Zinc-67 NMR study of tetrahedral and octahedral zinc sites with symmetrical oxygen, nitrogen, and sulfur ligands

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Abstract: We report a ^{67}Zn nuclear magnetic resonance (NMR) study of compounds containing zinc ions coordinated by oxygen, nitrogen, and sulfur ligands. New information concerning ^{67}Zn nuclear quadrupole coupling constants (NQCC) and chemical shift was obtained from magic-angle spinning (MAS) spectra of solid compounds containing both natural abundance and enriched ^{67}Zn isotopes. Rapid ligand exchange processes of $[Zn(thiourea)_4]^{2+}$ in aqueous solutions were also observed.

Key words: ^{67}Zn NMR, nuclear quadrupolar coupling constant, ligand exchange.

Résumé : On a mesuré les spectres de résonance magnétique nucléaire (RMN) du ^{67}Zn de composés contenant des ions zinc coordinés à des ligands oxygénés, azotés et sulfurés. Grâce aux spectres obtenus par la technique de rotation à l'angle technique (magique) de composés solides contenant du ^{67}Zn en abondance naturelle ou enrichie, on a obtenu de nouvelles informations relatives aux constantes de couplage quadripolaire nucléaire (CCQN) et les déplacements chimiques du ^{67}Zn. On a aussi observé des processus d'échange rapide de ligand pour le $[Zn(thiourée)_4]^{2+}$.

Mots clés : RMN du ^{67}Zn, constante de couplage quadripolaire nucléaire, échange de ligands.

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Introduction

Zinc is among the most important metal elements in biology and is an integral constituent of a large number of enzymes (1, 2). To study the catalytic or structural role of zinc ions in these enzymes, it is important to have a means of probing the nature of the zinc binding site. In the absence of X-ray crystallographic data, direct detection of diamagnetic d^{10} Zn^{2+} ions in biological systems is difficult because of the lack of a suitable spectroscopic probe. From an NMR perspective, ^{67}Zn (the only NMR-active zinc isotope) is among a number of potentially important but insensitive metal nuclei such as ^{43}Ca and ^{25}Mg. The insensitivity of ^{67}Zn NMR arises from the fact that ^{67}Zn is a quadrupolar nucleus (spin 5/2, $Q = 0.15 \times 10^{-28}$ m^{-2}) with low natural abundance (4.11%) and a small magnetogyric ratio ($\gamma = 1.6768 \times 10^7$ rad T^{-1} s^{-1}). Consequently, ^{67}Zn NMR experiments are remarkably difficult. In addition to the low intrinsic sensitivity, solution state ^{67}Zn NMR is further hampered by the fact that molecular tumbling motion always induces efficient ^{67}Zn quadrupole relaxation, resulting in short life times of Zeeman energy levels, which lead to broad NMR lines. To date, ^{67}Zn NMR of liquid samples has been limited to studies of either highly symmetric species or unsymmetrical complexes undergoing rapid exchange with large excessive $[Zn(H_2O)_6]^{2+}$ (3–6). Despite the biological relevance of zinc ions, the aforementioned practical difficulties have made ^{67}Zn NMR a nearly forgotten area. In the past, NMR studies of the metal binding sites in zinc-containing proteins have essentially relied on the utility of a surrogate nuclear probe, ^{113}Cd (7).

Solid-state NMR represents a useful approach to obtaining high-resolution NMR spectra for quadrupolar nuclei. In many aspects, it is more advantageous to study quadrupolar nuclei in the solid state than in solution. Since molecular motion is largely restricted in solids, quadrupole relaxation is not as efficient as in solution. As a result, the intrinsic resolution of solid-state NMR spectra is not limited by the lifetime of the quadrupole energy levels. However, solid-state ^{67}Zn NMR studies are still rare. Two solid-state ^{67}Zn NMR studies have appeared in the literature (8, 9); but the compounds under study are of cubic symmetry, so the electric field gradient (EFG) at the zinc site vanishes. The ^{67}Zn NMR study of $Zn(CH_3COO)_2 \cdot 2H_2O$ by Oldfield and coworkers (10) is the first report dealing with a noncubic zinc compound in the solid state. Later, Bastow and Stuart (11) obtained ^{67}Zn NMR spectra of both single-crystal and powdered ZnO samples. Recently, we reported some preliminary results of a natural abundance ^{67}Zn NMR study of zinc compounds with both tetrahedrally and octahedrally coordinated

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oxygen ligands (12). Here we extend our solid-state ^{67}Zn NMR study to compounds where the zinc center is coordinated by either nitrogen or sulfur ligands. To the best of our knowledge, ^{67}Zn nuclear quadrupole coupling constants (NQCC) have not been determined for any noncubic zinc center coordinated by nitrogen and sulfur ligands.

