regarding postulated intermediates along the reaction coordinate for proton transfer.

Conclusion

Heat capacities of protonation in sulfolane are negligible over a wide temperature range, 30 to 150 or 200 °C. If this result is general for other nonhydroxylic solvents, it implies that extrapolation of data for acid–base reactions near room temperature to elevated temperatures will be straightforward since large and variable heat capacities will not have to be contended with. Although limited by the present equipment and the stability of sulfolane to temperatures less than 200 °C, we suspect that heat capacities at much higher temperatures would become increasingly negative as the dielectric constant of the solvent decreases. Analysis of partial molar heat capacities of both electrolytes and nonelectrolytes in dipolar nonhydroxylic solvents suggests that most reactions in these media will have small heat capacity changes over wide temperature ranges. Since many types of catalytic processes involve proton transfer at elevated temperatures, it is important to test the generality of this simplifying conclusion.

Acknowledgment. We are pleased to acknowledge the support of this work by the Exxon Educational Foundation and by the U.S. Department of Energy under Grant No. DE-FG22-82PC50807. Professors Robert Wood and Cecil Criss provided helpful advice on the problems of high-temperature calorimetry.

Registry No. Quinoline, 91-22-5; 2-methylquinoline, 91-63-4; 4-amino-2-methylquinoline, 6628-04-2; 2-aminopyridine, 504-29-0; 2-amino-3-methylpyridine, 1603-40-3; 4-aminopyridine, 504-24-5; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; imidazole, 288-32-4; triethanolamine, 102-71-6; methanesulfonic acid, 75-75-2; sulfuric acid, 7664-93-9; sulfolane, 126-33-0.

Cadmium-113 Shielding Tensors of Cadmium–Oxo Compounds. 1. Single-Crystal Studies on $Cd(NO_3)_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$

Robert S. Honkonen, F. David Doty, and Paul D. Ellis*

Contribution from the Department of Chemistry, University of South Carolina,
Columbia, South Carolina 29208. Received December 13, 1982

Abstract: Diffraction-quality single crystals of $Cd(NO_3)_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$ have been investigated by ^{113}Cd Fourier transform NMR methods in a home-built single-crystal probe. As expected from point group symmetry arguments, the shielding tensors do not exhibit axial symmetry. The ^{113}Cd NMR of $Cd(NO_3)_2 \cdot 4H_2O$ gave rise to two cadmium resonances for the magnetically nonequivalent (but crystallographically equivalent) positions in the unit cell. The principal elements of the symmetry related tensors for $Cd(NO_3)_2 \cdot 4H_2O$ are −174.4, −154.3, and 22.2 ppm for σ_{11}, σ_{22}, and σ_{33}, respectively (the chemical shifts are reported with respect to solid $Cd(ClO_4)_2$). The ^{113}Cd NMR of $3CdSO_4 \cdot 8H_2O$ afforded three resonances as expected from the crystal symmetry. Two of the resonances are assigned to general positions within the lattice. These positions gave rise to symmetry-related tensors, which have principal elements −93.1, −76.7, and 25.5 ppm. The remaining resonance is assigned to cadmium in special position; the corresponding shielding tensor has principal elements −95.6, −85.3, and −3.4 ppm. These data are discussed in terms of the structure of the cadmium salts.

Introduction

Because of our interest in utilizing ^{113}Cd NMR spectroscopy[1] as a probe for calcium sites in biological systems,[2] we have been interested in obtaining a detailed understanding of the structural factors responsible for the isotropic ^{113}Cd chemical shifts in these molecules. In the systems studied (concanavalin A,[3] parvalbumin,[4] troponin C,[5] calmodulin,[6] and insulin[7]), the substitution of cadmium for calcium places cadmium in an environment in which the atoms in the primary coordination sphere are exclusively oxygens. Cadmium has been assumed to be six-coordinate. The isotropic chemical shifts for these compounds[8] fall in a characteristic range from −85 to −130 ppm with respect to 0.1 M $Cd(ClO_4)_2$. To date, there are no model compounds that can be studied in aqueous solution which have isotropic shifts within this range.[9]

If, however, one performs the ^{113}Cd NMR experiments in the solid state,[11] one finds a bewildering array of cadmium–oxo compounds that can be employed to model these biological systems. The coordination number for cadmium in these compounds is

---

(1) (a) Maciel, G. E.; Borzo, M. *J. Chem. Soc. Chem. Commun.* **1973**, 394. (b) Peters, C. S.; Codrington, R.; Walsh, H. C.; Ellis, P. D. *J. Magn. Reson.* **1973**, *11*, 431. (c) Kostlenik. R. J.; Bothner-by, A. A. *Ibid.* **1974**, *14*, 141. (d) Cardin, A. C.; Ellis, P. D.; Odom, J. D.; Howard, J. W., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 1672.

(2) A. A. Bothner-By actually proposed performing these experiments on Troponin C and Calmodulin more than 10 years ago. The basic approach is outlined in the Ph.D. thesis of R. J. Kostelnik. 1971, University Microfilms 72-21, 599.

(3) Palmer, A. R.; Bailey, D. B.; Cardin, A. D.; Yang, P. P.; Behnke, W. D.; Ellis, P. D. *Biochemistry* **1980**, *19*, 5063. Bailey, D. B.; Ellis, P. D.; Cardin, A. C.; Behnke, W. D. *J. Am. Chem. Soc.* **1978**, *100*, 5236.

(4) Darkenberg, T.; Lindman, B.; Cavé, A.; Parello, J. *FEBS Lett.* **1978**, *92*, 346. Cavé, A.; Parello, J.; Drakenberg, T.; Thulin, E.; Lindman, B. *Ibid.* **1979**, *100*, 148.

(5) Forsén, S.; Thulin, E.; Lilja, H. *FEBS Lett.* **1979**, *104*, 123.

(6) Forsén, S.; Thulin, E.; Drakenberg, T.; Krebs, J.; Seamon, K. *FEBS Lett.* **1980**, *117*, 189.

(7) Sudmeier, J. L.; Bell, S. J.; Strom, M. C.; Dunn, M. F. *Science* **1981**, *212*, 560.

