Zinc-67 nuclear magnetic resonance spectroscopy of solids

Gang Wu

Department of Chemistry, Queen’s University, Kingston, Ont. K7L 3N6, Canada

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Abstract

Solid-state $^{67}$Zn nuclear magnetic resonance (NMR) spectra have been reported for ZnO, ZnS, ZnSO$_4$·7H$_2$O and Zn(CH$_3$COO)$_2$. From the $^{67}$Zn NMR spectra obtained for stationary and magic-angle spinning (MAS) powder samples, useful parameters of chemical shift anisotropy (CSA) and nuclear quadrupole coupling constant (NQCC) are determined. The results demonstrate the feasibility of natural abundance $^{67}$Zn NMR studies on solids. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Zinc is among the most important metal ions in biology [1,2]. Zinc(II), a diamagnetic $d^{10}$ ion, is often referred to as being ‘spectroscopically silent’, since one cannot use electron spin resonance (EPR), UV or visible spectroscopic techniques to probe the nature of the Zn(II) site in an enzyme. In addition, the unfavorable NMR property of $^{67}$Zn nuclei ($I = 5/2$, natural abundance = 4.11%, $Q = 0.16 \times 10^{28}$ m$^{-2}$) has also prevented researchers from exploiting $^{67}$Zn as a nuclear probe to biological systems. In fact, $^{67}$Zn NMR studies are scarce even for simple zinc compounds [3]. For these reasons, $^{67}$Zn remains as one of the important but difficult nuclei in NMR spectroscopy.

To date, direct NMR detection of the metal binding sites in zinc-containing proteins has essentially relied on the utility of a surrogate nuclear probe, $^{113}$Cd, which is an NMR-friendly spin 1/2 nucleus [4]. However, the question as to the validity of using cadmium to model the zinc ion environment remains unanswered, because the connection between zinc ion environments and $^{67}$Zn NMR parameters in native zinc metalloproteins has not yet been established. It is not surprising that because of the low NMR sensitivity of $^{67}$Zn nuclei, very little is known about $^{67}$Zn NMR parameters such as chemical shift anisotropy (CSA), nuclear quadrupole coupling constant (NQCC) and indirect spin–spin ($J$) coupling constant. The only two zinc compounds with non-cubic symmetry having been studied by solid-state $^{67}$Zn NMR are Zn(CH$_3$COO)$_2$·2H$_2$O ($e^2\nu/\hbar = 5.3$ MHz, $\eta = 0.87$) [5] and ZnO ($e^2\nu/\hbar = 2.407$ MHz, $\eta = 0$) [6]. For systems where $J$-coupling involving $^{67}$Zn nuclei can be observed, $K_1$,Zn(CN)$_2$ represents the only zinc compound, $^1J(C,^{67}Zn) = 88$ Hz [7]. In this Letter, we present some preliminary results of a solid-state $^{67}$Zn NMR study of ZnO, ZnS, ZnSO$_4$·7H$_2$O and Zn(CH$_3$COO)$_2$. This study demonstrates the feasibility of natural abundance solid-state $^{67}$Zn NMR spectroscopy and the sensitivity of $^{67}$Zn NMR parameters to ion coordination environment.

E-mail: gangwu@chem.queensu.ca

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2. Experimental

The zinc compounds used in this study are commercially available. All $^{67}$Zn NMR experiments were performed on Bruker AM400 spectrometer operating at 25.036 MHz for $^{67}$Zn nuclei. Magic-angle spinning (MAS) experiments were carried out using a 5 mm MAS probe obtained from Doty Scientific (Columbia, South Carolina). Powder samples were packed into zirconium oxide rotors (5 mm o.d.). Zinc-67 chemical shift was referenced to 1.0 M Zn(NO$_3$)$_2$ aqueous solution (δ$_{iso}$ = 0 ppm). A pulse width of 5 μs was used and the recycle delay was typically 0.5–1.0 s. Spectral simulations were performed on a Pentium 200 personal computer using the SOLIDS program kindly provided by Dr. Klaus Eichele and Professor Rod Wasylishen (Dalhousie University, Canada).

3. Results and discussion

A $^{67}$Zn MAS spectrum of ZnO powder is shown in Fig. 1, which exhibits a typical line shape arising from the central transition (+1/2 ↔ −1/2) of a half-integer nucleus in the presence of second-order quadrupole interaction [8]. Unlike other cubic zinc-chalcogenides [9], the wurtzite structure of ZnO crystals is a hexagonal lattice belonging to space group P6$_3$mc [10]. The zinc atom is in tetrahedral coordination with four oxygen atoms (site symmetry C$_4v$). Two different types of Zn–O bonds exist, 1.9760 and 1.9915 Å, with the longer one being the unique Zn–O bond (also the c-axis). The O–Zn–O angles, 108.14 and 110.77°, deviate slightly from the perfect tetrahedral angle. The crystallographic symmetry of ZnO requires that the electric-field-gradient (EFG) tensor at the zinc nucleus be axially symmetric (i.e., η = 0) with the largest principal component along the unique Zn–O bond. From the experimental MAS spectrum shown in Fig. 1, the $^{67}$Zn NQCC and isotropic chemical shift were determined: e$^2$Q/h = 2.40 ± 0.02 MHz and δ$^{iso}$ = 240 ± 2 ppm.