Experimental section

All solid-state NMR spectra were obtained on a Bruker Avance-400 NMR spectrometer operating at 25.036 MHz for ^{67}Zn nuclei. Solution NMR spectra were obtained on Bruker Avance-500 and Avance-400 spectrometers. All ^{67}Zn chemical shifts were referenced to an external sample of 1.0 M $Zn(NO_3)_2$ aqueous solution (δ_{iso} = 0 ppm). Magic-angle spinning (MAS) ^{67}Zn NMR experiments were performed using a probe purchased from Doty Scientific Inc. (Columbia, S.C.). Powder samples were packed into zirconium oxide rotors (5 mm o.d.). Typical sample spinning speeds were between 7 and 9 kHz. A pulse width of 5 μs was used, and the recycle time was between 1 and 10 s. Samples of ZnSe and $Zn(CH_3COO)_2 \cdot 2H_2O$ were obtained from commercial sources and used without further purification. Anhydrous $Zn(CH_3COO)_2$ was obtained by heating the corresponding hydrate sample in oven for 2 days at 80°C. ZnO (88% ^{67}Zn-enriched) was purchased from Trace Science International (Toronto, Ont.). Crystals of $^{67}Zn(ClO_4)_2 \cdot 6H_2O$ were formed by dissolving 25 mg of ^{67}ZnO in 3.6 mL of 0.25 M $HClO_4$. A solid sample of tetrakis(imidazole)zinc(II) perchlorate, $Zn[ImH]_4(ClO_4)_2$ (ImH = imidazole), was then obtained by slow evaporation of a 1:4 molar ratio mixture of $^{67}Zn(ClO_4)_2 \cdot 6H_2O$ and imidazole (81 mg) from 1 mL of 95% ethanol. An aqueous solution of $^{67}Zn(NO_3)_2$ was prepared by dissolving 24 mg of ^{67}ZnO in 1.1 mL of 0.5 M HNO_3. To this solution, 93 mg of thiourea, $SC(NH_2)_2$, in 1 mL of distilled H_2O was added. Crystals of tetrakis(thiourea)zinc(II) nitrate, $^{67}Zn[SC(NH_2)_2]_4(NO_3)_2$, were then formed by slow evaporation of the solvent. For concentration-dependent experiments, the concentration of $[Zn]^{2+}$ was kept constant at 0.65 mM, and an appropriate amount of thiourea was added to the solution to form a specific $[Zn]^{2+}$ to thiourea concentration ratio. Solution ^{67}Zn NMR experiments were carried out at room temperature (298.5 K), using a pulse width of 55.0 μs and a recycle delay of 100 ms. Typically, 2000–3000 scans were collected. Prior to Fourier Transformation (FT), FIDs were left-shifted to remove data points due to probe ring-down, followed by 200–250 Hz exponential line broadening. Simulations of solid-state NMR spectra were performed on a Pentium 200 personal computer using the SOLIDS program package kindly provided by Dr. Klaus Eichele and Professor Rod Wasylishen (Dalhousie University, Halifax, N.S.).

Results and discussion

Figure 1 shows ^{67}Zn MAS spectra of solid ZnSe and $Zn(ClO_4)_2 \cdot 6H_2O$ obtained at 9.4 T. The cubic structure of ZnSe (13) yields a negligible ^{67}Zn NQCC at the zinc center, and therefore, the MAS spectrum of ZnSe shows a sharp isotropic peak centered at 276 ppm with a full width at the half-height (FWHH) of 16 Hz. Interestingly, this value is even smaller than that observed for the standard reference sample, $Zn(NO_3)_2$ (aq), which has a line width of 80 Hz. In an early study, Haller et al. (8) reported a 50 Hz line width for the ^{67}Zn NMR signal from a stationary ZnSe sample. Close inspection of the spectrum presented in Fig. 1(*a*) showed no indication of any indirect spin–spin coupling (*J*) between ^{67}Zn and ^{77}Se (spin 1/2, natural abundance = 7.58%) nuclei, suggesting that $^1J(^{67}Zn, ^{77}Se)$ must be smaller than the observed line width.

