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# A New Approach in 1D and 2D $^{13}C$ High-Resolution Solid-State NMR Spectroscopy of Paramagnetic Organometallic Complexes by Very Fast Magic-Angle Spinning

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Molecular structures of organometallic complexes in solids attract broad interest because of a wide variety of applications such as supramolecular science and solid-state reactions.[1] For providing detailed structural information on organometal complexes in solids, X-ray crystallography has been most useful, but only for compounds that can be successfully crystallized. Solid-state NMR (SSNMR) is a powerful technique for noncrystalline organic samples including diamagnetic organometal complexes.[2] However, only a handful of SSNMR studies have been performed for paramagnetic organometal complexes in rigid solids[3−6] because of low sensitivity/resolution and difficulties in $^{1}H$ decoupling associated with large paramagnetic shifts. Recent studies demonstrated that $^{13}C$, $^{1}H$, and $^{2}D$ magic-angle spinning (MAS) spectra of $^{2}D$-labeled paramagnetic complexes exhibit well-resolved lines without the requirement of $^{1}H$ decoupling.[4−6] Nevertheless, this method has not been widely employed because a large number of various selectively $^{2}D$- and/or $^{13}C$-labeled samples are required for signal assignments. Liu et al. reported line narrowing of $^{13}C$ MAS spectra for a nonlabeled sample without decoupling at a moderate spinning frequency ($\nu_R$) of 11 kHz.[6] However, the signals were still subject to considerable line broadening; hence, this approach requires a long-time signal accumulation to ensure sufficient sensitivity even for small molecules. Also, this is effective only for a sample with a large $^{1}H$ shift dispersion. Thus, SSNMR of paramagnetic-metal complexes remains challenging even for low molecular weight species.

In $^{13}C$ SSNMR of paramagnetic complexes, line broadening caused by insufficient $^{1}H$ RF decoupling due to large paramagnetic shifts has been a long-time problem. Also, a large anisotropic paramagnetic shift deteriorates sensitivity by splitting a signal into a number of sidebands under conventional MAS ($\nu_R = 5-10$ kHz). First, to solve these problems, we propose utilizing very fast MAS (VFMAS), in which $\nu_R$ exceeds 20 kHz, instead of $^{1}H$ RF decoupling, which is often not effective for paramagnetic complexes. As already demonstrated for organic compounds,[7] VFMAS removes a large part of $^{1}H-^{13}C$ dipolar couplings as well as $^{1}H-^{1}H$ dipolar couplings even for a nonparamagnetic sample having a small $^{1}H$ spectral distribution. This VFMAS approach also improves sensitivity by suppressing spinning sidebands. Second, we propose using a broadband ramped (or adiabatic) CP sequence to further enhance sensitivity by using a large $^{1}H$ polarization and a short $^{1}H$ $T_1$ in paramagnetic complexes. The problem in employing CP for a paramagnetic sample is the large spectral distribution due to paramagnetic shifts. The use of a VFMAS probe equipped with a small RF coil permits us to apply high-power $^{1}H$ and $^{13}C$ RF fields covering large bandwidths sufficient for many paramagnetic complexes. Adiabatic CP compensates for RF inhomogeneity and permits a variation of CP conditions appropriate for a large dispersion of paramagnetic shifts. Reported $^{1}H$ $T_1$ values in paramagnetic complexes are much shorter than $^{13}C$ $T_1$ values;[6] therefore, with CP we can further enhance sensitivity by increasing repetition rates.

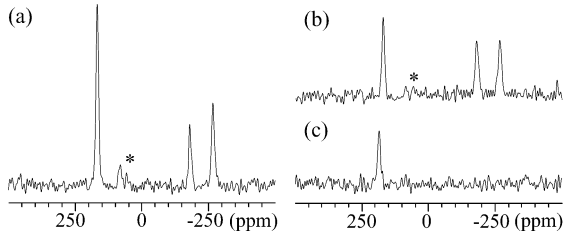


***Figure 1.*** $^{13}C$ MAS spectra of Cu(DL-alanine)$_2$·($H_2O$) obtained at $^{13}C$ NMR frequency of 100.6 MHz with (a) adiabatic CP at $\nu_R = 24$ kHz, (b) one-pulse excitation at $\nu_R = 24$ kHz, and (c) one-pulse excitation at $\nu_R = 5$ kHz, where cw $^{1}H$ decoupling (100 kHz) was applied only in (c). A total of 512 scans was recorded for each spectrum with recycle delays of 0.15 s in (a,b) and 0.3 s in (c). In all of the experiments, a rotor-synchronous spin−echo sequence was used prior to signal acquisition. In the CP experiment, the $^{13}C$ RF field was swept from 93 to 105 kHz during a contact time of 0.5 ms, while the $^{1}H$ RF was kept constant at 75 kHz. The spinning sidebands in (a,b) are indicated by *. The weak peak at 80 ppm in (a) is presumably attributed to impurities. The spectra are displayed on the same scale.

