NMR Studies of solid Pentachlorophenol-4-Methylpyridine Complexes exhibiting strong OHN Hydrogen Bonds: Geometric H/D Isotope Effects and Hydrogen Bond Coupling cause Isotopic Polymorphism

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Supporting Information

Synthesis of 2-Ethoxy-4-methyl-3,4-dihydro-2H-pyran (2)

1 mol of Crotonaldehyde and 1.16 mol of ethylvinylether were mixed together in a bomb in the presence of 1% Hydroquinone and heated for 15 hr at 175°C. The reaction mixture was separated by fractional distillation under normal pressure. The first fraction was ethylvinylether (38-40°C), the second fraction was a mixture of ethylvinylether and crotonaldehyde (42-58°C). The rest of the aldehyde was removed at 103°C. The pyran **2** was distilled off at 110°C at 172 mbar.

Synthesis of ^{15}N isotopic labeled 4-methylpyridine (1)

A 1-L three-neck flask equipped with a reflux condenser, addition funnel and magnetic stirrer was charged with 100 ml water and 250 ml EtOH, concentrated sulfuric acid (10 ml), methylene blue (33 g, 0.09 mol), and ^{15}N ammonium chloride (5 g, 0.09 mol). The solution was brought to a gentle reflux, and a solution of 2-ethoxy-4-methly-3,4-dihydro-2H-pyran **2** (11.5 g, 0.09 mol) in ethanol (11 ml) was added dropwise over a period of 1/2 hr. After addition of the acetal, the mixture was refluxed gently overnight. After cooling, the reflux condenser and addition funnel were replaced with a distilling head, condenser and receiver. Additional water (100 ml) was added, and about 200 ml of 3-methylglutaraldehyde was distillated off. The reaction mixture was allowed to cool and made basic by the gradual addition of 50% sodium hydroxide solution (50 ml) and then distilled until about 200 ml of the distillate was collected. The distillate was extracted a few times with CH_2Cl_2. The CH_2Cl_2 / pyridine mixture was separated by distillation with a vigreux column. CH_2Cl_2 was distillated off and the rest was 4-methylpyridine (**1**).

Tables

Table S1. Relative deuterium fraction x_D of 4-MPPCP samples

	Sample **d**	Sample **c**	Sample **b**	Sample **j**
Absolute intensity	74000	46000	4800	33800
Relative x_D	0.7	0.45	0.05	0.35

The ^{2}H MAS NMR spectra were measured at 92.10 MHz at room temperature; 1000 kHz spectral width, 1.5 s repetition time, 2048 scans, 18 kHz rotation frequency.

Table S2. Temperature calibration *via* ^{15}N CPMAS NMR of 95% enriched TTAA (1,8-dihydro-5,7,12,14-tetramethyldibenzo(b,i)-$^{15}N_4$-(1,4,8,11)- tetraazacyclotetra-deca-4,6,11,13- tetraene) at 60.6 MHz (Figure S8).

T/K[a]	δ_b/ppm[b]	δ_c/ppm[b]	δ_d/ppm[b]	δ_a/ppm[b]	T/K[c]
303	206.5	184.6	140.2	120.9	302

293	207.4	185.9	138.4	120.4	297
273	209.9	190.2	134.3	117.6	277
248	213.4	195.8	128.5	113.9	253
223	217.3	202	121.9	110	228

[a]Spectrometer temperature settings. Measured values.[b] Measured ^{15}N chemical shift values of lines a to d (see Figure S6 below) of TTAA. Corrected temperatures calculated from the chemical shift separations.[c]Corrected sample temperatures calculated from the ^{15}N chemical shifts according to eq 9 and eq 10 in Ref. [1].

Table S3. ^{15}N NMR chemical shift reference standards.

	δ ^{15}N vs. nitromethane /ppm	Ref.	δ^{15}N vs. NH_4Cl(solid) /ppm
Nitromethane	0	(2)	+341.168 ± 0.011
Sat. $^{15}NH_4Cl$ in H_2O 5.64M	-352.89 ± 0.17	(3)	-11.72 ± 0.18
Solid $^{15}NH_4Cl$	-341.168 ± 0.011	(2)	0
Glycine 10% ^{15}N-^{13}C		(2)	-6.37 ± 0.05
$^{15}NH_4Cl$ 2.9 mM in 1 M HCl at 25 °C	-358.1	(4)	16.9
liquid NH_3	-381.7	(4)	

Table S4. Acquisition parameters used to obtain the NMR spectra of pentachlorophenol-4-methylpyridine complexes in this work.

