized = $\Sigma_i w_i [(F_o)_i - (F_c)_i]^2$; where $w = 1/\sigma(F_o{}^2)$; hydrogen atoms were located from difference Fourier maps and included in structure factor calculations, but neither coordinates nor temperature factors were refined; final least-squares performed on MicrovaxII with f, f' and f'' from International Tables [12]; largest delta at end of refinement = 0.01 σ, no. of variables = 160; final $R = 0.039$, $R_w = 0.045$; error of observation of unit weight = 1.72; the final difference map showed a positive peak height of 0.66 e/Å^3; a negative of 0.65 e/Å^3; all computer programs used were either those in Enraf-Nonius SDP package [13] on the PDP 11/60 or the MicrovaxII. ORTEP II [14] calculated on Vax-11/780 and plotted on VT8222. The atomic coordinate parameters and errors are listed in Table I. Selected interatomic distances and angles and errors are listed in Table II. The experimental conditions and equipment for the solution ^{113}Cd NMR have been described elsewhere [15]. The principle components of the ^{113}Cd shielding tensor were determined by Simplex optimization of a two parameter fit of the chemical anisotropy and the asymmetry parameter, coupled with the rotor spinning speed and the spectrometer frequency to simulate the spinning side band intensities of the MAS spectra [8]. The simulated spectrum showed a good fit to the observed spectrum, Fig. 1, and the calculations, which were carried out on a Vax-11/780 with programs written by Marchetti [9], yielded the best estimates of the principal components of the chemical shift tensors.

TABLE I. Positional Parameters of Bis-dipyridylamine-dinitratocadmium(II)[a]

Atom	x	y	z	B (Å^2)[b]
Cd	0.000	0.000	0.000	3.331(7)
O(1)	0.2437(6)	–0.0882(2)	0.0729(5)	7.0(1)
O(2)	0.0606(4)	–0.1570(3)	0.1382(5)	7.8(1)
O(3)	0.2846(5)	–0.2074(2)	0.1721(6)	6.9(1)
N(1)	–0.0999(4)	0.0156(2)	0.2592(4)	3.26(7)
N(2)	–0.0284(4)	0.1536(2)	0.2708(5)	3.54(7)
N(3)	0.1741(4)	0.0932(2)	0.1325(4)	3.09(7)
N(4)	0.2013(4)	–0.1515(2)	0.1287(5)	3.83(8)
C(1)	–0.1144(5)	0.0890(2)	0.3255(5)	3.01(8)
C(2)	–0.2159(5)	0.1045(3)	0.4492(5)	3.54(9)
C(3)	–0.2989(5)	0.0416(3)	0.5075(6)	4.2(1)
C(4)	–0.2800(5)	–0.0363(3)	0.4425(6)	4.14(9)
C(5)	–0.1813(5)	–0.0452(3)	0.3225(6)	3.84(9)
C(6)	0.1239(5)	0.1539(2)	0.2250(5)	2.92(8)
C(7)	0.3254(5)	0.0960(3)	0.0979(6)	3.57(9)
C(8)	0.4246(5)	0.1584(3)	0.1464(6)	4.4(1)
C(9)	0.3695(6)	0.2212(3)	0.2367(6)	4.7(1)
C(10)	0.2193(6)	0.2194(3)	0.2784(6)	4.1(1)

[a] e.s.d.s given in parentheses. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE II. Bond Distances (Å) and Angles (°) of Bis-dipyridylamine-dinitratocadmium(II)^a