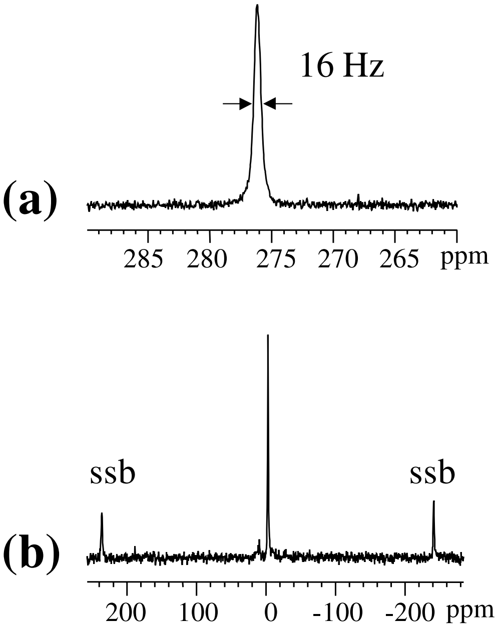
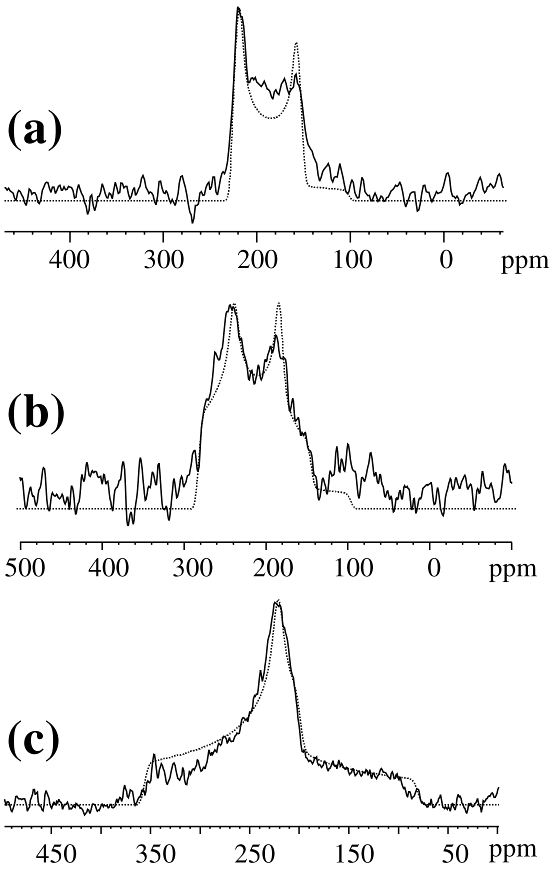


Fig. 1. ^{67}Zn MAS spectra of (*a*) natural abundance ZnSe (number of scans, 360; recycle delay, 1 s; spinning rate, 5.0 kHz) and (*b*) ^{67}Zn-enriched $Zn(ClO_4)_2 \cdot 6H_2O$ (number of scans, 128; recycle delay, 10 s; spinning rate, 6.0 kHz). Spinning sidebands are marked as "ssb."

The isotropic ^{67}Zn chemical shift observed for solid $^{67}Zn(ClO_4)_2 \cdot 6H_2O$ is –3 ppm, which suggests a similar zinc environment in both solid and solution state. The crystal structure of $Zn(ClO_4)_2 \cdot 6H_2O$ at room temperature (space group $P6_3mc$) (14) reveals that the zinc ion is coordinated by six water molecules with a nearly perfect O_h site symmetry. The Zn—O distances are 2.123 and 2.152 Å. The O-Zn-O angles are very close to those expected for a regular octahedron, e.g., 86.3°, 179.0°, 94.4°, and 84.9°. From the line width observed in the ^{67}Zn MAS spectrum, it is estimated that e^2qQ/h is less than 0.2 MHz.