Since the chemical shielding interaction is averaged by MAS, no information about $^{67}$Zn CSA can be obtained from the $^{67}$Zn MAS spectra. In order to determine CSA, it is necessary to obtain NMR spectra for a stationary sample. Fig. 2A shows the $^{67}$Zn NMR spectrum for a stationary powder sample of ZnO. Using the quadrupole parameters and the isotropic chemical shift derived from the MAS spectrum, one can calculate the static NMR line shape arising from the second-order quadrupole interaction as shown in Fig. 2C. However, the resultant spectrum clearly disagrees with the experimental spectrum given in Fig. 2A, indicating that the $^{67}$Zn chemical shift is anisotropic in ZnO. Similar to the case of the EFG tensor, the $^{67}$Zn chemical shift tensor in ZnO must also be axially symmetric, as required by the crystallographic symmetry. However, two possible situations may still exist. That is, the
unique component of the $^{67}$Zn chemical shift tensor could be either the most shielded or the least shielded. The best-fit spectrum shown in Fig. 2B is calculated by including a $^{67}$Zn chemical shift tensor with the unique component being the least shielded: $\delta_{11} = 270 \pm 2$, $\delta_{22} = \delta_{33} = 225 \pm 2$ ppm. The results on both $^{67}$Zn NQCC and CSA in ZnO are in excellent agreement with those from a single-crystal $^{67}$Zn NMR study by Bastow and Stuart [6]. It is noted that Bastow and Stuart [6] also obtained a $^{67}$Zn NMR spectrum for a stationary powder sample of ZnO. However, the quality of their static $^{67}$Zn powder spectrum was insufficient for deriving the $^{67}$Zn CSA parameter.

To illustrate the effects of interplay between CSA and quadrupolar interactions on the NMR line shape of a stationary powder sample, several calculated NMR spectra are presented in Fig. 3. Both the EFG and chemical shift tensors are assumed to be axially symmetric. In the cases of Fig. 3A–C, the unique component of the chemical shift tensor is the most shielded while in the cases of Fig. 3E–G it is the least shielded. As seen from Fig. 3A–G, the appearance of the NMR spectra is quite sensitive to the presence of the chemical shift tensor. Interestingly, the total line width of the spectrum arising from a combination of CSA and quadrupole interactions (e.g., Fig. 3G) can be smaller than that from the quadrupole interaction alone, Fig. 3D. Therefore, a general approach would be to obtain quadrupole parameters from MAS spectra of the central transition and subsequently analyze static line shapes by including CSA.

Fig. 4 shows solid-state $^{67}$Zn NMR spectra of ZnS, ZnSO$_4$·7H$_2$O and Zn(CH$_3$COO)$_2$. The solid-state $^{67}$Zn NMR data are summarized in Table 1. The $^{67}$Zn MAS spectrum of ZnS is shown in Fig. 4A, which exhibits two sharp peaks centered at 381.9 and 364.5 ppm, respectively. The line width of each of the two peaks is ~50 Hz. In contrast to ZnO, ZnS can exist in either cubic (sphalerite) or hexagonal (wurtzite) form. Solid-state $^{67}$Zn NMR parameters for the pure forms of cubic and hexagonal ZnS have