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cd	O(1)	2.599(4)	N(1)	C(5)	1.359(6)	C(2)	C(3)	1.366(7)
Cd	N(1)	2.310(4)	N(2)	C(1)	1.390(5)	C(3)	C(4)	1.398(7)
Cd	N(3)	2.316(3)	N(2)	C(6)	1.393(5)	C(4)	C(5)	1.344(7)
O(1)	N(4)	1.218(5)	N(3)	C(7)	1.356(5)	C(6)	C(10)	1.395(6)
O(2)	N(4)	1.226(5)	N(3)	C(6)	1.336(6)	C(7)	C(8)	1.365(6)
O(3)	N(4)	1.193(5)	C(1)	C(2)	1.397(6)	C(8)	C(9)	1.370(7)
N(1)	C(1)	1.330(5)				C(9)	C(10)	1.365(8)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
O(1)	Cd	O(1')	150.1(5)	O(1)	N(4)	O(2)	116.8(4)
O(1)	Cd	N(1)	103.5(1)	O(1)	N(4)	O(3)	123.8(4)
O(1)	Cd	N(1')	76.2(1)	O(2)	N(4)	O(3)	119.4(4)
O(1)	Cd	N(3)	78.1(1)	N(1)	C(1)	N(2)	120.1(4)
O(1)	Cd	N(3')	101.9(1)	N(1)	C(1)	C(2)	122.1(4)
N(1)	Cd	N(1')	180.1(3)	N(2)	C(1)	C(2)	117.8(4)
N(1)	Cd	N(3)	79.0(1)	C(1)	C(2)	C(3)	118.8(4)
N(1)	Cd	N(3')	101.0(1)	C(2)	C(3)	C(4)	119.3(4)
N(3)	Cd	N(3')	180.1(2)	C(3)	C(4)	C(5)	118.4(5)
Cd	O(1)	N(4)	105.3(3)	N(1)	C(5)	C(4)	123.6(4)
Cd	N(1)	C(1)	120.5(3)	N(2)	C(6)	N(3)	120.3(3)
Cd	N(1)	C(5)	119.6(3)	N(2)	C(6)	C(10)	117.6(4)
C(1)	N(1)	C(5)	117.7(4)	N(3)	C(6)	C(10)	122.2(4)
C(1)	N(2)	C(6)	128.8(3)	N(3)	C(7)	C(8)	123.6(5)
Cd	N(3)	C(6)	120.9(3)	C(7)	C(8)	C(9)	118.5(4)
Cd	N(3)	C(7)	121.3(3)	C(8)	C(9)	C(10)	119.7(4)
C(6)	N(3)	C(7)	117.1(3)	C(6)	C(10)	C(9)	119.0(4)

^{a}e.s.d.s given in parentheses.

Results and Discussion

Structure Description

The crystal structure of bis(2,2'-dipyridylamine)-dinitratocadmium(II) is composed of isolated neutral molecular units separated by normal van der Waals' distances, as shown in the packing diagram, Fig. 2. The six-coordinate cadmium atom which sits upon a crystallographic center of symmetry has four pyridine nitrogen atoms coplanar with it and two monodentate nitrate oxygen atoms are in the axial positions, Fig. 3. The Cd–N distances at 2.310(4) and 2.316(3) Å are similar to the value observed (2.326 Å) for Cd–N(pyridine) in a very closely related structure, bis(2-aminomethylpyridine)dinitratocadmium(II) [10]. The polymeric structure of cadmium bis(pyridine-2 carboxylate) also shows a Cd–N distance of 2.35(1) [16]. A more constrained ligand, 2,2'-dipyridyl, shows Cd–N distances of 2.33–2.43 Å for the nitrate structure and 2.37–2.40 Å for the isothiocyanate structure [5]. Unsubstituted pyridines yield slightly longer Cd–N distances at 2.35–2.37 Å as in tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) [15]. The bite angle, N(1)–Cd–N(3), is 79.0(1)° while the interligand angle N(1)–Cd–N(3') is 101.0(1)°. The axially bonded Cd–O(1) distances are at 2.599(4) Å, while Cd–O(2) distances are at 2.84 Å, too long to be considered covalent bidentate bonding but yet close enough to the cadmium and in an appropriate configuration to influence the chemical shielding tensor, *vide infra*. The bonding distance is consistent with this observation in that it is somewhat longer than the comparable Cd–O (axial, monodentate nitrate) distance of 2.450(3) Å in the bis(2-aminomethylpyridine)dinitratocadmium(II). In the dipyridyl complex [5] the nitrates are still monodentate, but in a *cis* configuration, at 2.41–2.435 Å. Possibly this longer than expected Cd–O distance is brought about by steric hindrance from the hydrogens of the pyridine rings. The two aromatic rings (planes) of the ligand have a dihedral angle of 33.6° relative to each other. All the atoms of the two nitrate groups together with the cadmium atom form a plane which is almost perpendicular to the CdN_4 plane, see Table III. It is somewhat surprising to find this planarity and it is probably electronic in origin, *i.e.* it is demanded by the use of the in-plane lone pair electrons of the oxygen atom of the nitrate group. The other bond distances and angles