Figure 2(*a*) shows the natural abundance ^{67}Zn MAS spectrum of $Zn(CH_3COO)_2$. The spectrum exhibits a typical line shape arising from the second-order quadrupolar interaction (15). The isotropic ^{67}Zn chemical shift of $Zn(CH_3COO)_2$ is found to be 245 ppm, which is similar to that found for ZnO (11, 12) where the zinc atom is tetrahedrally bonded to four oxygen atoms. No solution ^{67}Zn NMR data are available in the literature for zinc centers coordinated to four oxygen ligands. The crystal structure of $Zn(CH_3COO)_2$ (space group *Fdd*2) indicates that the zinc ion is in a slightly distorted tetrahedral environment (16). The Zn—O bond length varies from 1.914 to 1.955 Å, and the O-Zn-O angle ranges from

Fig. 2. Experimental (solid lines) and calculated (broken lines) ^{67}Zn MAS spectra of (*a*) natural abundance Zn(CH$_3$COO)$_2$ (number of scans, 32 225; spinning rate, 8.5 kHz; recycle delay, 1 s), (*b*) ^{67}Zn-enriched Zn(imidazole)$_4$(ClO$_4$)$_2$ (number of scans, 16 774; recycle time, 1 s; spinning rate, 8.1 kHz), and (*c*) ^{67}Zn-enriched Zn(thiourea)$_4$(NO$_3$)$_2$ (number of scans, 19 188, recycle time, 2 s; spinning rate, 9.1 kHz).



102.2° to 115.9°. Analysis of the MAS line shape shown in Fig. 2(*a*) yields that e^2qQ/h = 2.42 MHz and η = 0.1.

To explore the sensitivity enhancement by isotopic enrichment, we prepared two ^{67}Zn-enriched compounds: ^{67}Zn[ImH]$_4$(ClO$_4$)$_2$ and ^{67}Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$. The enrichment level is about 88% for both compounds. Figures 2(*b*) and (*c*) show the ^{67}Zn MAS spectra of the two ^{67}Zn-labeled compounds. For ^{67}Zn(ImH)$_4$(ClO$_4$)$_2$, the isotropic ^{67}Zn chemical shift is 291 ppm, which is comparable to the value of 264 ppm observed in acetone solution. The ^{67}Zn chemical-shift value for zinc ions coordinated by four nitrogen ligands is also in agreement with that observed in [Zn(NH$_3$)$_4$]$^{2+}$ from solution ^{67}Zn NMR studies (3). However, both the line width and peak position of the solution state ^{67}Zn spectrum of ^{67}Zn(ImH)$_4$(ClO$_4$)$_2$ were found to be solvent dependent. For example, the ^{67}Zn NMR spectrum of Zn(ImH)$_4$(ClO$_4$)$_2$ in methanol exhibits a peak at 280 ppm with a much larger line width, 2500 Hz, than that found in acetone, 500 Hz. Furthermore, we did not observe any ^{67}Zn NMR signal from an aqueous solution of Zn(ImH)$_4$(ClO$_4$)$_2$, presumably due to rapid ligand exchange (vide infra). The crystal structure of Zn(ImH)$_4$(ClO$_4$)$_2$ (space group *C*2/*c*) shows that the zinc ion lies on a crystallographic C_2 axis and is tetrahedrally coordinated by four nitrogen atoms from the imidazole molecules (17). The two independent Zn—N(imidazole) bond lengths are nearly identical, 1.997 and 2.001 Å. The N-Zn-N angles range from 105.3° to 113.3°. Analysis of the ^{67}Zn MAS line shape shown in Fig. 2(*b*) also yields that e^2qQ/h = 2.80 MHz and η = 0.4. To our knowledge, Zn(ImH)$_4$(ClO$_4$)$_2$ represents the only example where the ^{67}Zn NQCC for a ZnN$_4$ coordination environment is determined.

Figure 2(*c*) shows the ^{67}Zn MAS spectrum of ^{67}Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$. The isotropic ^{67}Zn chemical shift is 359 ppm, which is in agreement with those reported for zinc sites coordinated by four sulfur atoms (3). From analysis of the ^{67}Zn MAS spectrum, we obtained that the ^{67}Zn NQCC is 3.15 MHz with η = 1. The crystal structure of Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$ (space group *Pnaa*) indicates that the zinc ions are coordinated by four sulfur atoms from the thiourea ligands (18). The two Zn—S distances are 2.324 and 2.361 Å, which are considerably longer than the Zn—N distances in the zinc–imidazole complex. The S-Zn-S angle between the two longer Zn—S bonds is 100.0°, and the angle between the two shorter Zn—S bonds is 121.5°, both of which deviate considerably from the perfect tetrahedral angle. It is also noted that the ^{67}Zn EFG tensors in Zn(ImH)$_4$(ClO$_4$)$_2$ and Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$ exhibit very different asymmetry parameters. This observation is somewhat surprising, since the two compounds have a similar tetrahedral arrangement at the zinc center.