(8) The single exception of this chemical shift range is the shift observed for the calcium site in bovine insulin;[7] its chemical shift is −36 ppm. The X-ray data are definitive in this case for the Ca^{2+} to be six-coordinate: Blundell, T.; Dodson, G.; Hodgkin, D.; Mercola, D. *Adv. Protein Chem.* **1972**, *26*, 279.

(9) The problem arises because of the kinetic lability of the oxo ligands in aqueous solutions. The kinetic lability may be circumvented by employing supercooled aqueous solutions.[10] However, one still has the problem of how to relate those isotropic chemical shifts to structure!

(10) Ackerman, M. J. B.; Ackerman, J. J. H. *J. Phys. Chem.* **1980**, *84*, 3151. Jakobsen, H. J.; Ellis, P. D. *Ibid.* **1981**, *85*, 3367.

(11) (a) Nolle, A. *Z. Naturforsch. A* **1978**, *33*, 666. (b) Ackerman, J. J.; Orr, T. V.; Bartuska, V. J.; Maceil, G. E. *J. Am. Chem. Soc.* **1979**, *101*, 341. (c) Cheung, T. T. P.; Worthington, L. E.; Murphy, L. D.; Murphy, P. D. Gerstein, B. C. *J. Magn. Reson.* **1980**, *41*, 158. (d) Murphy, P. D.; Gerstein, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 3282. (e) Murphy, P. D.; Stevens, W. C.; Cheung, T. T. P.; Lacelle, S.; Gerstein, B. C.; Kurtz, D. M., Jr. *Ibid.* **1981**, *103*, 4400. (f) Mennit, P. G.; Shatlock, M. P.; Bartuska, V. J.; Maciel, G. E. *J. Phys. Chem.* **1981**, *85*, 2087. (g) Inners, R. R.; Doty, F. D.; Garber, A. R.; Ellis, P.D. *J. Magn. Reson.* **1981**, *45*, 503. (h) Ellis, P. D.; Inners, R. R.; Jakobsen, H. J. *J. Phys. Chem.* **1982**, *86*, 1506. (i) Jakobsen, H. J.; Ellis, P. D.; Inners, R. R.; Jensen, C. F. *J. Am. Chem. Soc.* **1981**, *104*, 7442.

either 6, 7, or 8, while the isotropic chemical shifts span a range from 150 to −100 ppm. There is no readily discernible relationship between cadmium coordination geometry or number and the isotropic chemical shift. The final approach that can be employed to understand this enigmatic situation is a detailed investigation of selected cadmium-oxo compounds via single-crystal NMR methods.[12]

The first compounds we investigated were $Cd(NO_3)_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$. These compounds were selected because they represent simple examples of cadmium in an all-oxygen environment with coordination numbers of 8 and 6, respectively. Further, the isotropic chemical shift of $Cd(NO_3)_2 \cdot 4H_2O$ is in the middle of the chemical shift range observed for biological systems. Additionally, powder spectra for both of these compounds have been reported by Gerstein and co-workers.[11d] These data were discussed in terms of axially symmetric ^{113}Cd shielding tensors. Rigorous axial symmetry for a shielding tensor requires the nucleus in question to lie on, at least, a threefold rotation axis (the presence of an irreducible representation with E symmetry). The respective space groups for $Cd(NO_3)_2 \cdot 4H_2O$[13] and $3CdSO_4 \cdot 8H_2O$[14] are F_{dd2} and $C_{2/c}$. The highest rotation axis in both groups is a twofold axis. Therefore, if the tensors were axially symmetric, it would have to occur in both compounds by a complicated set of conditions. We report here that neither tensor is axially symmetric. The tensors have small asymmetry parameters,[12] which would have been difficult to observe in the low-field powder studies previously reported.

Experimental Section

$Cd(NO_3)_2 \cdot 4H_2O$ and $3CdSO_4 \cdot 8H_2O$ were crystallized from aqueous solutions via slow evaporation at room temperature. Crystals of suitable volume (ca. 20 mm^3) required multiple seedings of saturated mother liquor. $Cd(NO_3)_2 \cdot 4H_2O$ crystals are orthorhombic ($a = 5.828$, $b = 25.86$, $c = 11.00$ Å; $Z = 8$) and belong to the space group F_{dd2} (C_{2v}^{19}).[13] $3CdSO_4 \cdot 8H_2O$ is, however, monoclinic ($a = 14.78$, $b = 11.91$, $c = 9.47$ Å, space group $C_{2/c}$ (C_{2h}^{6}); $Z = 4$) and hence has an inconvenient β angle of 97.34.[14] In the latter case, the monoclinic unit cell was transformed to an orthogonal a^*, b, c^* crystallographic reference frame.[15]

For data collection, diffraction-quality crystals of size 3 × 2 × 2 mm and 3 × 3 × 3 mm cadmium nitrate and sulfate, respectively, were chosen. The requisite rotations about three mutually perpendicular axes were readily achieved by mounting the crystal in an open three-sided cube measuring 4.2 mm on the outside edges. The cube was machined from full-density alumina ceramic. The 0.3-mm-thick walls provided sufficient strength for routine handling and occasional dropping. The cube was supported in the spectrometer by a holder similarly machined from alumina, having an outside diameter of 6.0 mm. This gave adequate clearance for rotation in a radio-frequency coil with an inside diameter of 6.2 mm. The rotation of the crystal was accomplished by a goniometer system consisting of two sets of right angle brass gears. The rotation apparatus represents a hybridization of the goniometer systems of Waugh[16] and Veeman.[17]

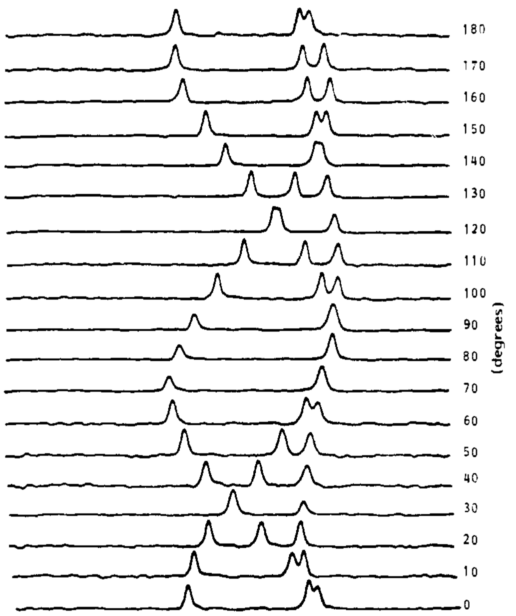

Figure 1. Representative rotation plot spectra for $3CdSO_4 \cdot 8H_2O$.