![Figure 3](image-url)  
**Fig. 3.** Effect of the interplay between chemical shielding tensor and second-order quadrupole interaction on the static line shape of the central transition. The $^{67}$Zn chemical shift tensors used in the calculations are as follows: (A) $\delta_{11} = \delta_{22} = 285$, $\delta_{33} = 150$ ppm; (B) $\delta_{11} = \delta_{33} = 270$, $\delta_{22} = 180$ ppm; (C) $\delta_{11} = \delta_{33} = 255$, $\delta_{22} = 210$ ppm; (D) $\delta_{11} = \delta_{33} = 270$, $\delta_{22} = 240$ ppm; (E) $\delta_{11} = \delta_{33} = 225$ ppm; (F) $\delta_{11} = 300$, $\delta_{22} = \delta_{33} = 210$ ppm; and (G) $\delta_{11} = 330$, $\delta_{22} = 195$ ppm. Other parameters used in the calculations are: $\eta = 0$, $^{67}$Zn Larmor frequency = 25.0 MHz. Both the EFG and chemical shift tensors are assumed to be axially symmetric.
Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zinc coordination environment</th>
<th>$\epsilon^2\gamma Q / h$ (MHz)</th>
<th>$\eta$</th>
<th>$\delta_{\text{iso}}$ (ppm)</th>
<th>$\delta^{+}$ (ppm)</th>
<th>$\kappa$</th>
<th>Ref.</th>
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<tr>
<td>Zn(CH$_3$COO)$_2$·2H$_2$O</td>
<td>6O</td>
<td>5.3</td>
<td>0.87</td>
<td>0</td>
<td>–</td>
<td>–</td>
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<td>ZnO (hexagonal)</td>
<td>4O</td>
<td>2.407</td>
<td>0</td>
<td>240.1</td>
<td>43.9</td>
<td>–1.0</td>
<td>[6]</td>
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<td></td>
<td></td>
<td>2.40</td>
<td>0</td>
<td>240</td>
<td>45</td>
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<td>ZnS (cubic)</td>
<td>4S</td>
<td>0</td>
<td>0</td>
<td>380.5</td>
<td>0</td>
<td>–</td>
<td>[6]</td>
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<tr>
<td></td>
<td></td>
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<td>0</td>
<td>378</td>
<td>0</td>
<td>–</td>
<td>[9]</td>
</tr>
<tr>
<td>ZnS (hexagonal)</td>
<td>4S</td>
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<td>0</td>
<td>365</td>
<td>16</td>
<td>–1.0</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 0.4</td>
<td>0</td>
<td>364.5</td>
<td>22</td>
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<td>0.2</td>
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<td>30</td>
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<td>Zn(CH$_3$COO)$_2$</td>
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<td>2.42</td>
<td>0</td>
<td>260</td>
<td>45</td>
<td>1.0</td>
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</table>

$^{a}$Span of the chemical shift tensor defined as: $\Omega = \delta_{11} - \delta_{33}$.

$^{b}$Skew of the chemical shift tensor defined as: $\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$.

been reported previously [6,9]. The $^{67}$Zn chemical shifts observed in Fig. 4A are in good agreement with those reported for the cubic and hexagonal forms of ZnS, respectively; see Table 1. Therefore, it is concluded that the commercial sample of ZnS used in this study contains both cubic and hexagonal forms in an approximate 1:1 ratio. The $^{67}$Zn NMR spectrum of a stationary sample of ZnS is shown in Fig. 4B. It is noted from Fig. 4B that, while the peak at 381.9 ppm (from the cubic ZnS) remains to exhibit an isotropic line shape, the peak at 364.5 ppm (from the hexagonal form) exhibits an anisotropic line shape, which suggests the presence of a small CSA. Analysis of the line shape yields an axially symmetric $^{67}$Zn chemical shift tensor for the hexagonal ZnS: $\delta_{11} = 380 \pm 2$ and $\delta_{22} = \delta_{33} = 358 \pm 2$ ppm. This finding is also consistent with a previous $^{67}$Zn NMR study of a pure hexagonal ZnS [6]. It is worth noting that CdSe and CdS also have a hexagonal (wurtzite) structure and that the span of the $^{113}$Cd chemical shift tensor in CdSe and CdS was found to be 54 and 64 ppm, respectively [11]. The values of 22 and 45 ppm observed in ZnS and ZnO are comparable to those in CdSe and CdS, respectively. Furthermore, the observation that the unique component of the $^{67}$Zn chemical shift tensor in ZnO and ZnS is the least shielded is also consistent with the solid-state $^{113}$Cd NMR results of CdSe and CdS [11]. The $^{67}$Zn NQCC in the hexagonal ZnS is, however, too small to be measured accurately at the field strength employed in this study, 9.4 T. From the line width of the peak at 364.5 ppm in the MAS spectrum shown in Fig. 4A, an upper limit for $^{67}$Zn NQCC in the hexagonal ZnS was estimated, $\epsilon^2\gamma Q / h < 0.4$ MHz. The fact that $^{67}$Zn NQCC is much smaller in ZnS than in ZnO can be explained by the structural difference of the two compounds. Although both compounds belong to the same space group, the unit-cell parameters of ZnS (c/a = 1.6378, u = 0.3748) [12] are considerably closer than those of ZnO (c/a = 1.6021, u = 0.3817) [10] to the values of an ideal wurtzite lattice (c/a = 0.16330, u = 0.3750) where perfect tetrahedra exist. Therefore, the significant departure from an ideal wurtzite structure is responsible for the large $^{67}$Zn NQCC and CSA values observed in ZnO.

