

7 Single-Crystal NMR of Low- γ Nuclei

Zinc plays an important role in several metalloproteins where the Zn^{2+} ion forms the active site. Information that leads to a better understanding of these sites may potentially be obtained from ^{67}Zn liquid (163) and solid state NMR (139). Unfortunately ^{67}Zn has a low natural abundance (4.11%) and low gyromagnetic ratio ($\gamma_{\text{H}}/\gamma_{\text{Zn}} \approx 16$) which results in a very poor NMR sensitivity. ^{95}Mo and ^{39}K are other examples of a low- γ nuclei of considerable chemical interest.

Considering the problems encountered in acquiring spectra at low larmor frequencies (low sensitivity and base line distortions caused by probe ringing) it is not surprising that, in spite of the great biological interest, only very few ^{67}Zn solid-state NMR studies have been carried out (139, 164–167). The normally quite broad lineshapes in ^{67}Zn (spin $I = 5/2$) spectra of polycrystalline samples, caused by the second-order quadrupolar broadening, further complicates ^{67}Zn solid-state NMR. In such a case SC NMR benefits from an improved sensitivity as all the intensity is collected in few discrete resonances while the powder spectrum may be spread over several tenth of kHz (139). Furthermore, while the analysis of powder spectra is critically dependent on the lineshape (and thereby an ideal baseline) the analysis of SC NMR spectra only relies on the position of discrete resonances and thus this technique appears ideal for studies of low- γ nuclei.

7.1 ^{67}Zn Single-Crystal NMR of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$

$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ has a monoclinic crystal structure (space group $C2/c$, $Z = 4$ (168)) with the Zn^{2+} ions located on the two-fold axes parallel to the b axis