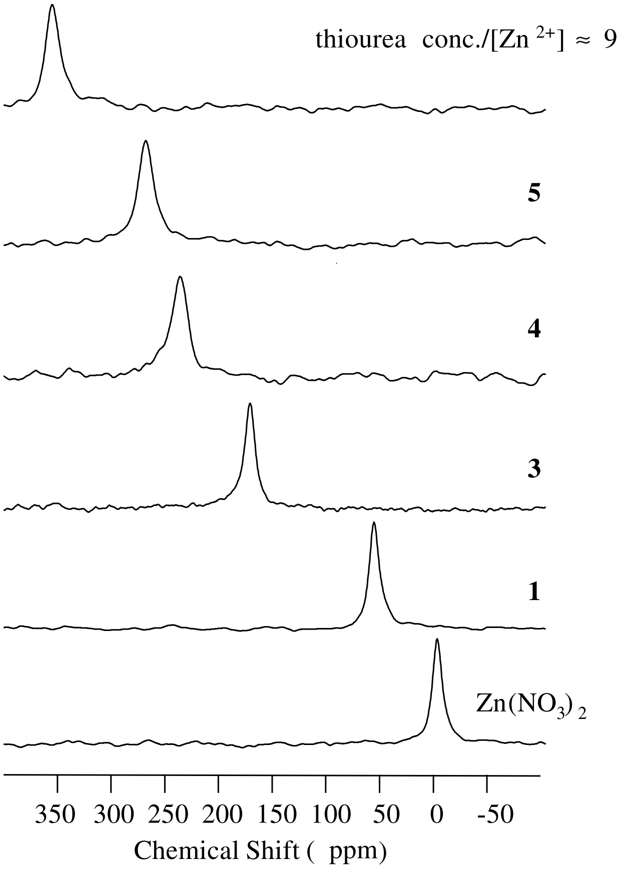
Compared with the ^{67}Zn MAS spectrum of natural abundance Zn(CH$_3$COO)$_2$, as shown in Fig. 2(*a*), the overall sensitivity enhancement in the ^{67}Zn MAS spectra of the two ^{67}Zn-enriched compounds does not appear as dramatic as expected from the enrichment level, i.e., a factor of 20. Although solution ^{67}Zn NMR did prove that the ^{67}Zn enrichment procedure was successful, several other factors may contribute to the apparent lack of full signal enhancement in the ^{67}Zn spectra of ^{67}Zn(ImH)$_4$(ClO$_4$)$_2$ and ^{67}Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$. First, the molecular size of Zn(ImH)$_4$(ClO$_4$)$_2$ (FW = 536) and Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$ (FW = 493) is larger than that of Zn(CH$_3$OO)$_2$ (FW = 183). Second, in the case of ^{67}Zn(ImH)$_4$(ClO$_4$)$_2$, a small sample of the enriched compound (ca. 50 mg) was used, which is much less than ca. 150 mg used for the natural abundance Zn(CH$_3$COO)$_2$ sample. Third, the ^{67}Zn spin-lattice relaxation time (T_1) is much longer in ^{67}Zn(ImH)$_4$(ClO$_4$)$_2$ and ^{67}Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$ than in Zn(CH$_3$COO)$_2$. By performing ^{67}Zn MAS experiments with different recycle delays, we were able to provide an estimate for ^{67}Zn T_1 in ^{67}Zn[SC(NH$_2$)$_2$](NO$_3$)$_2$, $T_1 \approx 2$ s. In Zn(CH$_3$COO)$_2$, however, the T_1 was estimated to be less than 0.5 s (12). After considering all these factors, the sensitivity enhancement in Figs. 2(*b*) and (*c*) seems reasonable. It is worth pointing out that our attempts to record ^{67}Zn MAS spectra for natural abundance samples of Zn(ImH)$_4$(ClO$_4$)$_2$ and Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$ were unsuccessful, presumably due to the long T_1 values.

Similar to the case of the zinc imidazole complex, we also observed rapid ligand exchange in the aqueous solution of Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$. Figure 3 shows the result of the concentration study to examine the rapid ligand exchange process in Zn[SC(NH$_2$)$_2$]$_4$(NO$_3$)$_2$. When the concentration of thiourea is low, the ^{67}Zn chemical shift is close to 0 ppm, in-

Table 1. Solid-state ^{67}Zn NMR data for zinc compounds.