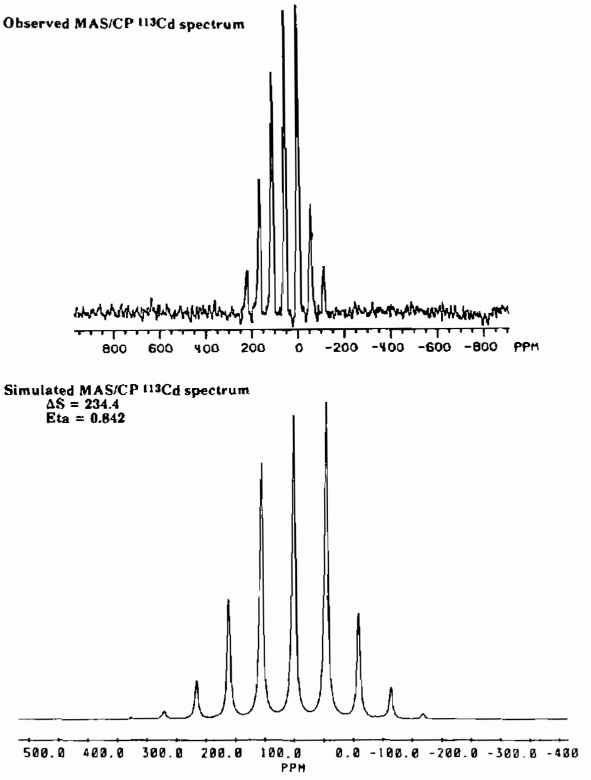

Fig. 1. Simulated and observed ^{113}Cd NMR spectra. Unfortunately, they are on different scales. Optimized values of the chemical anisotropy and the asymmetry parameter are indicated on the simulated spectrum.

of both the nitrate groups and the bidentate *N,N'*-dipyridylamine ligands show expected values.

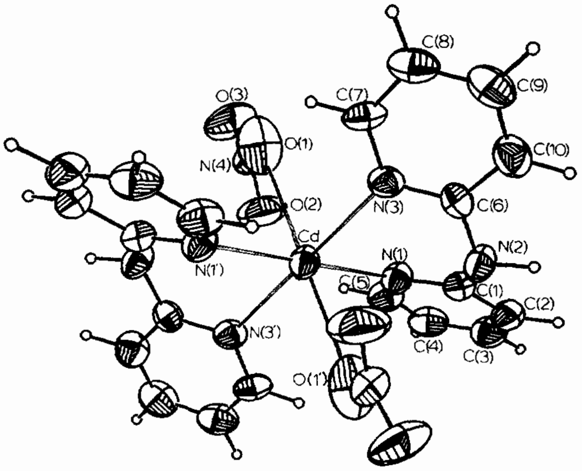

Fig. 3. An ORTEPII [14] drawing of an isolated molecule of bis(2,2'-dipyridylamine)dinitratocadmium(II). The thermal ellipses are drawn at the 50% probability level. The hydrogen atoms are drawn with an arbitrary radius of 0.1 Å and are represented by open circles. The Cd atom is on a crystallographic center of symmetry and the primed atoms are related to the unprimed by this symmetry operation. The pyridine ring notation is such that N(1) is bound to C(1) and proceeds to C(5) also bound to N(1) in a clockwise manner. N(3) is bound to C(7) and proceeds through C(8), C(9), C(10), C(6), N(3) in a clockwise fashion.