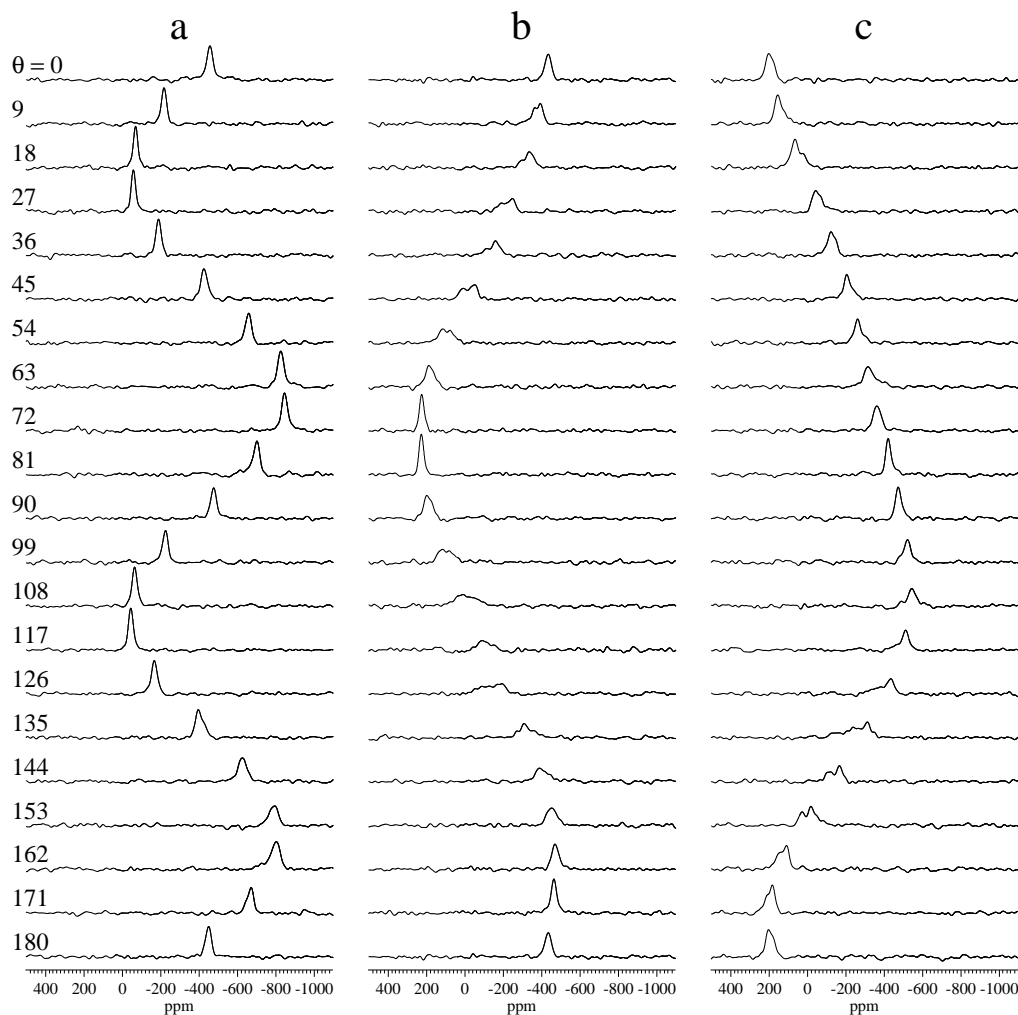


Figure 7.1: 14.1 T ^{67}Zn SC NMR spectra of the central transition for a crystal of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ resulting from rotation about the $-x^{\text{T}}$ (a), y^{T} (b), and $-z^{\text{T}}$ (c) axis. Each spectrum is followed by an increment in the rotation angle of 9° .

(position 4(e)). The four Zn^{2+} ions in the unit cell are related by inversion and/or translation and thus we expect only one ^{67}Zn resonance in the SC spectra. Because of the local two-fold symmetry the Zn NMR tensors must have one principal element aligned along the b axis.

Figure 7.1 shows the experimental ^{67}Zn spectra of a crystal of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (size $1.5 \times 5 \times 5 \text{ mm}^3$) recorded at 14.1 T (37.5 MHz) using the three-axis goniometer probe.¹ The time required for acquisition of each spectrum is approximately 50

¹All spectra employed single-pulse excitation ($\tau_p = 1 \mu\text{s}$) followed by a pre-acquisition delay of $32 \mu\text{s}$ for damping of the probe to ringing, a spectral width of 500 kHz, and 6000 scans with a repetition delay of 0.5 s.

minutes. In most of the 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 a doublet.

By consulting the XRD structure report on $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (168) we learn that this material usually grows twins consisting of elongated plates which stack together to form prismatic needles along the unique (b) axis. 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}Zn resonances measured from the experimental spectra gives the same parameters for the magnitude of the quadrupole coupling tensor (summarized in table 7.1) while the orientation of the two tensors varies by approximately 4° . 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}Zn quadrupole coupling tensor aligned along the b axis. This assumption is independently verified by an XRD study of the same crystal which shows that the crystallographic b axis is parallel to the orientation 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 other crystallographic axes with respect to the tenon frame. Thereby we may determine the orientation of the quadrupole tensor with respect to the crystal frame. This orientation is summarized by the direction cosines in table 7.2 that describe the orientation of the $V_{\alpha\alpha}$ principal elements relative to the crystal frame. For visualization of these direction cosines fig. 7.2 shows a plot of the $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ crystal structure with indication of the orientation of the V_{zz} element.

Introducing the CSA in the simulation 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 this analysis are shown in table 7.1. Although the ^{67}Zn CSA is very small ($\delta_\sigma = -33 \pm 6$ ppm)

Table 7.1: ^{67}Zn quadrupole coupling (C_Q, η_Q), chemical shielding ($\delta_\sigma, \eta_\sigma, \delta_{\text{iso}}$), and relative tensor orientation (ψ, χ, ξ) in $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$.

Method	C_Q [MHz]	η_Q	δ_σ [ppm]	η_σ	δ_{iso} [ppm] ^a	ψ [°]	χ [°]	ξ [°]	Reference
SC ^b	5.20 ± 0.03	0.898 ± 0.017			-125 ± 3				This work
SC ^c	5.34 ± 0.03	0.819 ± 0.018	-33 ± 6	0.5 ± 0.3	-123 ± 3	0^d	1 ± 4	0^d	This work
Static	5.3 ± 0.1	0.87 ± 0.03			0				139

^a Isotropic chemical shifts are relative to an 1.0 M solution of ZnCl_2 . ^b Parameters resulting from simulations including only the quadrupole coupling interaction. ^c Parameters resulting from iterative fitting including the combined effect of quadrupole coupling and CSA. ^d Parameter fixed during optimization (see text).

Table 7.2: Direction cosines describing the orientation of the principal elements of the ^{67}Zn quadrupole coupling tensor in $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with respect to the crystal frame. An orthogonal representation of the monoclinic crystal frame (a , b , c^*) has been chosen.

