

**SUPPORTING INFORMATION**

**Title:** The Added Value of Solid-State Pb NMR Spectroscopy to Understand the 3D Structures of Pb Amino Acid Complexes

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## Fit of the chemical shift anisotropy parameters for $[\text{Pb}(\text{Hile})_2(\text{NO}_3)(\text{H}_2\text{O})_2]\text{NO}_3$ , **1**

The chemical shift anisotropy parameters of compound **1** have been fitted with an iterative SIMPSON/MINUIT procedure that takes into account the pulse strength of  $\sim 75$  kHz and the phase cycling that was used in the NMR experiment. The fitting procedure is described on page S5 of this Supporting Information. The results for compound **1** are shown below:

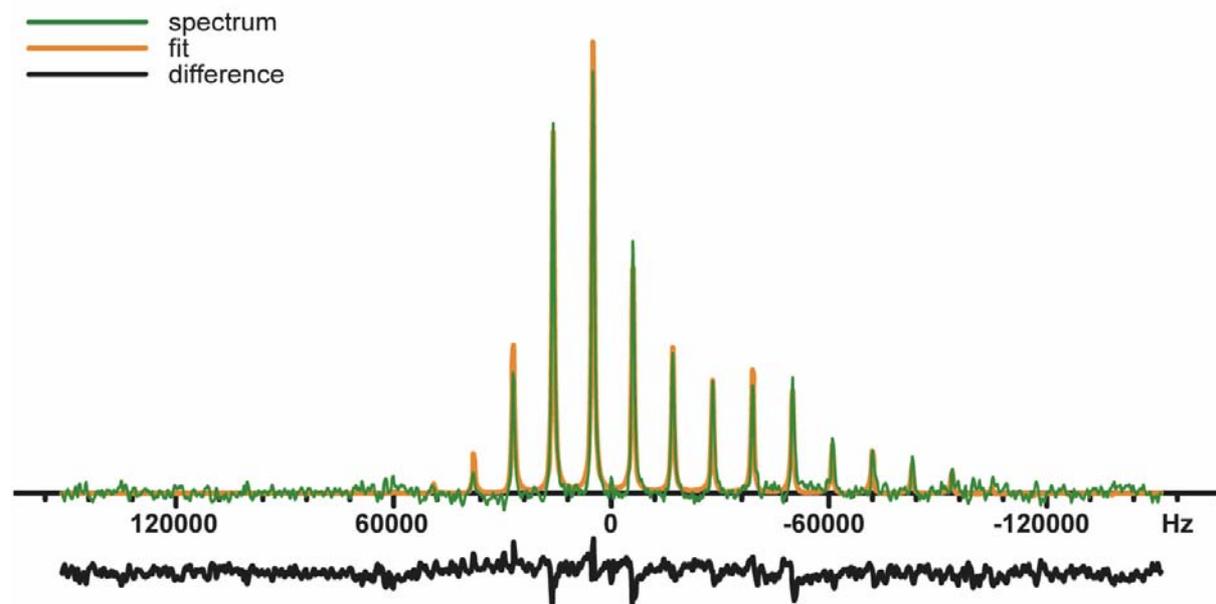


Figure S1 Graphical representation of the result of the iterative fitting of the solid-state NMR spectrum of compound **1** with SIMPSON/MINUIT. The input (green) and the fit (orange) are superimposed, the difference (black) is shown under the axis. The origin represents the frequency offset of the NMR experiment. The isotropic value of theoretical spectrum was initially set to around -28000 Hz to be in agreement with the determined isotopic shift. The final normalized root-mean-square deviation was 8.2

Table S1 Result of the iterative fitting of the NMR spectrum of compound **1** with a theoretical spectrum using SIMPSON/MINUIT. The error values were calculated with the HESSE function available in MINUIT.