		temperature	nucleus	recycle delay/s	number of scans	experiment	pulse durations
Figure 3	a	160 K	^{1}H	1.5s	4	90° pulses	7 µs
		140 K	^{1}H	1.5s	4	90° pulses	7 µs
		130 K	^{1}H	1.5s	4	90° pulses	7 µs
	b	130 K	^{15}N	2s	128	90° pulses	7 µs
Figure 4	a	297 K	^{1}H	60s	4	90° pulses	2 µs
			^{2}H	5s	10240	90° pulses	2 µs
		277 K	^{1}H	60s	16	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		253 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		228 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
	b	297 K	^{15}N	300s	24	90° pulses	3.5 µs
		277 K	^{15}N	300s	24	90° pulses	3.5 µs
		253 K	^{15}N	300s	24	90° pulses	3.5 µs
		228 K	^{15}N	300s	24	90° pulses	3.5 µs
Figure 5	a	297 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs

		277 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		253 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		228 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
	b	297 K	^{15}N	300s	24	90° pulses	3.5 µs
		277 K	^{15}N	300s	24	90° pulses	3.5 µs
		253 K	^{15}N	300s	24	90° pulses	3.5 µs
		228 K	^{15}N	300s	24	90° pulses	3.5 µs
Figure 6	a	297 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		277 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		253 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		228 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
	b	297 K	^{15}N	300s	24	90° pulses	3.5 µs
		277 K	^{15}N	300s	24	90° pulses	3.5 µs
		253 K	^{15}N	300s	24	90° pulses	3.5 µs
		228 K	^{15}N	300s	24	90° pulses	3.5 µs
Figure 7	a	297 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		277 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		253 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
		228 K	^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	10240	90° pulses	2 µs
	b	297 K	^{15}N	300s	24	90° pulses	3.5 µs
		277 K	^{15}N	300s	24	90° pulses	3.5 µs
		253 K	^{15}N	300s	24	90° pulses	3.5 µs
		228 K	^{15}N	300s	24	90° pulses	3.5 µs
Figure 10	a		^{1}H	60s	4	90° pulses	3.6 µs
	b		^{15}N	5s	10240	{^{1}H} CP	5.5 µs
	c		^{1}H	60s	4	90° pulses	3.6 µs
			^{2}H	5s	20480	90° pulses	2 µs
	d		^{15}N	5s	10240	{^{1}H} CP	2.5 µs
	e		^{1}H	60s	4	90° pulses	3.6 µs
	f		^{15}N	5s	10240	{^{1}H} CP	5.5 µs
	g		^{1}H	60s	4	90° pulses	3.6 µs
Figure S1	a		^{1}H	2s	16	90° pulses	5 µs
Figure S2	b		^{1}H	2s	8	90° pulses	5 µs
Figure S3	c		^{1}H	60s	4	90° pulses	3.6 µs

Figure S4		323 K	^{1}H	60s	4	90° pulses	3.6 µs
		297 K	^{1}H	60s	4	90° pulses	3.6 µs
		277 K	^{1}H	60s	4	90° pulses	3.6 µs
		253 K	^{1}H	60s	4	90° pulses	3.6 µs
		228 K	^{1}H	60s	4	90° pulses	3.6 µs
		temperature	nucleus	recycle delay/s	number of scans	experiment	pulse durations

CP: cross polarization from ^{1}H. {^{1}H}: ^{1}H decoupling.

