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Supporting Information for: Rapid Acquisition of Wideline MAS Solid-state NMR

Spectra with Fast MAS, Indirect Proton Detection, and Dipolar HMQC Pulse Sequences

Aaron J. Rossini,<sup>1,2</sup>\* Michael P. Hanrahan<sup>1,2</sup> and Martin Thuo<sup>2,3</sup>

<sup>1</sup>Iowa State University, Department of Chemistry, Ames, IA, USA 50011

<sup>2</sup>US DOE Ames Laboratory, Ames, Iowa, USA, 50011

<sup>3</sup>*Iowa State University, Materials Science and Engineering Department, Ames, IA, USA 50011* 



**Figure S1**. (A) 2D <sup>1</sup>H-<sup>195</sup>Pt D-HMQC correlation spectrum of cisplatin (Alfa Aesar) acquired with an MAS frequency of 40 kHz, 32 scans per increment, a 0.8 s recycle delay, m = 27 ( $2m^*\tau_r = 1.35$  ms), n = 6 ( $n^*\tau_r = 150$  µs), 514 individual  $t_1$  increments and  $t_1$  was incremented in steps of 1.0 µs (1.00 MHz indirect dimension spectral width).  $\theta$  pulses 0.6 µs in duration with a 278 kHz rf field (60° tip angle) were used. The total experiment time was 3.65 hours. (B) Comparison of the indirectly detected <sup>195</sup>Pt wideline MAS sideband manifolds obtained from 2D D-HMQC correlation spectra acquired with 40 and 50 kHz MAS. The isotropic chemical shift of –1834 ppm is indicated.



**Figure S2**. 2D <sup>1</sup>H-<sup>195</sup>Pt constant echo time D-HMQC correlation experiment on cisplatin (Alfa Aesar) with a 50 kHz MAS frequency. The directly observed <sup>1</sup>H dimension was Fourier transformed and the resulting real component of the indirectly detected <sup>195</sup>Pt free induction decay (FID) is shown. Rotary echoes are clearly visible and separated by the rotor period of 20  $\mu$ s. The indirect dimension *t*<sub>1</sub>-increment was 0.8  $\mu$ s (1.25 MHz indirect dimension spectral width). Fourier transformation of the indirect dimension results in the 2D spectrum shown in Figure 2B of the main text.



Figure S3. Numerical simulations (SIMPSON) of 50 kHz MAS <sup>1</sup>H-<sup>195</sup>Pt D-HMQC experiments for an isolated  ${}^{1}\text{H}-{}^{195}\text{Pt}$  spin pair with a dipolar coupling of -2000 Hz. (A) Simulation of the normalized efficiency of <sup>1</sup>H-<sup>195</sup>Pt D-HMQC experiment as a function of transmitter offset for several different <sup>195</sup>Pt excitation/reconversion pulses with different length/tip angle. The <sup>195</sup>Pt rf field was 278 kHz in all cases. An isotropic <sup>195</sup>Pt resonance  $(\Omega = 0 \text{ ppm})$  was used in these simulations. (B) Numerical simulation of the efficiency of <sup>1</sup>H-<sup>195</sup>Pt D-HMQC experiments as a function of the pulse length/tip angle for <sup>195</sup>Pt sites with different anisotropic chemical shifts ( $\Omega = 8885$  ppm,  $\Omega = 3750$  ppm, and  $\Omega = 375$ ppm). Axial tensor asymmetry was assumed ( $\kappa = -1.00$  or  $\eta_{CSA} = 0.00$ ). For simulations with  $\Omega = 8885$  ppm and  $\Omega = 3750$  ppm, the <sup>195</sup>Pt isotropic chemical shift was set to – 1200 ppm so that the <sup>195</sup>Pt pules were applied at approximately the center of the shielding patterns. (C) Comparison of experimental and simulated <sup>1</sup>H-<sup>195</sup>Pt D-HMQC spectra as a function of the <sup>195</sup>Pt pulse length. The experiments and simulations used <sup>195</sup>Pt pulses with a 278 kHz rf field. The simulation curve was taken from (B) and the experiment was performed on the sample of transplatin from Sigma Aldrich. Each experimental point was acquired with 16 scans and an 8 s recycle delay. (D) Comparison of the experimental <sup>195</sup>Pt sideband manifold obtained from the 2D<sup>1</sup>H-<sup>195</sup>Pt D-HMQC spectrum of cisplatin (Figure 2, main text) and simulated sideband manifolds calculated in SIMPSON. The red trace is <sup>195</sup>Pt NMR spectrum calculated for the indirect dimension of a <sup>1</sup>H-<sup>195</sup>Pt D-HMQC spectrum and the green trace is the <sup>195</sup>Pt NMR spectrum calculated from a 60° pulseacquire experiment.