Parameter	Value	Error
Isotropic chemical shift ( $\delta_i$ )	-1774 <sup>a</sup>	36
Anisotropy ( $\delta_{\text{aniso}}$ )	-1220	32
Asymmetry ( $\eta_{\text{aniso}}$ )	0.17	0.09
Line width	782	92

<sup>a</sup> This is the value from the NMR experiment

## Estimation of the chemical shift anisotropy parameters for [Pb(lev)(NO<sub>3</sub>)] , 2

The fitting of the chemical shift anisotropy parameters of compound **2** with the SIMPSON/MINUIT procedure has resulted in an unrealistic overestimation of the anisotropy and multiple solution for the asymmetry. The anisotropy parameters are therefore estimated from spectra recorded with different irradiation frequencies. From the spectra below it was estimated that the chemical shift envelope extends 8 spinning side bands to the downfield edge and 14 to the upfield edge for both resonances. This results in the estimated values that are reported in the paper and indicated in Table S2.

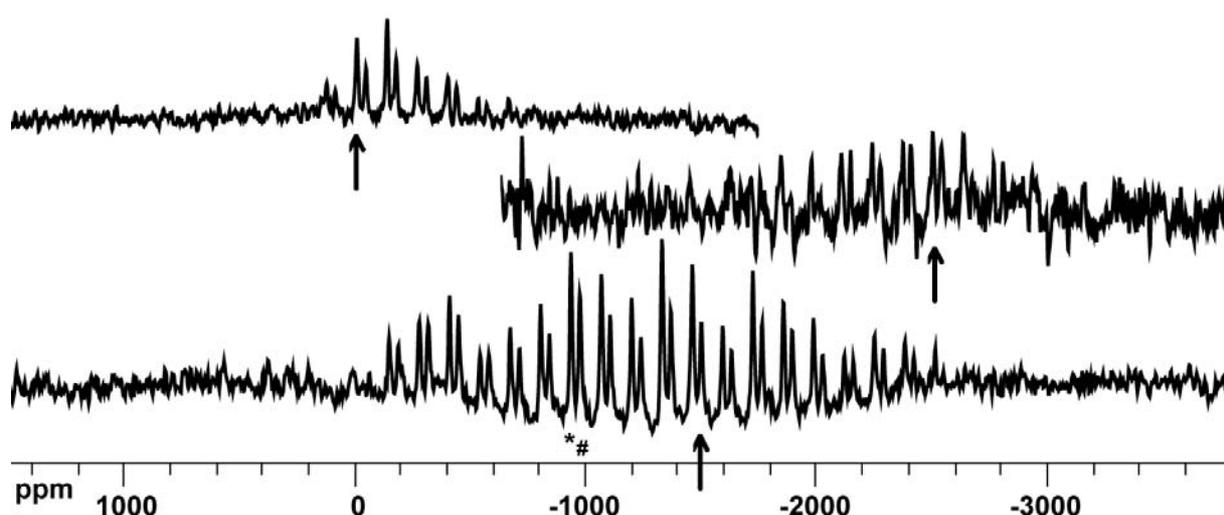


Figure S2 Solid-state spectra of compound **2** at different irradiation frequencies to estimate the upfield and downfield edge of the chemical shift envelope. The arrows indicate the respective irradiation frequencies at -1500 ppm (bottom), -2500 ppm (middle) and 0 ppm (top). The \* and # indicate the isotropic chemical shifts. All spectra were recorded with 75 kHz pulse strength and processed using 500 Hz exponential broadening. The spectra were recorded by adding 20000, 1500 and 1500 transients, respectively.