^{113}*Cd NMR Data*

A summary of NMR data and relevant interatomic distances is given in Table IV.

To find correctly the orientation of these components of the chemical shift tensor, one would have

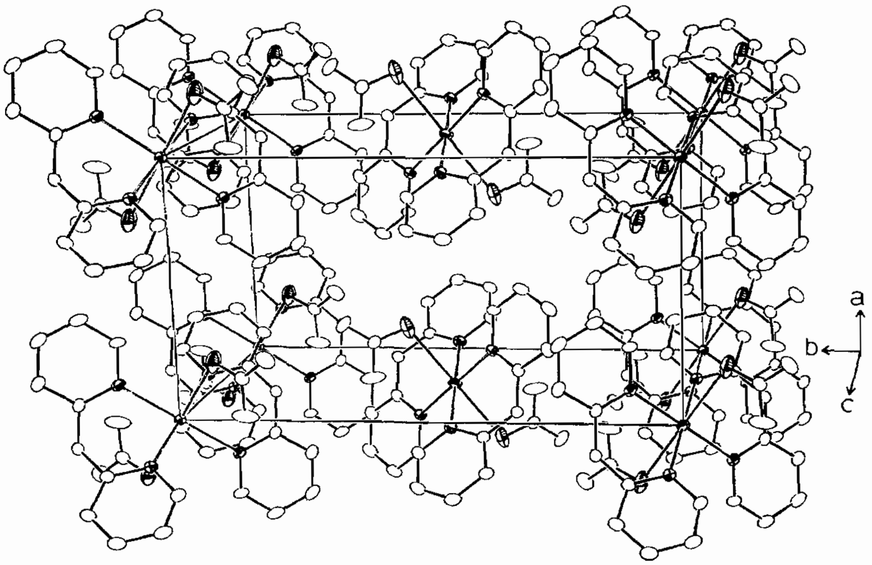

Fig. 2. An ORTEPII [14] drawing of the contents of the unit cell. The coordination sphere atoms and the Cd atom are shown by shaded ellipses, whereas all the other atoms are open ellipses. Hydrogen atoms have been omitted for clarity. The origin of the unit cell is at the lower right rear of the drawing with cell directions as indicated.

TABLE III. Least-squares Planes of Bis-dipyridylamine-dinitratocadmium(II)[a]

Plane number P, Q, R, S	Atoms in plane and deviations from plane (Å)		Atoms out of plane and deviations (Å)	
1 ($X^2 = 42.0$)	N(3)	0.016(3)	N(2)	−0.035(4)
−1.7965	C(6)	−0.009(4)	Cd	0.444(0)
7.9829	C(7)	−0.009(4)		
−6.4868	C(8)	−0.004(5)		
−0.4442	C(9)	0.011(5)		
	C(10)	−0.004(5)		
2 ($X^2 = 48.8$)	N(1)	0.018(3)	N(2)	−0.052(4)
−5.8345	C(1)	−0.015(4)	Cd	0.691(1)
2.9410	C(2)	0.002(4)		
−5.0226	C(3)	0.008(5)		
−0.6907	C(4)	−0.005(5)		
	C(5)	−0.008(4)		
3 ($X^2 = 0.8$)	N(4)	−0.003(4)	Cd	0.060(0)
−0.2809	O(1)	0.001(4)		
−6.1147	O(2)	0.001(4)		
−7.2458	O(3)	0.001(4)		
−0.0597				
4 ($X^2 = 0.0$)	N(1)	0.000(3)	Cd	0.000(−)
−4.6699	N(3)	−0.000(3)		
12.3369	N(1′)	0.000(3)		
−2.5405	N(3′)	−0.000(3)		
−0.0000				
5 ($X^2 = 92.6$)	N(4)	−0.006(4)		
−0.1982	O(1)	−0.015(4)		
−6.3497	O(2)	−0.012(4)		
−7.2104	O(3)	0.020(4)		
−0.0000	Cd	0.000(0)		
	N(4′)	0.006(4)		
	O(1′)	0.015(4)		
	O(2′)	0.012(4)		
	O(3′)	−0.020(5)		