Figures

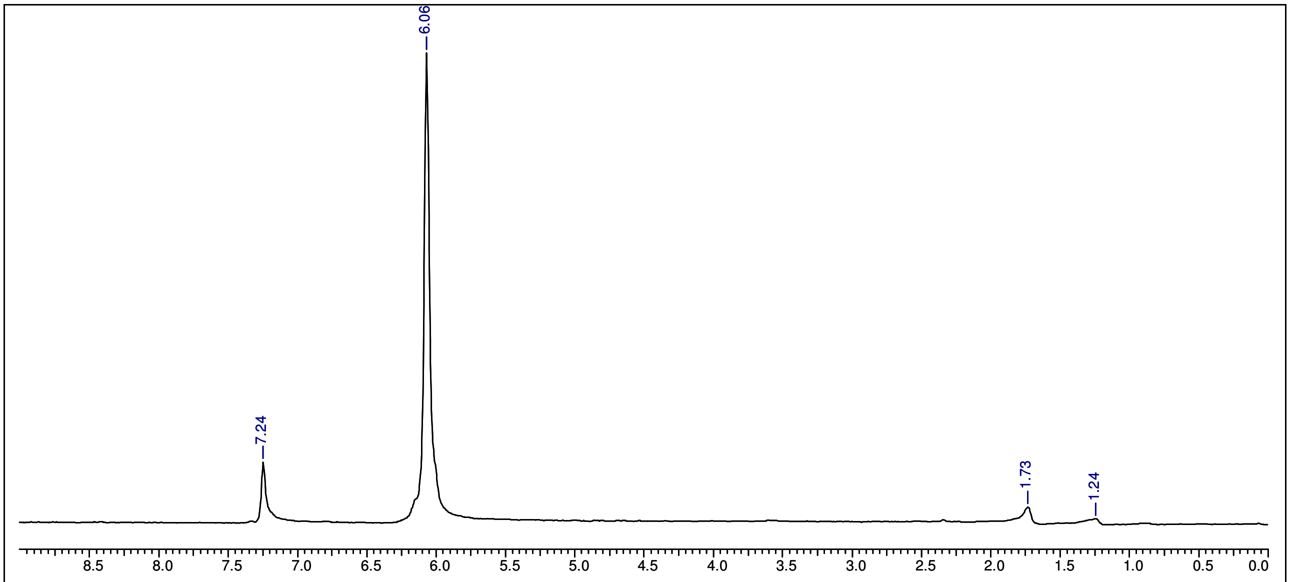

Figure S1. Liquid state ^1H NMR spectra (500 MHz) of pentachlorophenol in $CDCl_3$.

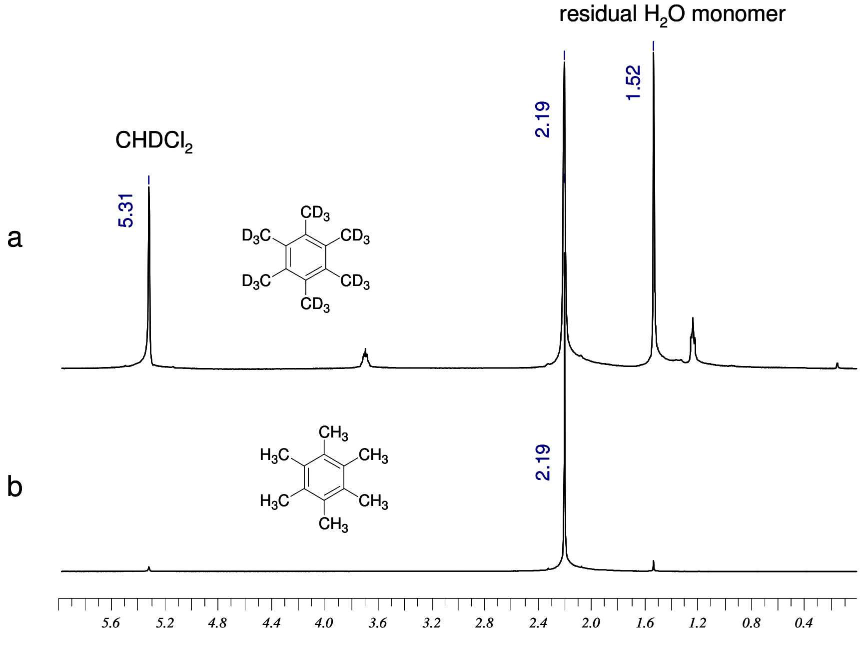

Figure S2. Liquid state ^1H NMR spectra (500 MHz) of **(a)** HMB-d_{18} and **(b)** HMB in CD_2Cl_2. The peak at 1.52 ppm arises from residual water monomer.[5]