Table S2 Estimated values for upfield and downfield edges for the resonances of compound **2**

	$\delta_i$	$n^{\text{th}}$ side band at downfield edge	$m^{\text{th}}$ side band at upfield edge	$\delta_{11}$ (= $\delta_i + n \cdot \omega_r$ ) <sup>a</sup>	$\delta_{33}$ (= $\delta_i - m \cdot \omega_r$ )
site 1	* -929	8	14	121 ppm (-929 + 8 • 11 kHz)	-2773 ppm (-929 - 14 • 11 kHz)
site 2	# -969	8	14	84 ppm (-969 + 8 • 11 kHz)	-2814 ppm (-969 - 14 • 11 kHz)

<sup>a</sup>  $\omega_r$  is the spin rate of the experiment

## Fit of the chemical shift anisotropy parameters for $[\text{Pb}(\text{Hasp})(\text{NO}_3)]$ , **3**

The chemical shift anisotropy parameters of compound **3** have been fitted with an iterative SIMPSON/MINUIT procedure identical to compound **1** (see page S2)

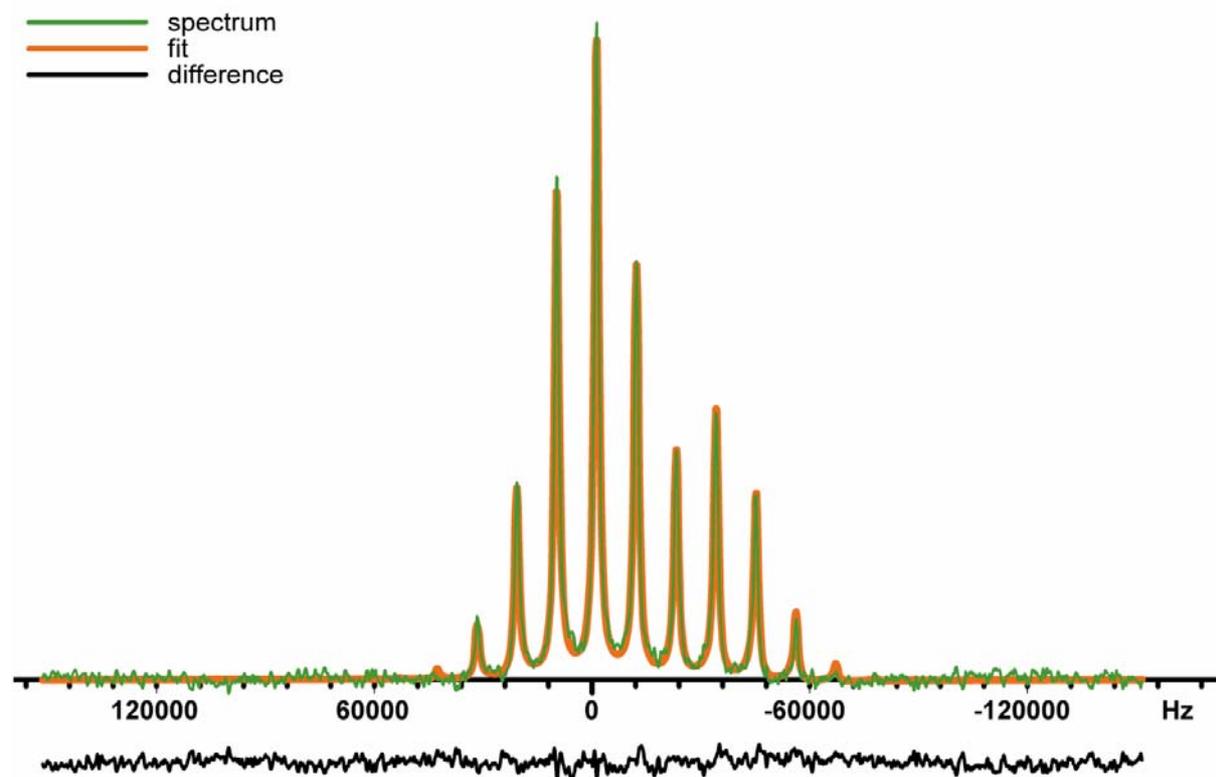


Figure S3 Graphical representation of the result of the fitting of the solid-state NMR spectrum of compound **3** with SIMPSON/MINUIT. The input (green) and the fit (orange) are superimposed, the difference (black) is shown under the axis. The origin represents the frequency offset of the NMR experiment, while the isotropic value of fit was initially set to around -12200 Hz to be in agreement with the determined isotopic shift. The final normalized root-mean-square deviation was 1.0

Table S3 Result of the iterative fitting of the NMR spectrum of compound **3** with a theoretical spectrum using SIMPSON/MINUIT. The error values were calculated with the HESSE function in MINUIT.

