

## Improved $^{67}\text{Zn}$ Solid-State NMR from Single-Crystal Studies. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

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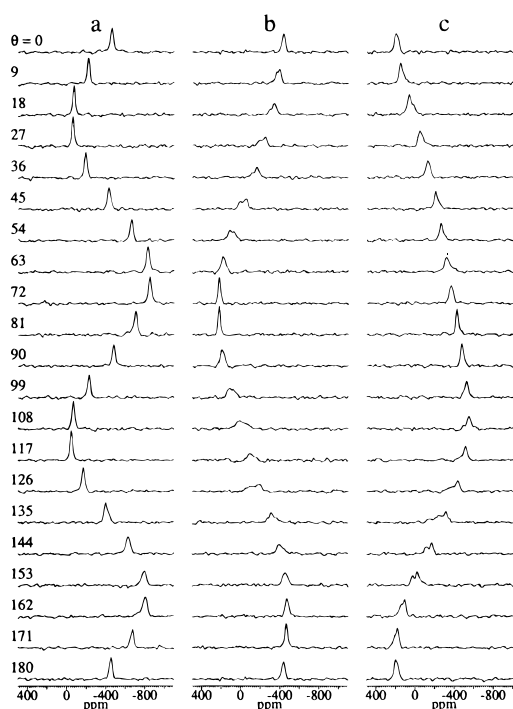
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Solid-state NMR spectroscopy has had a longstanding potential of playing a significant role in the biostructural chemistry of Zn-metalloproteins and in the chemistry of important inorganic zinc-containing materials. Unfortunately, the low natural abundance (4.11%) and low gyromagnetic ratio of  $^{67}\text{Zn}$  (spin  $I = 5/2$ ) combined with its fairly large quadrupole moment have prevented solid-state  $^{67}\text{Zn}$  NMR from developing into a routine analytical method. Broad second-order quadrupolar line shapes for the central transition, low sensitivity, and acoustic probe ringing are the main reasons for the problems encountered in solid-state  $^{67}\text{Zn}$  NMR of powders and thus for the very few studies reported.<sup>1–3</sup> Improving sensitivity by, for example,  $^{67}\text{Zn}$ -isotope enrichment is costly; however, working at cryogenic temperatures and at the highest available magnetic field strength may help to overcome these problems. Generally, the broad  $^{67}\text{Zn}$  resonances are detected using the quadrupolar echo (QE) pulse sequence as, for example, for the 40-kHz wide powder pattern observed for  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  at 11.7 T.<sup>1</sup> As an alternative, narrow and discrete resonances should be obtainable employing  $^{67}\text{Zn}$  single-crystal (SC) NMR. Especially, taking advantage of the improved sensitivity for the new SC probes constructed in our laboratory<sup>4,5</sup> and using a magnetic field strength of 14.1 T, several of the difficulties in solid-state  $^{67}\text{Zn}$  NMR may be reduced or circumvented. This paper demonstrates the improved performance and information which may be achieved using natural abundance  $^{67}\text{Zn}$  SC NMR employing a crystal of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (**1**) as an example.

**1** has a monoclinic crystal structure (space group  $C2/c$ ,  $Z = 4$ ) with the  $\text{Zn}^{2+}$  ions located on the 2-fold axes parallel to the  $b$  axis (position 4( $e$ )).<sup>6</sup> The four  $\text{Zn}^{2+}$  ions in the unit cell are related by inversion and translation, and thus we expect only one resonance in the SC NMR spectra. Because of the local two-fold symmetry of the  $\text{Zn}^{2+}$  ions, the NMR tensors (quadrupole and chemical shielding) must have one principal element aligned along the  $b$  axis.<sup>7</sup>

Figure 1 shows the experimental  $^{67}\text{Zn}$  spectra for the central transition of a crystal of **1** (size  $1.5 \times 5 \times 5 \text{ mm}^3$ ) recorded at 37.5 MHz on a Varian INOVA-600 spectrometer with a 14.1 T widebore magnet using a three-axis goniometer SC NMR probe of a new design and described elsewhere.<sup>4</sup> This probe is fully automated with respect to rotation of the crystal about the,  $-x^T$ ,  $y^T$ , and  $-z^T$  axis of the tenon (T) frame for the crystal.<sup>8</sup> The time required for acquisition of each spectrum is approximately 50



**Figure 1.**  $^{67}\text{Zn}$  single-crystal NMR spectra of the central transition for a crystal of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  resulting from rotation about the  $-x^T$  (a),  $y^T$  (b), and  $-z^T$  (c) axis of the tenon frame (T) as described elsewhere.<sup>4</sup> Each spectrum follows an increment in the rotation angle of  $9^\circ$  and employs single-pulse excitation ( $\tau_p = 1 \mu\text{s}$  for  $\gamma B_1/2\pi \approx 40 \text{ kHz}$ ) and 6000 scans with a repetition delay of 0.5 s. Minor baseline distortions have been removed by a baseline correction routine. We note the significant broadening of the resonances for certain orientations, a broadening particularly pronounced for one of the twins.