The cube was readily transferred from the spectrometer goniometer to a modified crystallography goniometer compatible with Weissenberg and precession cameras. The orientation of the crystallographic reference frame with respect to the cube frame was determined by a combination of Weissenberg and Laue techniques with Cu Kα radiation for $Cd(NO_3)_2 \cdot 4H_2O$. The orientation data for cadmium sulfate were obtained on an automated Enraf-Nonius CAD-4 diffractometer.

The NMR experiments for both crystals were performed on a modified wide-bore WP-200 spectrometer which has been previously described.[19] Data acquisition was via a standard matched Hartman–Hahn[20] spin-locked cross-polarization[21] pulse sequence. Contact times were optimized for both compounds and correspond to 5 and 10 ms, for nitrate and sulfate, respectively. An acquisition time of 102.4 ms with a 4-s recycle time was uniformly employed. Typically, addition of 75–100 transients was required to achieve the signal:noise ratio demonstrated in Figure 1.

The determination of the elements of the chemical shielding tensor in the crystallographic reference frame from chemical shift data is a well-documented procedure.[12] The salient features are reviewed here. A single crystal is mounted in a rigorously orthogonal cube. The unitary transformation matrix, R, which brings the unit cell reference frame into coincidence with the cube frame, is determined via the techniques mentioned above. The cube is subsequently mounted in a matching receptacle that supports the crystal in the spectrometer. NMR spectra are taken at 10° increments for positive rotations about the three orthogonal cube axes. The typical sinusoidal rotation plot of chemical shift vs. rotation angle is seen in Figure 1. The observed shift depends solely upon the zz component of the shielding tensor in the laboratory frame, σ_{zz}^{lab}. The variation of the secular part of a second rank tensor with orientation is well known and leads to the following expression:

$$\sigma_{zz}^{\text{lab}} = \tfrac{1}{2}(\sigma_{11}^{\text{cube}} + \sigma_{22}^{\text{cube}}) + \tfrac{1}{2}(\sigma_{11}^{\text{cube}} - \sigma_{22}^{\text{cube}}) \cos 2\theta - \tfrac{1}{2}(\sigma_{12}^{\text{cube}} + \sigma_{21}^{\text{cube}}) \sin 2\theta$$

where the rotation angle, θ, is about the 3-axis of the cube frame. The rotation axis is required to be perpendicular to B_0. Least-squares fitting of the lab response to this sinusoidal function for three rotation plots uniquely determines the six distinct elements of σ^{cube}. The resulting tensor is then transformed to the unit cell (xtal) reference frame via the general transformation

$$\sigma^{\text{xtal}} = R^{-1}\sigma^{\text{cube}}R$$

Diagonalization of σ^{xtal} provides the desired eigenvalues and eigenvectors.

---

(12) (a) Haeberlen, U. "High Resolution NMR in Solids", Suppl. 1 in "Advances in Magnetic Resonance"; by Waugh, J. S., Ed., Academic Press: New York, 1976. (b) Mehring, M. "High Resolution NMR Spectroscopy in Solids"; Springer-Verlag: New York, 1976.

(13) Matkovic, B.; Ribar, B.; Zelenko, B.; Peterson, S. W. *Acta Crystallogr.* **1966**, *21*, 719.

(14) Richardson, J. W.; Jacobsen, R. A.; personal communication.

(15) "Computing Methods in Crystallography"; Rollett, J. S., Ed.; Pergamon Press: New York, 1975; pp 22–26. The author discusses the orthogonalization of a general triclinic cooridnate system. To avoid confusion concerning our notation in the sulfate molecular reference frame, a brief discussion of the transformation is given. Consider a monoclinic reference frame denoted **a b c** with an angle β, different than 90°, between the unit vectors **a** and **c**. The transformation from the monoclinic frame to an orthogonal frame, $a^* b c^*$, is given by

$$\begin{pmatrix} a^* \\ b \\ c^* \end{pmatrix} = \begin{pmatrix} a \sin\beta & 0 & 0 \\ 0 & b & 0 \\ a \cos\beta & 0 & c \end{pmatrix} \begin{pmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \end{pmatrix}$$

Here a, b, c are the dimension (Å) of the monoclinic cell in the **a**, **b**, **c** directions. Note that a^* and c^* are simply the transformed **a** and **c** vectors and should not be interpreted as reciprocal lattice vectors. This transformation preserves the magnitude and relative directions of vectors in the monoclinic system when expressed in the orthogonal frame. Hence, bond lengths, angles, and the magnitude and direction of shielding tensors are invariant.

(16) Pausak, S.; Tegenfeldt, J.; Waugh, J. S. *J. Chem. Phys.* **1974**, *61*, 1338.

(17) Veeman, W. S. *Phil. Trans. R. Soc. London, Ser. A* **1981**, *229*, 629.

(18) Stout, G. H.; Jensen, L. H. "X-ray Structure Determination"; Macmillan: New York, 1965.

(19) Inners, R. R.; Doty, F. D.; Garber, A. R.; Ellis, P. D. *J. Magn. Reson.* **1981**, *45*, 503.

(20) Hartman, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042.

(21) Pines, A.; Gibby, M. E.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

Table I. Principal Elements of the ^{113}Cd Shielding Tensors and Corresponding Direction Cosines Assigned to Cadmium in Special and General Positions for 3CdSO$_4$·8H$_2$O

tensor element (ppm)^a		direction cosines			angles (deg)		
		a^*	b	$c^{*\,b}$	a^*	b	$c^{*\,b}$
			Cd$_s$				
σ_{11}	−95.6	0.0299	0.9995	0.0090	88	2	90
σ_{22}	−85.3	0.8336	−0.0199	−0.5520	34	91	124
σ_{33}	−3.4	−0.5515	0.0240	−0.8338	124	89	146
$\bar{\sigma}^c$	−61.4						
			Cd$_g$				
σ_{11}	−93.1	0.4675	0.8082	−0.3580	62	36	111
σ_{22}	−76.7	0.5277	0.0698	0.8466	58	86	32
σ_{33}	25.5	0.7092	−0.5847	−0.3939	45	126	113
$\bar{\sigma}^c$	−48.1						

^{a} All chemical shifts are relative to solid Cd(ClO$_4$)$_2$. ^{b} The starred axis system represents the orthogonalized monoclinic unit cell axes (see ref 15). ^{c} $\bar{\sigma} = {}^1/_3\mathrm{Tr}(\sigma)$.