Figure S4. (A) 2D <sup>1</sup>H-<sup>195</sup>Pt D-HMQC correlation spectrum of cisplatin (Sigma Aldrich) acquired with an MAS frequency of 50 kHz, 32 scans per increment, a 0.5 s recycle delay,  $m = 27 (2m^*\tau_r)$ 1.08 ms), n = 6 ( $n \star \tau_r = 120 \mu s$ ), 512 individual  $t_1$  increments and  $t_1$  was incremented in steps of 0.8 μs (1.25 MHz indirect dimension spectral width). θ pulses 0.6 μs in duration with a 278 kHz rf field (60° tip angle) were used. The total experiment time was 2.3 hours. (B) Comparison of the positive projections of the indirectly detected <sup>195</sup>Pt wideline MAS sideband manifolds obtained from the samples of cisplatin obtained from Sigma Aldrich and Alfa Aesar. Asterisks denote additional peaks arising from an unidentified secondary phase/impurity. (C) 2D <sup>1</sup>H-<sup>195</sup>Pt D-HMQC correlation spectrum of transplatin (Sigma Aldrich) acquired with an MAS frequency of 50 kHz, 32 scans per increment, a 4.0 s recycle delay,  $m = 24 (2m^*\tau_r = 0.96 \text{ ms}), n = 6 (n^*\tau_r = 0.96 \text{ ms})$ 120 µs), 360 individual  $t_1$  increments and  $t_1$  was incremented in steps of 0.8 µs. The total experiment time was 12.8 hours. (D) Comparison of the positive projections of the indirectly detected <sup>195</sup>Pt wideline MAS sideband manifolds obtained from the samples of transplatin obtained from Sigma Aldrich and Alfa Aesar. An intense <sup>195</sup>Pt isotropic NMR signal is observe at -430 ppm in the Sigma Aldrich sample. This signal must correspond to an octahedral Pt(IV) site since its chemical shift is close to 0 ppm and it possess a small CSA. Note that the sideband manifold which should correspond to transplatin in the Sigma Aldrich sample has a significantly different isotropic chemical shift. This could occur because a different phase of transplatin is present. Secondary and tertiary sideband manifolds are also observed in this sample.

0 0	
NMR	<sup>71</sup> Ga
Parameter <sup>a</sup>	
$\delta_{iso}$ (ppm)	-15(20)
$C_0$ (MHz)	16.9(3) / 26.9(3)
ηο	0.14(5)
$\Omega$ (ppm) <sup>b</sup>	340
κ	0.53
α (°)	-10
β (°)	25
γ(°)	30
<i>a</i>	

**Table S1.** Chemical shift (CS) and electric field gradient (EFG) tensor parameters obtained from simulations of <sup>71</sup>Ga static and MAS solid-state NMR spectra of **1**.

<sup>a</sup>The CS tensor is defined by three principal components ordered such that  $\delta_{11} \ge \delta_{22} \ge \delta_{33}$ ,  $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$ ,  $\Omega = \delta_{11} - \delta_{33}$  and  $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$ . The EFG tensor is described by three principal components ordered such that  $|V_{11}| \le |V_{22}| \le |V_{33}|$ ,  $C_Q = eQV_{33}/h$  and  $\eta_Q = (V_{22} - V_{11})/V_{33}$ . The Euler angles describe the relative orientations of the EFG and CS tensors. Uncertainties in experimental parameters are indicated in parentheses. <sup>b</sup>The uncertainties associated with the CS and EFG tensor parameters and Euler angles are very large (±50%) and are included as adjustable parameters to improve the quality of the simulations. Acquisition of data at multiple magnetic fields could improve the uncertainties associated with these parameters.