min (6000 scans). We should note that the somewhat lower sensitivity generally associated with the conventional “cube” goniometer SC probes, and resulting from a poorer filling factor,<sup>8</sup> would be compensated by employing a large-size crystal, similar to the one used here. Thus we expect such probes (e.g., commercially available from Doty Scientific, Inc.) to give comparable results for large crystals. As usual, degradation in sensitivity and acoustic ringing effects on going to lower-field magnets obviously must be taken into account. For most of the present  $^{67}\text{Zn}$  spectra, a single resonance with a line width of 1–2 kHz is observed in accordance with the crystal symmetry. However, for some orientations of the crystal, the resonance quite surprisingly splits into broadened doublets generally with one of the resonances being broader than the other.

Consulting the XRD structure report for **1**,<sup>6</sup> we learn that good single crystals of **1** are the exception and that this material usually grows twins consisting of elongated plates which stack together to form prismatic needles along the unique ( $b$ ) axis.<sup>6</sup> Thus, if our crystal is a twin we may assume that each twin has the same orientation for the  $b$  axis. A preliminary analysis of the two sets of  $^{67}\text{Zn}$  resonances measured from the experimental spectra gives the same parameters for the magnitude of the quadrupole coupling tensor ( $C_Q = 5.20 \pm 0.03 \text{ MHz}$ ,  $\eta_Q = 0.90 \pm 0.02$ ) while the orientation of the two tensors varies by approximately  $4^\circ$ . However, we note that the  $V_{xx}$  elements for the two tensors are parallel within error limits. This indicates that our crystal is most likely a twin following the twin-law described above and with the  $V_{xx}$  element of the  $^{67}\text{Zn}$  quadrupole coupling tensor aligned along the  $b$  axis. This assumption has been independently verified by an XRD study of the same crystal setup employing a precession

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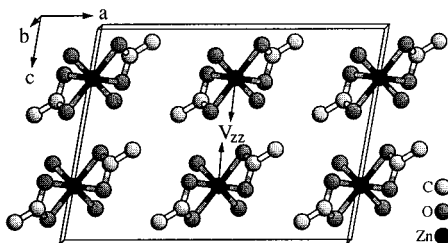
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**Table 1.** Parameters for  $^{67}\text{Zn}$  Quadrupole Coupling ( $C_Q$ ,  $\eta_Q$ ) and Chemical Shielding Anisotropy ( $\delta_\sigma$ ,  $\eta_\sigma$ ) in  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ 

method	$C_Q$ [MHz]	$\eta_Q$	$\delta_{\text{iso}}$ [ppm] <sup>a</sup>	$\delta_\sigma$ [ppm]	$\eta_\sigma$	reference
SC <sup>b</sup>	$5.34 \pm 0.03$	$0.819 \pm 0.018$	$-123 \pm 3$	$-33 \pm 6$	$0.5 \pm 0.3$	this work
SC <sup>c</sup>	$5.20 \pm 0.03$	$0.898 \pm 0.017$	$-125 \pm 3$			this work
static	$5.3 \pm 0.1$	$0.87 \pm 0.03$	$0^d$			1

<sup>a</sup> Isotropic chemical shifts are relative to an aqueous 1.0 M solution of  $\text{ZnCl}_2$ . <sup>b</sup> Parameters resulting from iterative fitting including the combined effect of quadrupole coupling and CSA. The resulting Euler angles for the relative orientation of the two tensors are  $\psi = \xi = 0^\circ$  and  $\chi = 1 \pm 4^\circ$  (see text). <sup>c</sup> Parameters resulting from iterative fitting including only the quadrupole coupling interaction. <sup>d</sup> Relative to an aqueous 1.0 M solution of  $\text{Zn}(\text{NO}_3)_2$ .



**Figure 2.** Projection of the crystal structure of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  onto the  $ac$  plane. Each  $\text{Zn}^{2+}$  ion is surrounded by oxygens from two water molecules and from the carboxyl groups of two acetate ions. The  $V_{xx}$  elements are oriented along the  $b$  axis (perpendicular to the plane of the paper) while the  $V_{zz}$  and  $V_{yy}$  (not shown) elements are located in the  $ac$  plane. It is noted that the quadrupole coupling and chemical shielding tensors coincide (see text).