Figure 1 shows the $^{13}C$ MAS spectra of Cu(II)(DL-alanine)$_2$·($H_2O$) (a) with CP at $\nu_R = 24$ kHz, (b) with one-pulse excitation at $\nu_R = 24$ kHz, and (c) with one-pulse excitation at $\nu_R = 5$ kHz, where no decoupling was applied in (a) and (b). It is apparent that VFMAS and CP dramatically enhanced sensitivity as well as resolution for the paramagnetic metal-amino acid complex. In contrast, in Figure 1c, the signals at −180 and −270 ppm are within the noise levels because of line broadening and spectral splitting into many sidebands (also, see the Supporting Information). The sensitivity enhancement factor by CP in (a) is about 1.5−2.3 and 1.1 for protonated and nonprotonated $^{13}C$ spins, respectively. Considering that it took up to a day to obtain similar sensitivity under moderately fast MAS,[6] it is noteworthy that the good sensitivity in (a) was obtained in 1.3 min for only 15 mg of nonlabeled paramagnetic complex. Removal of $^{1}H$ high-power decoupling also helps to increase the maximum repetition rate of signal acquisition, which is often limited by the duty factor of the NMR probe rather than the $T_1$ of $^{1}H$ spins (∼1.5 ms in this case) or that of $^{13}C$ (10−30 ms). It is possible to further increase the repetition rate by up to 20 times using a probe with a smaller coil, which generally tolerates a higher duty factor.

The major challenges in analysis of SSNMR spectra of paramagnetic complexes are in signal assignments. In many cases, large paramagnetic shifts mask diamagnetic shifts specific to chemical groups. To solve this fundamental problem, we propose performing *signal editing* on the basis of $^{13}C-^{1}H$ dipolar recoupling techniques under VFMAS. Removal of $^{1}H-^{13}C$ and $^{1}H-^{1}H$ dipolar couplings by VFMAS enables us to employ recoupling methods, which form a basis of modern SSNMR, yet have not been applied to


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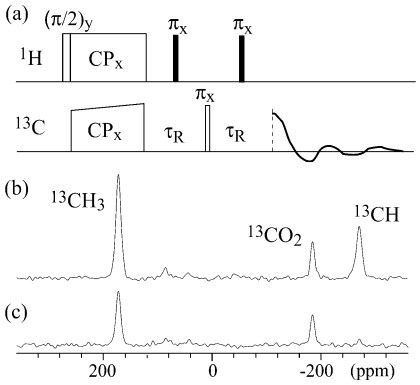


***Figure 2.*** (a) A pulse sequence for $^{13}C-^{1}H$ dipolar filter signal editing, where $\tau_R$ denotes one rotation cycle. Dipolar dephasing is introduced when the $^{1}H$ $\pi$-pulses (filled boxes) are applied. $^{13}C$ CPMAS spectra of Cu(DL-alanine)$_2$·($H_2O$) obtained at $\nu_R = 22\,989 \pm 3$ Hz without (b) and with (c) $^{13}C-^{1}H$ dipolar dephasing. $^{1}H$ and $^{13}C$ $\pi$-pulse widths are 5 $\mu$s.

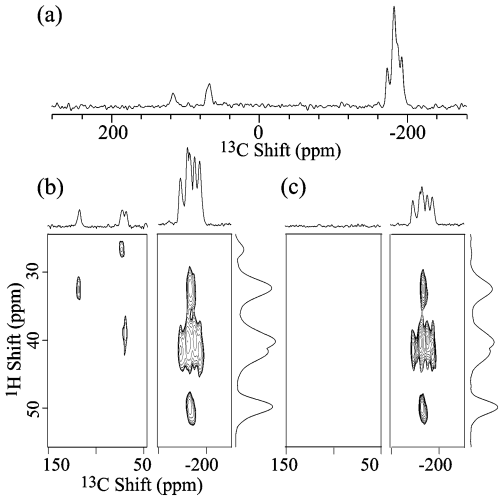


***Figure 3.*** (a) 1D $^{13}C$ CPMAS and (b,c) 2D $^{13}C/^{1}H$ correlation NMR spectra of V(acac)$_3$ obtained at $\nu_R = 22\,989 \pm 2$ Hz together with projections in (b,c). In (c), a $^{13}C-^{1}H$ dipolar dephasing filter was applied. For (b,c), the $t_1$ period was inserted between the $^{1}H$ $\pi/2$-pulse and the CP period in Figure 2 (a), without (b) and with (c) $^{1}H$ $\pi$-pulses (see the Supporting Information about the pulse sequence). The sample quantity was 15 mg. The experimental time was (a) 2 min and (b,c) 2.1 h.