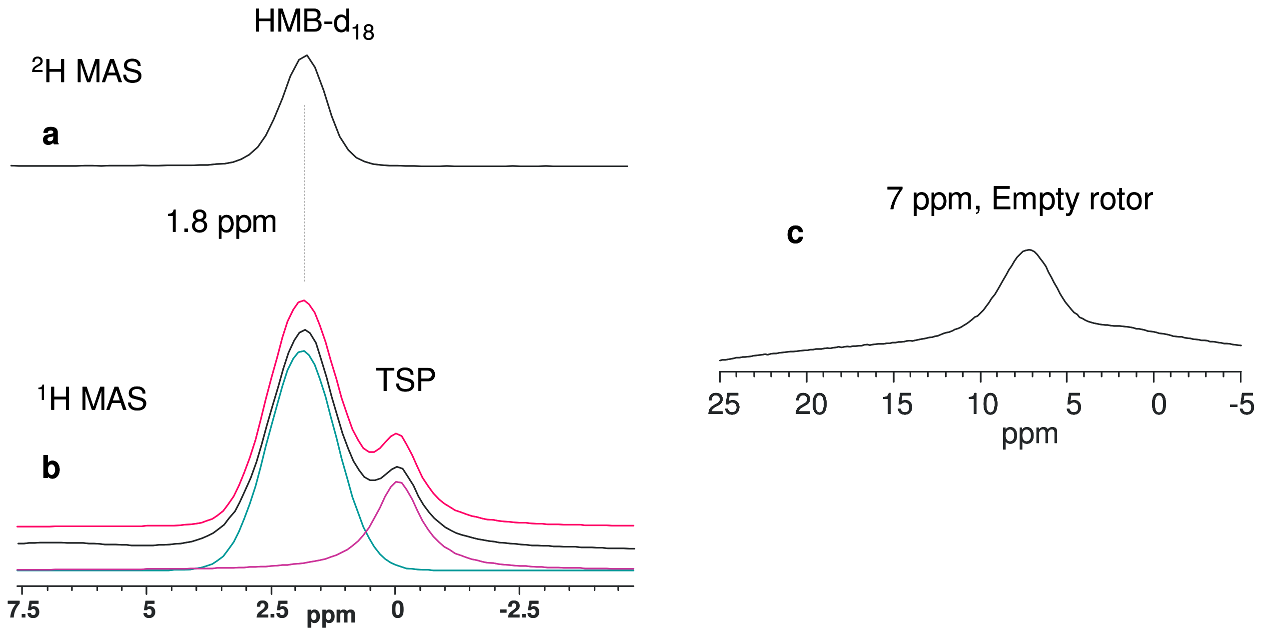

Figure S3. (a) ^{2}H MAS solid state NMR spectra of hexamethylbenzene-d_{18} (92.10 MHz, 16 kHz spinning speed). **(b)** ^{1}H MAS solid state NMR spectra of hexamethylbenzene mixed with solid 3-(trimethylsilyl)propionic acid sodium salt (TSP, $Si(CH_3)_3$-CD_2-CD_2-COO^-Na^+) (599.97 MHz, 16 kHz spinning speed) relative to TSP. **(c)** ^{1}H MAS signal of an empty rotor (599.97 MHz, 16 kHz spinning speed).

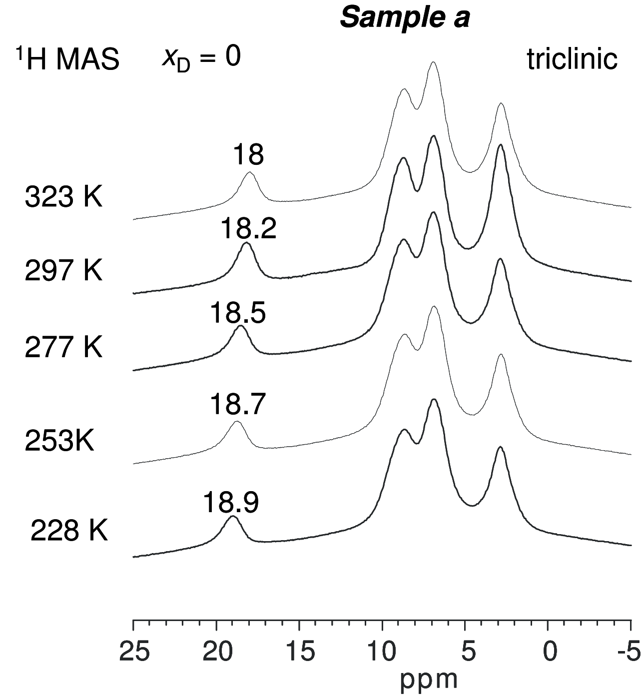

Figure S4. Variable temperature solid state (a) ^{1}H (599.97 MHz, 16 kHz spinning speed) of sample **a**, the 1:1 triclinic 4-MPPCP-*h*, obtained from recrystalization of 1:1 equivalent of 4-methylpyridine and pentachlorophenol in acetonitrile (Procedure A).