The eigenvalues correspond to the principal elements (σ_{11}, σ_{22}, σ_{33}) of the shielding tensor and the eigenvectors to the direction cosines of the elements with respect to the orthogonal crystal reference frame.

An estimate of the error in the orientation of the shielding tensors is indicated in Tables I and IV. Symmetry requires one principal element of the cadmium nitrate shielding tensor to be coincidental with **c**. σ_{11} is 3° from this orientation. Therefore the orientation of the nitrate tensor is good to with 3°. Similar arguments indicate that the special position sulfate shielding tensor orientation is good to within 2°. An estimate of the error associated with the general position ^{113}Cd shielding tensor orientation is obtained by comparing the eigenvectors of the second distinguishable general position tensor with the eigenvectors generated by applying the point group mirror operator to the reported eigenvectors. The discrepancy in this case is 2°. The uncertainty in the eigenvalues reported is less than 1 ppm.

Results and Discussion

The ^{113}Cd shielding tensor symmetry and orientation relative to the position of the symmetry operators in the lattice are determined by the Cd site symmetry.[22] Analysis, therefore, of the tensor and lattice symmetries affords an understanding of the number of magnetically distinguishable nuclei and also the possible orientational constraints imposed upon the shielding tensors. Consequently, the format for this section is a discussion of the aforementioned symmetries followed by a description of the tensor orientation in the molecular reference frame. Three distinct ^{113}Cd shielding tensors have been determined of which only the shielding tensor corresponding to CdSO$_4$ special position can be unambiguously assigned to the appropriate reference frame. As the assignment of the nitrate tensors was based on criteria determined in the analysis of cadmium sulfate, we discuss this case first.

Richardson and Jacobsen[14] recently solved the crystal structure of 3CdSO$_4$·8H$_2$O under the standard monoclinic $C_{2/c}$ space group. The general equivalent positions for this space group are given in I and II below. There are two independent cadmium per unit

I			II		
a	b	c	a	b	c
x	y	z	x	$\bar{y}$	$^1/_2 + z$
$x + {}^1/_2$	$y + {}^1/_2$	z	$x + {}^1/_2$	$\bar{y} + {}^1/_2$	$^1/_2 + z$
$\bar{x}$	$\bar{y}$	$\bar{z}$	$\bar{x}$	y	$\bar{z} + {}^1/_2$
$\bar{x} + {}^1/_2$	$\bar{y} + {}^1/_2$	$\bar{z}$	$\bar{x} + {}^1/_2$	$y + {}^1/_2$	$\bar{z} + {}^1/_2$

cell. One cadmium, Cd$_g$, lies in general position, the second, Cd$_s$, in special position on the twofold. The unit cell, therefore, contains 12 Cd atoms with 8 corresponding to general positions and 4 to special positions. The crystallographically equivalent positions are equally divided into two sets of magnetically distinguishable sites corresponding to groups I and II. The members of each group are related by a center of inversion or a translation. Neither transformation is discernible by the NMR experiment. This results in a single distinguishable[23] shielding tensor for each group. Hence, for general orientations of the crystal with respect to the field, three lines of equal intensity are expected in the NMR spectrum (I and II are degenerate for Cd in special position). Three resonances are observed (see Figure 1) and a shielding tensor was determined for each. Neglecting the translational components of the symmetry elements, I and II are related by the point group mirror normal to **b**. Since the shielding tensors transform under the symmetry operations of the point group relating the crystallographically equivalent positions, the tensors corresponding to Cd in general position must similarly be mirror related. The principal elements of ^{113}Cd shielding tensors and the appropriate direction cosines are found in Table I. A single set of direction cosines is reported for the tensors corresponding to cadmium in general position. The eigenvectors for the second tensor are generated by the mirror operator reflecting in the plane normal to **b**. The eigenvalues and eigenvectors corresponding to Cd$_g$ indicate that the shielding tensor is not axially symmetric and that the principal elements assume general orientations with respect to the crystallographic reference frame. This configuration is expected considering the C_1 site symmetry for general position cadmium. Similarly, the shielding tensor for Cd$_s$ has three distinct principal elements as anticipated from the C_2 site symmetry. Further, the C_2 site symmetry constrains one of the principal elements to be coincidental with **b**, the unique crystallographic axis. Referring to Table I, σ_{11} is seen to be colinear with **b**.

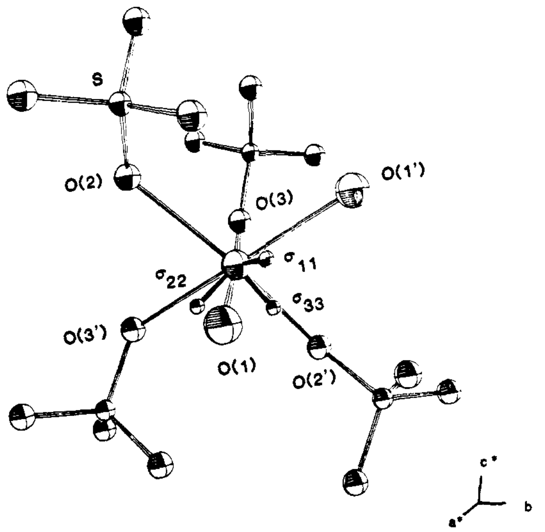

Figure 2. ORTEP showing the orientation of the ^{113}Cd shielding tensor corresponding to Cd in special position with respect to the 3CdSO$_4$·8H$_2$O molecular reference frame. Primed labels indicate symmetry related atoms. The thermal ellipsoids in this work are solely intended to illustrate the position of atoms. For clarity, the ellipsoids are not necessarily drawn at the 50% probability level.