Compound	Zinc coordination	δ_{iso} (ppm)	e^2qQ/h (MHz)	η	Ref.
ZnO (hexagonal)	ZnO_4	240.1	2.407	0.0	11
		240	2.40	0.0	12
ZnS (cubic)	ZnS_4	378	0	—	8
		380.5	0	—	11
		381.9	0	—	12
ZnS (hexagonal)	ZnS_4	365	<0.5	0	11
		364.5	<0.4	0	12
ZnSe (cubic)	$ZnSe_4$	273	—	—	8
		276	—	—	This work
ZnTe (cubic)	$ZnTe_4$	85	—	—	8
$K_2Zn(CN)_4$ (cubic)	ZnC_4	291	0	—	9
$Zn(CH_3COO)_2 \cdot 2H_2O$	ZnO_6	0	5.3	0.85	10
$ZnSO_4 \cdot 7H_2O$	ZnO_6	10	1.70	0.2	12
$Zn(CH_3COO)_2$	ZnO_4	245	2.42	0.1	This work
$Zn(imidazole)_4(ClO_4)_2$	ZnN_4	291	2.80	0.4	This work
$Zn(thiourea)_4(NO_3)_2$	ZnS_4	359	3.15	1.0	This work
$Zn(ClO_4)_2 \cdot 6H_2O$	ZnO_6	–3.0	<0.2	—	This work

Fig. 3. ^{67}Zn NMR spectra of aqueous solutions of $Zn(NO_3)_2$ and thiourea at different thiourea conc./[Zn^{2+}] ratios. The pH value of the solution varies from 4.20 (1:1) to 3.78 (1:9).



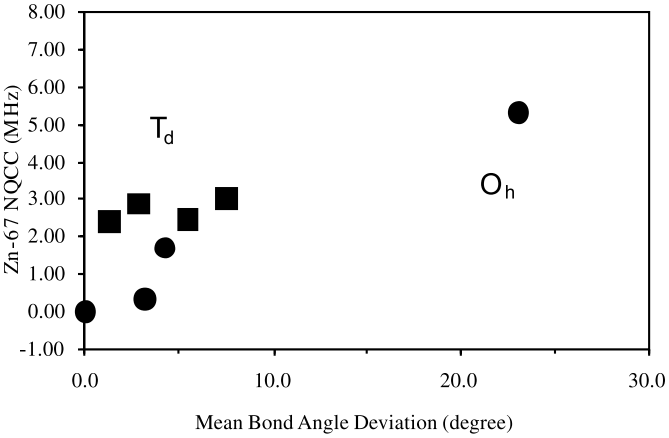
dicating the existence of $[Zn(H_2O)_6]^{2+}$ species. As the concentration of the thiourea ligand is increased, the ^{67}Zn NMR signal is shifted toward higher frequencies. At the highest metal–ligand ratio used in this study, thiourea conc./[Zn^{2+}] ≈ 9, the ^{67}Zn chemical shift of 355 ppm for the solution sample is practically identical to that observed in the solid state, 359 ppm.

To examine possible trends in solid-state ^{67}Zn NMR parameters, we summarize in Table 1 the presently available data in the literature for zinc compounds. It is noted that the ^{67}Zn NQCC has also been determined in zinc metal, e^2qQ/h = 11.983 MHz (19–21); however, it is reasonable not to compare this value with those obtained for zinc compounds. With this exception, the largest ^{67}Zn NQCC found in zinc compounds is that in $Zn(CH_3COO)_2 \cdot 2H_2O$, e^2qQ/h = 5.3 MHz (10). The crystal structure of $Zn(CH_3COO)_2 \cdot 2H_2O$ (22) indicates that the zinc ion is coordinated by six oxygen atoms in a very distorted octahedral environment. Four of the six oxygen atoms are from the acetate groups. The other two oxygen atoms are those from the water molecules. Whereas, the Zn—O bond length varies slightly from 2.14 to 2.18 Å, a significant distortion from perfect O_h symmetry exists in the O-Zn-O bond angles. For example, large distortions are found when the two mutually *trans* oxygen atoms are due to the acetate and water, respectively, i.e., O(Ac)-Zn-O(W) = 152°, or when the two *cis* oxygen atoms are from the same acetate group, O(Ac)-Zn-O(Ac) = 61°. The distortion is, however, smaller when the two *cis* oxygen atoms arise from the acetate and water, respectively, i.e., O(Ac)-Zn-O(W) = 108°. To study the possible correlation between ^{67}Zn NQCC and molecular structure, we have used a parameter called the mean deviation of bond angles as a measure of the degree of deviation of the zinc site of interest from a perfect symmetry, T_d or O_h. The mean deviation of bond angles can be defined for a tetrahedral site as