paramagnetic complexes because the large paramagnetic shifts cause difficulty in $^{1}H$ and $^{1}H-^{1}H$ decoupling. Figure 2a shows a pulse sequence for $^{13}C$ signal editing using a $^{13}C-^{1}H$ REDOR-type recoupling sequence.[8] When two $\pi$-pulses (filled boxes) are applied to $^{1}H$ spins in Figure 2a, $^{13}C-^{1}H$ dipolar dephasing of $^{13}C$ signals is induced by the restored $^{13}C-^{1}H$ dipolar couplings; on the other hand, no dephasing is induced without the $\pi$-pulses. The dephasing depends on spin topology reflecting the type of chemical groups. In a control experiment on L-valine, dephasing ratios $S/S_0$ of 90, 47, and 8% were obtained for $CO_2^-$, $CH_3$, and CH groups, respectively, where $S$ and $S_0$ denote the signal intensities obtained with and without the $^{1}H$ $\pi$-pulses, respectively. Little dephasing is induced for nonprotonated $CO_2^-$. The dephasing for $CH_3$ groups is smaller than that for CH groups due to motional averaging caused by fast rotation of the $CH_3$ groups along the symmetry axis. Figure 2b,c shows the $^{13}C$ CPMAS spectrum for Cu(alanine)$_2$·($H_2O$) without (b) and with (c) $^{13}C-^{1}H$ dephasing on the same scale. $S/S_0 = 52$, 83, and 12% for the signals at 173, $-183$, and $-269$ ppm, respectively. The signal assignments based on this result are indicated in the figure. These assignments agree with those by Liu et al. on the basis of selective $^{2}D$- and $^{13}C$-labeling.[6] In contrast to the selective labeling approach, our approach can provide reliable assignments for a small quantity of *nonlabeled* sample. Although our numerical simulation indicated that distinction of CH and $CH_2$ groups by the present sequence is difficult, there are recent examples of the sequences designed for this purpose.[9]

Because of the sensitivity limitation, applications of 2D SSNMR of paramagnetic organometal complexes in rigid solids have been long limited to labeled materials even for small molecules.[5] However, on the basis of the superior sensitivity in the above experiments, we propose performing 2D $^{13}C/^{1}H$ correlation NMR for nonlabeled paramagnetic complexes. A pulse sequence for the proposed experiments is shown in the Supporting Information. Because VFMAS largely averages out strong $^{1}H-^{1}H$ dipolar couplings as well as $^{1}H-^{13}C$ dipolar couplings, it enables high-resolution $^{1}H$ SSNMR without $^{1}H-^{1}H$ homonuclear RF decoupling. Figure 3a and b shows 1D $^{13}C$ CPMAS and 2D $^{13}C/^{1}H$ correlation NMR spectra of V(III)(acac)$_3$ (acac = $CH_3-CO-CH-CO-CH_3$), respectively. In (b), six lines and three lines, which are overlapping in (a), are resolved around $^{13}C$ shifts of $-180$ and 100 ppm. Figure 3c shows the 2D spectrum obtained with $^{13}C-^{1}H$ dipolar dephasing. The six lines were reduced to ~50%, while the three lines were dephased to ~0%.

This clearly demonstrates that the three lines and the six lines are assigned to CH and $CH_3$ groups, respectively. It is most likely that three acac molecules coordinating to $V(III)^{3+}$ have the six $CH_3$ groups and the three CH groups all in magnetically *nonequivalent* environments, and signals for CO are broadened out by strong hyperfine couplings (they were also missing in a one-pulse experiment). This agrees with the results of a recent high-resolution X-ray diffraction study,[10] which revealed nonequivalence of the three acac molecules. This experiment also provides assignments of $^{1}H$ signals, which are not resolved in a 1D $^{1}H$ MAS spectrum. To the best of our knowledge, this is the first 2D correlation NMR experiment involving detection of dilute spins (i.e., $^{13}C$) in nonlabeled paramagnetic complexes in rigid solids. Considering the natural abundance of $^{13}C$ (~1%), it is possible to apply similar 2D techniques to selectively $^{13}C$-labeled biomacromolecules such as ~300-residue paramagnetic metal proteins.

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**Supporting Information Available:** Further details of the experiments and supplemental data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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