Plane no.	Plane no.	Dihedral angle
Dihedral angles between planes		
1	2	33.6(2)
1	3	52.0(1)
1	4	36.9(2)
1	5	52.9(1)
2	3	51.9(2)
2	4	39.3(2)
2	5	52.8(1)
3	4	84.6(2)
3	5	1.0(4)
4	5	85.6(1)

[a]Equation of the planes are in the form: $Px + Qy + Rz - S = 0$ in crystallographic space.

to do the single crystal ^{113}Cd NMR experiment in which the ^{113}Cd NMR is observed at incremental angles of rotation about the crystallographic directions which can be related to the molecular frame of ref. 17. However, this experiment requires crystals of the size of several millimeters on an edge, which are all too frequently difficult to obtain and require considerable amounts of NMR time. Many Cd structures possess sufficient local symmetry about the metal atom to entice one to attempt making reasonable estimates of the orientation of the components of the chemical shift tensor. We have made some progress along these lines and wish to extend that attempt to the present structure. A component of the chemical shift tensor reflects contributions from atoms in the plane perpendicular to that component. It has been found that oxygen atoms of monodentate nitrate groups contribute approximately −50 ppm each to the chemical shift tensor component. In addition, each nitrogen of aromatic nitrogen donor ligands contributes approximately +50 ppm. Therefore, in this compound the largest positive component should have a value of ~+200 ppm directed normal to the 4N plane, approximately along the O–Cd–O direction. The largest negative component should be perpendicular to the plane containing the Cd atom and the two nitrate groups, have a value of ~−100 ppm, and bisect the N(1)–Cd–N(3) angle of ~90°. The third component should be perpendicular to the other two at $4 \times 50 \cos 45° + (-100) = +41$ ppm. The agreement with the observed values of +208, −92 and +39 ppm is better than we have any right to expect considering the nature of the approximations and the present state of the art.

For comparison purposes the analogous ^{113}Cd NMR data is presented for bis(2-aminomethylpyridine)dinitratocadmium(II) which has essentially the same structure as the present compound and the orientation of the tensor components are probably similar. When this structure and the MAS/CP results were originally reported, we had not the capability to retrieve the components of the chemical shift tensor. Eventually we plan to establish a relationship between Cd–O distances and contributions to the ^{113}Cd chemical shift tensor, but data at present are insufficient to report such a correlation. However, the large deshielded value of +558 ppm which is normal to the plane of the four nitrogens is striking. The contribution of an aliphatic nitrogen to the tensor component, in contrast to +50 ppm for an aromatic nitrogen donor, is more like +225 ppm. The implication is that we can tell the difference between aromatic and aliphatic nitrogen donors using ^{113}Cd NMR via the components of the chemical shielding tensor. The component at +238 ppm also reflects this greater deshielding value from the aliphatic nitrogen donor. These results give us considerable hope for the utility of ^{113}Cd NMR as a structural tool as well as encouragement to continue this research path.

TABLE IV. Summary of NMR Data and Relevant Interatomic Distances

	Isotropic shift (ppm)	Tensor components (ppm)			Distances (Å)		
		S_{11}	S_{22}	S_{33}	Cd–O(1)	Cd–N(pyr)	Cd–N(amine)
This structure	+51.4	−92	+39	+208	2.599(4)	2.310(3) 2.316(3)	
Aminomethylpyridine [10]	+218.0	−128	+224	+558	2.450(3)	2.326(2)	2.279(2)

Supplementary Material

Tables SI, SII and SIII listing the thermal parameters, the derived hydrogen positions and bond distances and angles involving hydrogens (3 pages); and Tables of observed and calculated structure factors (36 pages) are available from the authors on request.

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