$$[1] \qquad \Delta(T_d) = \frac{1}{4}\sum_i \left| \theta_i - 109.5° \right|$$

where θ_i is the *i*th bond angle across the zinc center. In a similar fashion, one can define a mean deviation of bond angles for an octahedral site using 90° and 180° as perfect angles. In Fig. 4, ^{67}Zn NQCC is plotted against the mean deviation of bond angles as defined in eq. [1] for presently available ^{67}Zn NMR data. As seen in Fig. 4, the octahedral

Fig. 4. Plot of ^{67}Zn NQCC versus mean bond angle deviation from perfect T_d (■) and O_h (●) symmetry.



compounds appear to show a correlation between the magnitude of the ^{67}Zn NQCC and the degree of deviation from the O_h symmetry, whereas the tetrahedral compounds are insensitive to the mean deviation of bond angles, at least within the presently available data. It is also somewhat surprising that a very small distortion from the perfect T_d symmetry in ZnO (O-Zn-O: 108.14° and 110.77°) (23) results in a reasonably large ^{67}Zn NQCC, 2.40 MHz. However, $ZnSO_4 \cdot 7H_2O$ exhibits larger distortion (O-Zn-O: 80.6°, 97.5°, 172.3°) than ZnO but has a smaller ^{67}Zn NQCC, 1.7 MHz. It is clear that using the mean deviation of bond angles alone to explain the results may be oversimplified because the model does not consider the nature of the Zn—ligand bond. For the octahedral compounds examined in this study, the zinc ions are coordinated to six oxygen atoms with similar bond lengths, 2.09 ± 0.10 Å. Thus, it is perhaps not surprising that a reasonable correlation is observed among octahedral compounds. However, the Zn—ligand distance for the tetrahedral compounds varies from 1.914 to 2.000 to 2.361 Å for Zn—O (acetate), Zn—S (thiourea), and Zn—N (imidazole), respectively. This discrepancy may be responsible for the lack of correlation between ^{67}Zn NMR parameters and molecular structure among tetrahedral compounds. Nevertheless, more investigations are definitely required before one can draw any conclusion about the correlation between ^{67}Zn NMR parameters and molecular structure.

Based on the presently available solid-state ^{67}Zn NMR data, it seems that the value of 5.3 MHz found in $Zn(CH_3COO)_2 \cdot 2H_2O$ may represent an upper limit of the ^{67}Zn NQCC for zinc ions coordinated octahedrally by *symmetrical* ligands but a lower limit for octahedral compounds with *unsymmetrical* ligands. The zinc binding geometry in the zinc–insulin complex belongs to the latter case, since each of the two zinc sites in the two-zinc insulin hexamer is coordinated by three imidazolyl nitrogen atoms and three water oxygen atoms (24). In light of the new solid-state ^{67}Zn NMR data, it appears that the value of 1.86 MHz suggested for the ^{67}Zn NQCC in insulin by Shimizu and Hatano (25) may be grossly underestimated.

Conclusions

In this study, we have focused on the solid-state ^{67}Zn NMR spectra of tetrahedral and octahedral zinc centers that are symmetrically coordinated by water, acetate, imidazole, and thiourea ligands. It is well known that the active zinc sites in metalloproteins usually contain *unsymmetrical* ligands. Therefore, it would be desirable, although technically challenging, to extend these solid-state ^{67}Zn NMR studies to some model compounds where the zinc center resembles those in zinc-containing proteins. Unfortunately, to this date, our efforts in recording solid-state ^{67}Zn NMR signals for unsymmetrical zinc sites have been unsuccessful, presumably due to the large quadrupole coupling constants associated with those sites. It should be noted that the solid-state ^{67}Zn NMR results reported in this study were obtained at a relatively low magnetic field, 9.4 T. Since the second-order quadrupolar broadening is inversely proportional to the applied magnetic field strength, the availability of very high-field instrument (18.8 T or greater) holds the promise of making unsymmetrical coordination zinc sites accessible.[2]

Acknowledgments

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