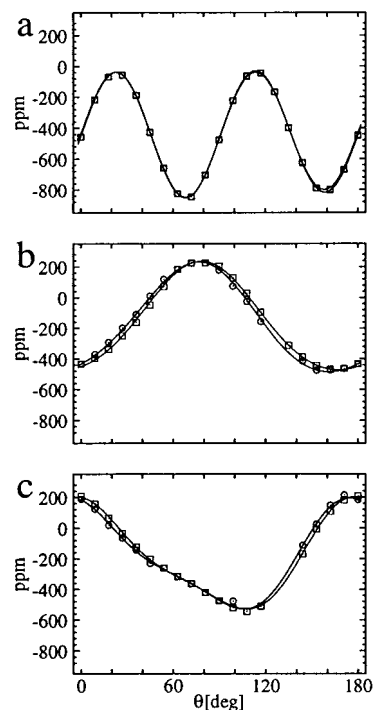
camera.<sup>4</sup> This shows that the crystallographic  $b$  axis is parallel to the direction of the  $V_{xx}$  elements. However, in this XRD investigation we have only observed one of the twins. The XRD investigation furthermore allows a determination of the orientation of the crystallographic  $a$  and  $c$  axes with respect to the tenon frame. Thereby we may determine the orientation of the quadrupole tensor with respect to the crystal frame. The result of this analysis is visualized in Figure 2 which shows a projection of the crystal structure of **1** onto the  $ac$  plane and the orientation of the quadrupole coupling  $V_{zz}$  principal elements.<sup>9,10</sup>

Introducing the chemical shielding anisotropy (CSA) as an additional interaction in the simulations of the rotation patterns for the central transitions decreases the *rms* deviation between the experimental and simulated rotation plots from 503 to 344 Hz. The resulting parameters from the iterative fitting including both the quadrupole coupling and CSA interactions are shown in Table 1 along with their error limits (95% confidence intervals).<sup>8</sup> The requirement that one CSA principal element must be parallel to the  $b$  axis, and thus to  $V_{xx}$ , is fulfilled by  $\psi = n \times 90^\circ$  ( $n = 0$  or 1) and  $\xi = 0^\circ$ . Of the two combinations  $\psi = 0^\circ$  yields the lower *rms* deviation. Therefore, these two Euler angles have been fixed ( $\psi = \xi = 0^\circ$ ) during the iterative fitting. We note that the CSA and quadrupole coupling tensors coincide since the value  $\chi = 1 \pm 4^\circ$  ( $0^\circ$ ) is obtained from the iterative fitting. Although the  $^{67}\text{Zn}$  CSA is quite small ( $\delta_\sigma = -33 \pm 6$  ppm) and represents the first determination of a  $^{67}\text{Zn}$  CSA, it leads to a noticeable change in the quadrupole constant which increases from  $5.20 \pm 0.03$  to  $5.34 \pm 0.03$  MHz by introducing the CSA in the simulations. We note that a similar effect is observed for the  $^{87}\text{Rb}$  static-powder investigation of  $\text{RbVO}_3$  for which  $\delta_\sigma$  is also negative.<sup>10</sup> The

(9) The direction cosines of the quadrupole coupling principal elements with respect to the crystal frame expressed in the orthogonal frame  $a$ ,  $b$ , and  $c^*$ .

	$a$	$b$	$c^*$
$V_{xx}$	0.000	1.000	0.000
$V_{yy}$	0.996	0.000	0.087
$V_{zz}$	-0.087	0.000	0.996

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**Figure 3.** Rotation plots for the  $^{67}\text{Zn}$  spectra of the central transition in  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , resulting from rotation about the  $-x^T$  (a),  $y^T$  (b), and  $-z^T$  (c) axis. The experimental resonances are marked with  $\circ$  and  $\square$  for the two twins, while the solid lines correspond to the optimized quadrupole coupling and CSA parameters in Table 1. Because of the line broadening noted in Figure 1 for certain crystal orientations, some of the resonances are poorly defined and are omitted (e.g., in the region from  $108$  to  $138^\circ$  for rotation about  $-z^T$ ) in the rotation plots. The twin exhibiting the narrower resonance of the two is marked by  $\circ$ .

rotation plots for the  $^{67}\text{Zn}$  spectra of the central transitions in **1** are shown in Figure 3 with the experimental resonances marked as circles and squares for the two twins while the optimized quadrupole coupling and CSA parameters are represented by the solid lines.

In conclusion, single-crystal NMR with its high-resolution properties, is shown to overcome many of the experimental problems encountered in powder NMR studies of broad  $^{67}\text{Zn}$  line-shape patterns for the central transition. This can be of particular importance in natural abundance  $^{67}\text{Zn}$  NMR studies. The single-crystal NMR technology may be of special advantage in solid-state NMR studies using crystals of Zn-complexes which serve as models for Zn-metalloproteins.

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