The MAS spectrum for 3CdSO$_4$·8H$_2$O contains two resonances with intensities having a 2:1 ratio and isotropic chemical shifts of −48 and −61 ppm (relative to solid Cd(ClO$_4$)$_2$), respectively. Comparison of the isotropic chemical shifts from the MAS experiment and the shifts calculated from the shielding tensors provided a straightforward and unambiguous assignment of the Cd$_s$ shielding tensor to the appropriate cadmium sulfate lattice site. The orientation of ^{113}Cd shielding tensor in the Cd$_s$ molecular reference frame is illustrated in Figure 2. The special position Cd-coordination sphere geometry and tensor-ligand geometry are detailed in Table II. Referring to Figure 2, the Cd$_s$ coordination

---

(22) (a) Weil, J. A.; Buch, T.; Clapp, J. E. *Adv. Magn. Reson.* **1973**, *7*, 183. (b) Nye, J. F., Physical Properties of Crystals"; Oxford University Press: London, 1957. (c) Sands, D. E., "Tensors and Vectors in Crystallography"; Addison-Wesley: Reading, Mass., 1982. (d) Gaylord, T. K. *Am. J. Phys.* **1975**, *43*, 861. (e) Schonland, D. S. *Proc. Phys. Soc., London, Sect. A* **1959**, *A73*, 788.

(23) We have adopted the convention that distinct tensors have different eigenvalues and, clearly, different eigenvectors. A problem, however, occurs for symmetry related tensors. Here, the eigenvalues are the same but the eigenvectors differ. We refer to the latter case as distinguishable tensors.

Table II. Structural Data for Cadmium Sulfate: Selected Interatomic Distances and Angles for the Coordination Sphere of Cadmium in Special Position and Details of the Orientation of the Principal Elements of the ^{113}Cd Shielding Tensor with Respect to the Molecular Reference

bond distances (Å)		bond angles (deg)		tensor element-ligand angles (deg)	
Cd-O(1)	2.291	O(1)-Cd-O(1′)	87.0	σ_{11}-Cd-O(1)	42
Cd-O(2)	2.295	O(1)-Cd-O(2)	88.0	σ_{11}-Cd-O(1′)	45
Cd-O(3)	2.300	O(1)-Cd-O(2′)	103	σ_{11}-Cd-O(2)	96
		O(1)-Cd-O(3)	177	σ_{11}-Cd-O(2′)	99
		O(1)-Cd-O(3′)	96.4	σ_{11}-Cd-O(3)	141
		O(2)-Cd-O(2′)	165	σ_{11}-Cd-O(3′)	139
		O(2)-Cd-O(3)	90.6	σ_{22}-Cd-O(1)	48
		O(2)-Cd-O(3′)	77.8	σ_{22}-Cd-O(1′)	135
		O(3)-Cd-O(3′)	80.3	σ_{22}-Cd-O(2)	81
				σ_{22}-Cd-O(2′)	98
				σ_{22}-Cd-O(3)	129
				σ_{22}-Cd-O(3′)	49
				σ_{33}-Cd-O(1)	91
				σ_{33}-Cd-O(1′)	88
				σ_{33}-Cd-O(2)	169
				σ_{33}-Cd-O(2′)	12
				σ_{33}-Cd-O(3)	90
				σ_{33}-Cd-O(3′)	92

sphere can be seen to be a distorted octahedron consisting of four monodentate sulfate and two water oxygens. The cadmium-oxygen distances are uniform (2.291 to 2.300 Å) with the Cd-OH$_2$ distances being only slightly shorter. If O(2) and O(2′) constitute axial positions, the only distinguishing structural feature is the cis orientation of the twofold related water oxygens (O(1), O(1′)) in the equatorial plane. Again referring to Figure 2, the orientation of ^{113}Cd$_s$ shielding tensor is seen to be dominated by the local C_2 symmetry. The more shielded elements, σ_{11} and σ_{22}, lie in the equatorial plane with σ_{11} being coincidental with **b** and necessarily bisecting the O(1)-Cd-O(1′) angle. The least shielded element, σ_{33}, is directed normal to the plane containing the waters oxygens. The ^{113}Cd$_s$ shielding tensor approximates axial symmetry with σ_{11} and σ_{22} differing by only 10 ppm. This requires the shielding environments normal to σ_{11} and σ_{22} to be similar; reference to Table II reveals this to be the case. σ_{11} makes angles of 96 and 99° with the Cd-O(2) and Cd-O(2′) internuclear vectors, respectively, and 88° from the best least-squares line[24] (BLL) through O(2)-Cd-O(2′). Similarly, σ_{22} is directed 81 and 98° from the Cd-O(2), Cd-O(2′) internuclear vectors, respectively, and makes an angle of 81° with the O(2)-Cd-O(2′) BLL. Further, the shielding contributions from equatorial ligands to σ_{11} and σ_{22} are expected to be comparable because of the inherent site symmetry. The orientation of σ_{33} is unique as anticipated from its eigenvalue. σ_{33} is normal (within experimental limits) to O(1), O(1′), O(3), and O(3′) resulting in an angle of 81° with the best least-squares plane (BLP) containing the equatorial oxygen atoms and cadmium. Two orientational features need to be emphasized. First, the tensor elements with comparable eigenvalues are normal to similar shielding environments. Second, the least shielded element is nearly orthogonal to the plane containing the water oxygens. No assumptions were required for this shielding tensor-lattice site assignment. We, therefore, have employed these observations as criteria in assigning the shielding tensors corresponding to general position cadmium sulfate and cadmium nitrate to the appropriate molecular reference frames.

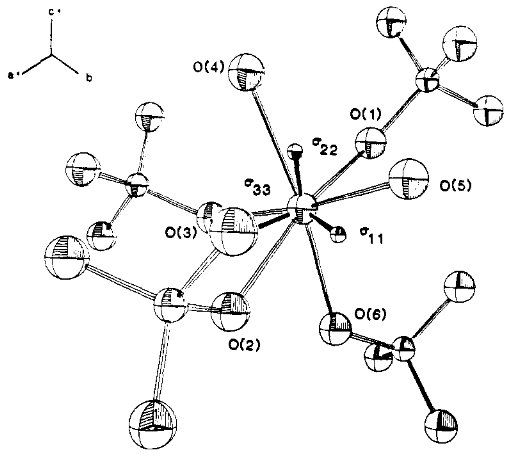

Figure 3. ORTEP indicating the orientation of the ^{113}Cd shielding tensor with respect to the general position molecular reference frame.