Parameter	Value	Error
Isotropic shift ( $\delta_i$ )	-2439 <sup>a</sup>	69
Anisotropy ( $\delta_{\text{aniso}}$ )	-606	31
Asymmetry ( $\eta_{\text{aniso}}$ )	0.55	0.18
Line width	1526	210

<sup>a</sup> This is the value from the NMR experiment

## SIMPSON input file

The SIMPSON Tcl-script below is representative for the iterative fitting procedure for the NMR spectra of compound **1** and **3** taking into account the pulse length and phase cycling. The script contains a procedure 'spectrum' that is introduced to apply the phase cycling. The initial magnetization is set along the z-axis with the variable 'rf' to reflect the finite pulse length used in the NMR experiment. The Tcl-script that was used to fit compound **3** is shown:

```

# Hahn-echo pulse program with phase
# cycling

spinsys {
  channels 207Pb
  nuclei 207Pb
  shift 1 -12280.1 -606p 0.55 0 0 0
}

par {
  proton_frequency 399681918
  spin_rate 11000
  gamma_angles 50
  sw 303030
  np 2048
  crystal_file repl100
  start_operator Ilz
  detect_operator Ilp
  variable rf73964
  verbose 1
}

proc pulseseq {} {
  global par

  set t90 [expr 0.25e6/$par(rf)]
  set t180 [expr 0.5e6/$par(rf)]
  set d6 [expr 1e6/$par(spin_rate) \
    -0.5*$t90-0.5*$t180]
  set d7 [expr 1e6/$par(spin_rate) \
    -0.5*$t180]
  maxdt [expr $t90/16]

  pulse $t90 $par(rf) \
    [lindex {x y -x -y} $par(ph)]
  delay $d6
  pulse $t180 $par(rf) \
    [lindex {x x x x} $par(ph)]
  delay $d7

  for {set i 1} {$i <= $par(np)} \
    {incr i} {
    acq [lindex {x -y -x y} $par(ph)]
    delay [expr 1e6/$par(sw)]
  }
}

proc spectrum {piso pcsa peta plb} {
  global par

  for {set par(ph) 0} {$par(ph) <4}\
    {incr par(ph)} {
    set f [fsimpson [list \
      [list shift_1_iso $piso] \
      [list shift_1_aniso $pcsa] \
      [list shift_1_eta $peta] \
    ]]
    if [info exist g] {
      fadd $g $f
      funload $f
    } else {
      set g [fdup $f]
    }
  }
  faddlb $g $plb 0
  fft $g
  return $g
}

proc minuit {} {
  global mn h par

  set s [spectrum $mn(iso) $mn(csa)p $mn(eta) $mn(lb)]
  fphase $s -rp 90
  fautoscale $s $h \
    -re {{-90000 70000}}
  set rms [frms $s $h \
    -re {{-90000 70000}}]
  funload $s
  return $rms
}

```

```
}  
proc main {} {  
  global mn h par  
  
  set h [fload "NMR SPECTRUM.spe"]  
  mnlog $par(name).minuit.log  
# mnpars name val step [min max]  
  mnpars iso -12280.1 1 -12500 -12000  
  mnpars csa -606 1  
  mnpars eta 0.55 0.01 0.35 0.59  
  mnpars lb 1526 10 1500 2500  
  
  mnminimize  
  mnhesse  
  
  set s [spectrum $mn(iso) $mn(csa)p \  
        $mn(eta) $mn(lb)]  
  fphase $s -rp 90  
  fautoscale $s $h -re  
  fsave $s $par(name).final.spe  
  fsub $s $h  
  fsave $s $par(name).diff.spe  
  funload $s  
}
```