The $^{67}$Zn NMR spectrum of a stationary sample of ZnSO$_4$·7H$_2$O is presented in Fig. 4C together with the best-fit spectrum. From the $^{67}$Zn MAS spectrum of ZnSO$_4$·7H$_2$O (data not shown), the $^{67}$Zn NQCC was determined to be 1.70 ± 0.02 MHz with a small departure from axial symmetry, $\eta = 0.2$. The zinc ion in ZnSO$_4$·7H$_2$O is coordinated by six water molecules in a distorted octahedral environment [13]. The observed isotropic $^{67}$Zn chemical shift of 10 ppm is typical of zinc ions in octahedral environment. To reproduce the static spectrum shown in Fig. 4C, it is necessary to include a small $^{67}$Zn.
It was also assumed that the $^{67}$Zn chemical shift tensor is axially symmetric and approximately coincident with the EFG tensor. However, given the low signal-to-noise ratio of the static spectrum, it is difficult to determine precisely the relative orientation between the two tensors in ZnSO$_4$·7H$_2$O. Fig. 4D shows the $^{67}$Zn NMR spectrum of Zn(CH$_3$COO)$_2$. The Zn(CH$_3$COO)$_2$ crystals form a three-dimensional polymeric network with the zinc ion being in a slightly distorted tetrahedral environment [14]. The four Zn–O bond lengths are 1.914, 1.929, 1.937 and 1.955 Å and the O–Zn–O bond angles range from 102.2 to 115.9°. Analysis of the $^{67}$Zn NMR spectra of Zn(CH$_3$COO)$_2$ yields both $^{67}$Zn NQCC and CSA: $e^2 q Q / h = 2.42 ± 0.02$ MHz, $\eta = 0$, $\delta_{11} = \delta_{22} = 275 ± 2$ and $\delta_{13} = 230 ± 2$ ppm. Since both the $^{67}$Zn EFG and chemical shift tensors are axially symmetric, it is reasonable to assume that the two tensors have the same principal-axis system.

It is interesting to note that, in contrast to the case of ZnO, the unique component of the $^{67}$Zn chemical shift tensor in Zn(CH$_3$COO)$_2$ is the most shielded. For ZnSO$_4$·7H$_2$O and Zn(CH$_3$COO)$_2$, the $^{67}$Zn spin–lattice relaxation time was estimated to be $<$ 0.5 s.

It is of interest to compare the observed $^{67}$Zn NMR parameters in ZnO, ZnSO$_4$·7H$_2$O and anhydrous Zn(CH$_3$COO)$_2$ with those previously reported for Zn(CH$_3$COO)$_2$·2H$_2$O by Kunwar et al. [5]. The crystal structure of Zn(CH$_3$COO)$_2$·2H$_2$O [15] indicates that the zinc ion is in a very distorted octahedral environment. Two of the six coordination oxygen atoms are from water molecules. The O–Zn–O angles deviate significantly from those expected for the perfect O$_6$ symmetry with the Zn–O bond length varying from 2.14 to 2.18 Å [15]. Consequently, a large $^{67}$Zn NQCC is observed, 5.3 MHz [5]. However, it is somewhat surprising that the rather small departure from T$_h$ or O$_h$ symmetry in ZnO, ZnS and Zn(CH$_3$COO)$_2$ or in ZnSO$_4$·7H$_2$O, respectively, results in measurable $^{67}$Zn CSAs, but no indication of $^{67}$Zn CSA was observed for Zn(CH$_3$COO)$_2$·2H$_2$O where large distortion from O$_h$ symmetry is present. The $^{67}$Zn NMR parameters for zinc ions in a tetrahedral environment seem to be more sensitive to the degree of departure from perfect symmetry than those in an octahedral environment. Furthermore, based on the very limited $^{67}$Zn NMR data, there does not seem to exist any simple correlation between $^{67}$Zn NQCC and CSA. Clearly, a complete understanding of the anisotropic nature of the NMR parameters in transition metals would require further theoretical studies. The zinc compounds in the present study may serve as test examples for future ab initio calculations of zinc NMR parameters.

4. Conclusions

We have presented results of a solid-state $^{67}$Zn NMR study of several zinc compounds at natural abundance. The distorted zinc environments in ZnO, the hexagonal (wurtzite) form of ZnS, ZnSO$_4$·7H$_2$O and Zn(CH$_3$COO)$_2$ cause non-vanishing $^{67}$Zn quadrupole and CSA interactions. Solid-state $^{67}$Zn NMR is capable of yielding useful information about $^{67}$Zn quadrupole and CSA interactions. These NMR parameters are sensitive measures of the immediate coordination environment of the metal nucleus. We anticipate that a combination of high magnetic field strength and high-speed MAS will make $^{67}$Zn an accessible nuclear probe in the study of metal ion binding in a variety of systems including biological systems. We hope that the results presented in this work will encourage additional solid-state $^{67}$Zn NMR studies.

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