Table III. Structural Data for Cd$_g$ Molecular Reference Frame: Selected Interatomic Distances and Angles and the Orientation of ^{113}Cd Shielding Tensor with Respect to the Molecular Reference Frame

interatomic distances (Å)		interatomic angles (deg)		tensor element-ligand angle (deg)	
Cd-O(1)	2.246	O(1)-Cd-O(2)	170	σ_{11}-Cd-O(1)	116
Cd-O(2)	2.263	O(1)-Cd-O(3)	86.1	σ_{11}-Cd-O(2)	60
Cd-O(3)	2.279	O(1)-Cd-O(4)	86.7	σ_{11}-Cd-O(3)	151
Cd-O(4)	2.287	O(1)-Cd-O(5)	95.7	σ_{11}-Cd-O(4)	104
Cd-O(5)	2.292	O(1)-Cd-O(6)	92.0	σ_{11}-Cd-O(5)	33
Cd-O(6)	2.317	O(2)-Cd-O(3)	94.5	σ_{11}-Cd-O(6)	82
		O(2)-Cd-O(4)	103	σ_{22}-Cd-O(1)	89
		O(2)-Cd-O(5)	85.0	σ_{22}-Cd-O(2)	99
		O(2)-Cd-O(6)	78.7	σ_{22}-Cd-O(3)	110
		O(3)-Cd-O(4)	90.5	σ_{22}-Cd-O(4)	20
		O(3)-Cd-O(5)	173	σ_{22}-Cd-O(5)	63
		O(3)-Cd-O(6)	78.7	σ_{22}-Cd-O(6)	171
		O(4)-Cd-O(5)	82.4	σ_{33}-Cd-O(1)	154
		O(4)-Cd-O(6)	169	σ_{33}-Cd-O(2)	32
		O(5)-Cd-O(6)	108	σ_{33}-Cd-O(3)	70
				σ_{33}-Cd-O(4)	84
				σ_{33}-Cd-O(5)	107
				σ_{33}-Cd-O(6)	93

The general position cadmium sulfate coordination sphere is illustrated in Figure 3 and detailed in Table III. The coordination sphere geometry is again a distorted octahedron; however, the C_1 site symmetry results in six distinct Cd-O bonding distances varying from 2.246 to 2.317 Å. Considering O(1) and O(2) to be axial, the equatorial plane consists of O(3) through O(6). The orientation of the shielding tensor, assignment based upon the aforementioned criteria, within the general site reference frame is seen in Figure 3 and detailed in the last column of Table III. In this configuration σ_{11} is oriented 96° from the O(4), Cd, O(6) BLL making angles of 104 and 82° with the Cd-O(4) and Cd-O(6) internuclear vectors, respectively. The nearly perpendicular orientation of the most shielded element with O(6), the longest Cd-O bond, is also consistent with current single-crystal work in our lab on CdCa(OAc)$_4$·6H$_2$O (one Cd per unit cell and one distinguishable tensor) and results discussed later for cadmium nitrate. σ_{22} is directed nearly orthogonal to the Cd-O(1), Cd-O(2) internuclear vectors with angles of 89 and 99°, respectively. The corresponding σ_{22}-O(1), Cd, O(2) BLL angle is 85°. It must be pointed out that the least shielded element makes an angle of 93° with the Cd-O(6) bond. The influence of O(6) upon the shielding environment of σ_{33}, however, is clearly modulated by the remaining ligands in the equatorial plane, principally the two water oxygens. The significant feature of this assignment is the orientation of σ_{33} which makes angles of 70, 84, 107, and 93° with the equatorial ligands and an angle of 74° with the corresponding BLP.

The alternative assignment corresponds to a reflection of the shielding tensor in the a^*, c^* plane. This orientation results in a σ_{33}-equatorial BLP angle of 49° and concomitantly orients σ_{11} 84° from this same equatorial plane. Both of these orientational features are inconsistent with the observations in the Cd$_s$ case.

Before discussing the cadmium nitrate shielding tensor, it should be pointed out that the rationalization for the number of distinguishable[23] tensors observed in the single-crystal experiment may

---

[24] The X-Ray System. Technical Report TR-455. Program: LSQPL; Stewart, J. M., Ed.; Computer Science Center, University of Maryland: College Park, Md., 1979.

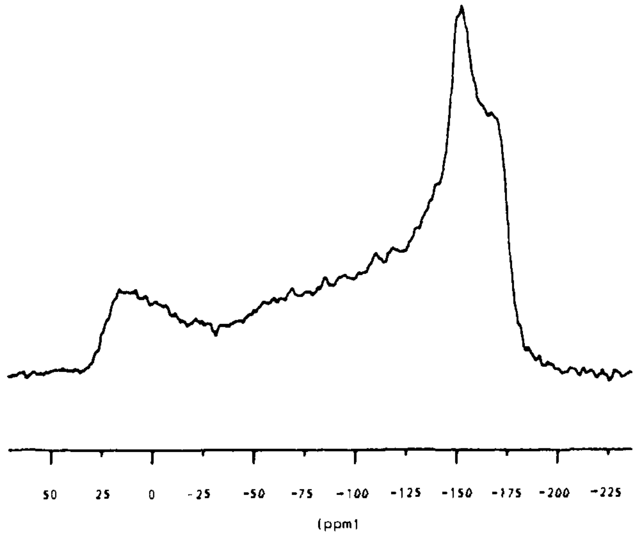

Figure 4. ^{113}Cd powder spectrum for Cd(NO$_3$)$_2$·4H$_2$O (obtained at 200 MHz). The shielding tensor has three distinct elements: $\sigma_{11} = -174$, $\sigma_{22} = -154$, $\sigma_{33} = 22$ ppm.

Table IV. Principal Elements of the ^{113}Cd Shielding Tensor and Corresponding Direction Cosines for Cd(NO$_3$)$_2$·4H$_2$O

tensor element (ppm)[a]		direction cosines			angles (deg)		
		a	*b*	*c*	*a*	*b*	*c*
σ_{11}	−174.4	0.0561	0.0036	0.9984	87	90	3
σ_{22}	−154.3	−0.8552	0.5162	0.0462	149	59	87
σ_{33}	22.2	0.5152	0.8564	−0.0320	59	31	92
$\bar{\sigma}$[b]	−102.2						

[a] All shifts are reported relative to solid Cd(ClO$_4$)$_2$. [b] $\bar{\sigma} = {}^1/_3\mathrm{Tr}(\sigma)$.

be performed at the space-group or the point-group level. The sulfate was discussed at the former level. The point-group level is now applied to the nitrate.