	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

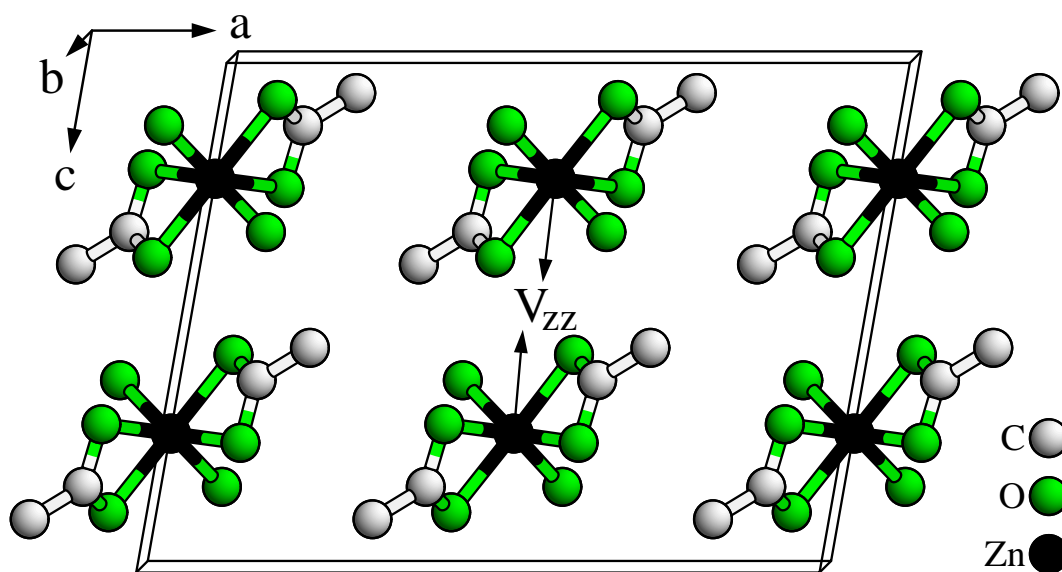


Figure 7.2: Projection of the $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ crystal structure onto the ac plane. Each Zn^{2+} ion is surrounded by the oxygen atoms of two water molecules and by the carboxyl group of two acetate ions. The V_{xx} elements are oriented along the b axis (perpendicular to the plane of the paper), and the V_{zz} elements are oriented towards the nearest neighboring Zn^{2+} ion as indicated by arrows.

it leads to a remarkable change in the quadrupole constant which increases from 5.20 ± 0.03 to 5.34 ± 0.03 MHz by introducing the CSA in the simulations. We note that a similar effect is observed in the ^{87}Rb static-powder investigation of RbVO_3 where δ_σ is also negative (45). The rotation plots for the central ^{67}Zn transitions in $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ are shown in fig. 7.3 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, we have taken advantage of the high-resolution properties of SC NMR to improve solid-state ^{67}Zn NMR. This may be useful in studies of e.g., Zn-

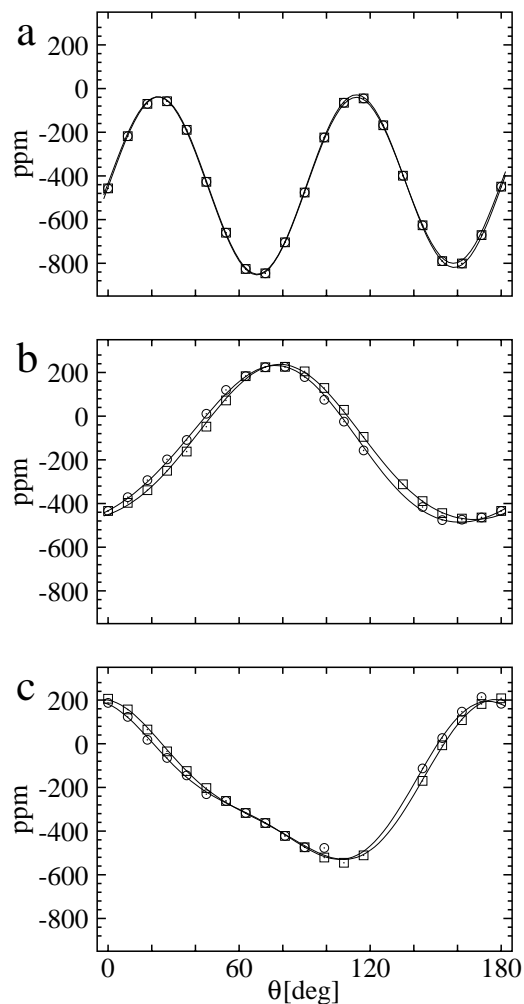


Figure 7.3: Rotation plots of the ^{67}Zn central transitions of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ for rotation about $-x^T$, y^T , and $-z^T$, showing the experimental resonances as circles and squares. The solid lines correspond to the optimized quadrupole coupling and CSA parameters in table 7.1.

complexes which serve as models for Zn-metalloproteins. As the low sensitivity of ^{67}Zn implies the need for quite large crystals this may limit the number of Zn-complexes available by ^{67}Zn SC NMR.