As indicated above, the number of distinguishable shielding tensors per unit cell depends upon the tensor symmetry and location relative to the point-group symmetry opertors. The static powder spectrum of Cd(NO$_3$)$_2$·4H$_2$O at 200 MHz is an $\eta = 0.16$ spectrum with three readily resolved tensor elements (see Figure 4). Further, cadmium nitrate crystals belong to the *mm*2 crystallographic point group. As the shielding tensors of symmetry related cadmium transform under the symmetry operations of the point group, the number of distinguishable tensors can either be four or two. For cadmium in general position the point group operators (xyz, $\bar{x}yz$, $x\bar{y}z$, $\bar{x}\bar{y}z$) generate four distinguishable shielding tensors with one corresponding to the application of each operator. In special position, cadmium occupies a site of C_2 symmetry and consequently only two distinguishable tensors result. The reduction in the number of distinguishable tensors in this latter case is easily understood if one considers the constraints imposed upon the components, σ_{ij}, of the shielding tensor, σ, by the C_2 site symmetry.[22] Specifically, if R_2 is the matrix representation of the twofold operator and $\bar{R}_2$ the inverse, then the site symmetry demands

$$\sigma = R_2 \sigma \bar{R}_2$$

From the resulting matrix algebra it can be seen that an element of the shielding tensor must be coincidental with the twofold, and shielding tensors thus related (i.e., xyx, $\bar{x}\bar{y}z$ and $\bar{x}yz$, $x\bar{y}z$) are no longer distinguishable. Matkovic et al.[13] refined the crystal structure with Cd on special position. Two distinguishable tensors with one principal element coincidental with the point group twofold are therefore required. Two shielding tensors were determined and found to have the suggested orientations relative to **c**, the unique crystallographic axis. The ^{113}Cd shielding tensor elements and the corresponding direction cosines are given in Table IV. The shielding tensors are distinguishable, not distinct;[23] therefore only one is reported. The eigenvectors for the second tensor are generated by the mirror operator ($\bar{x}yz$). It is interesting to note that rotation about the cube axis determined to be coincidental with **a** resulted in rotation plot spectra with a single resonance. Rotation about **a** necessarily places the magnetic field in the mirror. Shielding tensors related by the mirror are no longer distinguishable, and therefore only one line is observed. Distinguishable tensors necessarily result in an assignment ambiguity. The preferred orientation of the principal elements of the shielding tensor within the cadmium nitrate reference frame is illustrated in Figure 5 and the rationale for this assignment is discussed subsequently. The details of the coordination geometry and the tensor-coordination sphere geometry are given in Table V.

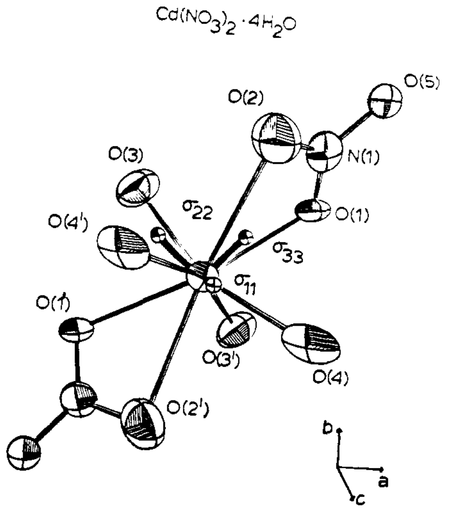

Figure 5. ORTEP illustrates the relative orientation of the principal axes of the ^{113}Cd shielding tensor to the Cd(NO$_3$)$_2$·4H$_2$O molecule. O(3), O(4), O(3′), O(4′) are water oxygens. Primed labels indicate atoms related by the twofold along *c*.

Table V. Structural Data for Cd(NO$_3$)$_2$·4H$_2$O: Selected Bond Distances and Angles for the Cadmium Coordination Sphere in Cd(NO$_3$)$_2$·4H$_2$O and Details of the Orientation of the Principal Elements of the Shielding Tensor with Respect to the Molecular Reference Frame

bond distances (Å)		bond angles (deg)		tensor element-ligand angles (deg)	
Cd–O(1)	2.435	O(1)–Cd–O(1′)	146	σ_{11}–Cd–O(4)	42
Cd–O(2)	2.593	O(1)–Cd–O(2)	49.0	σ_{11}–Cd–O(4′)	48
Cd–O(3)	2.333	O(1)–Cd–O(3)	83.9	σ_{11}–Cd–O(2)	76
Cd–O(4)	2.260	O(1)–Cd–O(3′)	72.5	σ_{11}–Cd–O(2′)	78
		O(1)–Cd–O(4)	79.4	σ_{11}–Cd–O(1)	104
		O(1)–Cd–O(4′)	127	σ_{11}–Cd–O(1′)	110
		O(2)–Cd–O(2)	154	σ_{22}–Cd–O(4′)	43
		O(2)–Cd–O(3)	78.1	σ_{22}–Cd–O(3)	50
		O(2)–Cd–O(3′)	121	σ_{22}–Cd–O(1)	117
		O(2)–Cd–O(4)	83.8	σ_{22}–Cd–O(1′)	65
		O(2)–Cd–O(4′)	78.1	σ_{22}–Cd–O(2)	78
		O(3)–Cd–O(3′)	91.4	σ_{33}–Cd–O(2′)	101
		O(3)–Cd–O(4′)	92.6	σ_{33}–Cd–O(1)	31
		O(4)–Cd–O(4′)	89.7	σ_{33}–Cd–O(2)	19
				σ_{33}–Cd–O(3)	75
				σ_{33}–Cd–O(4)	86
				σ_{33}–Cd–O(3′)	102
				σ_{33}–Cd–O(4′)	97

The Cd coordination geometry in Cd(NO$_3$)$_2$·4H$_2$O was described by Matkovic et al.[13] as a distorted dodecahedron. The coordination sphere consists of four pairs of twofold related oxygen atoms from four water molecules and two bidentate nitrate anions. As noted earlier, Cd lies on the twofold along **c**. The molecular symmetry is clearly illustrated in Figure 5. The Cd–O distances are much less uniform than in either sulfate, varying from 2.26 to 2.59 Å (see Table V), with Cd–OH$_2$ distances being significantly shorter. Figure 5 illustrates the ^{113}Cd shielding tensor orientation with respect to the molecular reference frame. This assignment resulted by requiring that σ_{11} and σ_{22}, with eigenvalues differing by only 20 ppm compared to a total anisotropy of 197 ppm, have similar orthogonal shielding environments. The second criterion required σ_{33}, the least shielded element, to be oriented normal to the water-oxygen plane. In this case compliance with one criterion guaranteed the second. The tensor element, σ_{11} is coincidental with **c** (the C_2 axis) and hence bisects the O(4)–Cd–O(4′) angle (see Table V). The two shielded elements lie in the water-oxygen plane making angles of 88 and 84°, σ_{11} and σ_{22}, respectively, with the normal to the BLP defined by Cd and the four water oxygens. Further, σ_{11} is oriented 76 and 78° from the Cd–O(2) and Cd–O(2′) internuclear vectors, respectively, and 104 and 110° from the Cd–O(1) and Cd–O(1′) vectors, respectively. This corresponds to σ_{11}-best-line angles of 87 and 88°, respectively. Again, the perpendicular orientation of the most shielded element with the longest Cd–O bond should be noted. σ_{22} has a comparable orientation relative to the Cd–O_2NO^- bonds. However, as might be anticipated, the σ_{22}- BLL angles are less (63 and 78° for lines corresponding to O(1)–Cd–O(1′) and O(2)–Cd–O(2′) than the corresponding σ_{11} angles. Finally, σ_{33}, the least shielded element, makes an acute angle of 83° with the BLP defined by Cd–O(3), O(3′), O(4), and O(4′).

The alternative assignment, which is easily visualized in Figure 5, corresponds to reflection of the shielding tensor in the *b*,*c* plane. This assignment results in σ_{11} and σ_{33}, the most shielded and deshielded elements, having similar orthogonal environments. We contend that this is an unreasonable configuration.

Conclusion

The orientation of three distinct ^{113}Cd shielding tensors relative to the corresponding oxo–cadmium molecular reference frames has been determined. The local Cd site symmetry has been observed to dominate the orientation of the tensor. The orientation of the shielding tensor corresponding to the special position in $3CdSO_4{\cdot}8H_2O$ was unambiguously determined by NMR and crystallographic data. The shielding tensor–molecular reference frame orientation for cadmium sulfate general position and cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$) required assumptions. Three observations correlating shielding tensor element orientation with molecular features were made and are reiterated. First, shielding tensor elements of comparable magnitude have similar molecular environments normal to the elements. Second, the least shielded tensor elements are aligned nearly perpendicular to planes containing water oxygen. Third, the more shielded tensor elements are oriented perpendicular to the longer Cd–O bonds. Clearly, additional single-crystal NMR data for oxo–cadmium complexes are required to determine whether these orientational features are general or unique to the compounds investigated in this work.

Finally, correlations between bond-length dispersion and shielding anisotropy have been suggested.[11d] At this point, our data on ^{113}Cd shielding tensors, do not indicate a direct correlation between bond-length variation and the magnitude of the shielding anisotropy. Bond-length dispersion, local site symmetry, and ligand type are all contributory structural parameters in determing the value of $\Delta\sigma$.

Acknowledgment. The authors thank Dr. J. W. Richardson and Professor R. A. Jacobsen for kindly supplying the crystal structure data for $3CdSo_4{\cdot}8H_2O$. Further, we thank the crystallography group at U.S.C., Professor E. L. Amma and Drs. E. H. Griffith, R. C. Paslay, and N. G. Charles, for the helpful discussions during the course of this work and for supplying access to the necessary diffraction equipment. The use of the facilities at the University of South Carolina NMR Center, funded by the National Science Foundation (CHE 78-18723), is acknowledged. Finally, we acknowledge the National Institutes of Health (GM 26295) for partial support of this research.

Registry No. ^{113}Cd, 14336-66-4; $Cd(NO_3)_2{\cdot}4H_2O$, 10022-68-1; $3CdSO_4{\cdot}8H_2O$, 7790-84-3.

The Interaction of Lanthanide Shift Reagents with Cationic Sites: A ^{1}H and ^{13}C NMR Study of the Solution Geometry of Nicotine *N*-Methiodide

Ronald L. Bassfield

Contribution from the Philip Morris U.S.A. Research Center, Richmond, Virginia 23261.
Received August 20, 1982

Abstract: The use of lanthanide shift reagents as proton and carbon-13 NMR shift and relaxation probes has enabled the determination of the solution geometry of the nicotine *N*-methiodide complex. A series of experiments were performed to illustrate the applicability of induced shift and T_1 relaxation data derived from the interaction between Ln(fod)$_3$ and a quaternary ammonium salt. The results indicate that the lanthanide/anion moiety complexes with quaternary salts via the positively charged center and adheres principally to the pseudocontact model.

We previously reported the interaction of lanthanide shift reagents (LSR) with bifunctional ammonium salts containing both a positive quaternary nitrogen and a neutral amine nitrogen.[1] The results of that study revealed that the LSR complexes preferentially with the negative counterion rather than with the lone pair of electrons of the amine nitrogen. It was suggested that the observed paramagnetic shifts in the cationic moiety resulted from the tight ion pairing of the LSR–anion adduct and the cationic species. The ion pairing phenomenon is enhanced by the use of a nonpolar solvent such as chloroform-*d*. Although ion pairing of LSR–anion complexes with positively charged centers has been reported,[2-9] to our knowledge no detailed structural analysis has

---

(1) J. I. Seeman and R. L. Bassfield, *J. Org. Chem.*, **42**, 2337 (1977).

(2) K. B. Lipkowitz, T. Chevalier, B. P. Mundy, and J. J. Theodore, *Tetrahedron Lett.*, **21**, 1297 (1980).

(3) F. Lefevre, C. Rabiller, A. Mannshreck, and G. J. Martin, *J. Chem. Soc., Chem. Commun.*, 942, (1979).

(4) Alexandru T. Balaban, *Tetrahedron Lett.*, **50**, 5055 (1978).

(5) G. Montavdo, *Tetrahedron Lett.*, **21**, 1841 (1974).