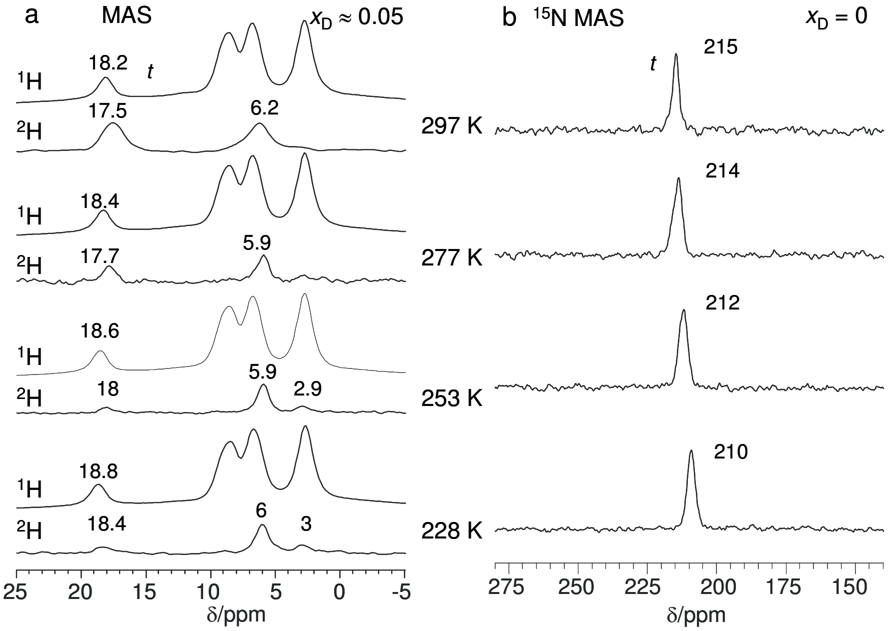

Figure S5. Temperature-dependent solid state MAS NMR spectra of triclinic (*t*) 4-MPPCP. (a) One-pulse ^{1}H and ^{2}H MAS NMR spectra (2.5 mm rotors, 16 kHz spinning speed) of Sample **b** (4-MPPCP -$d_{0.05}$) exhibiting a deuterium fraction of $x_D = 0.05$. (b) 90° pulse ^{15}N MAS NMR spectra (2.5 mm rotors, 18 kHz spinning speed) of Sample **a** (4-MPPCP, $x_D = 0$).

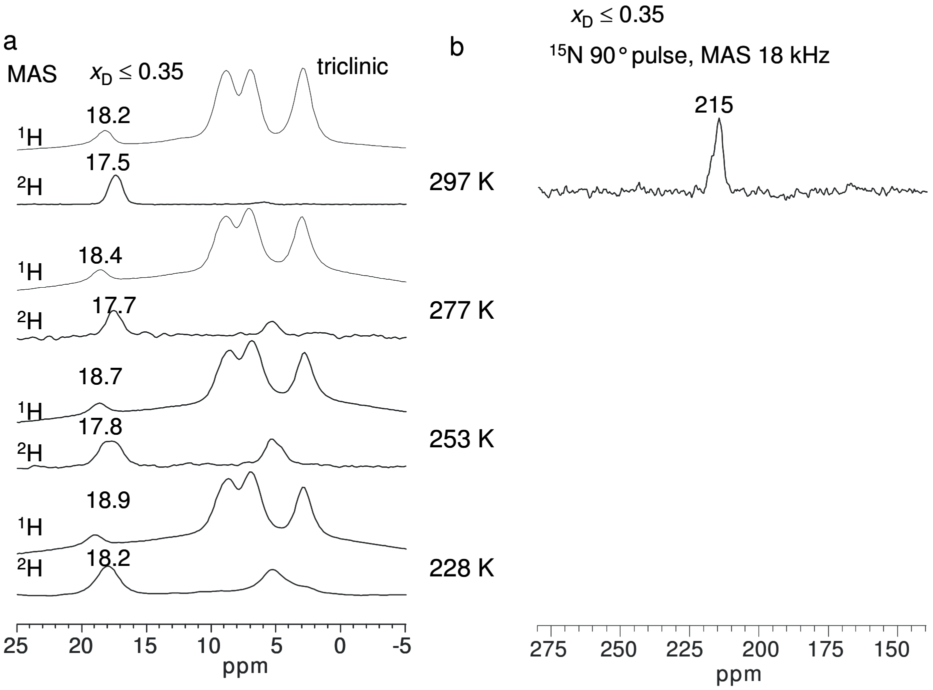

Figure S6. Variable temperature solid state (a) ^{1}H (599.97 MHz, 16 kHz spinning speed) and one-pulse ^{2}H MAS NMR spectra (92.10 MHz, 16 kHz spinning speed) and (b) ^{15}N 90° pulse MAS NMR spectra (60.8 MHz, 18 kHz spinning speed) of sample **j**, 4-MPPCP-$d_{0.35}$, with a deuterium fraction of $x_D \approx 0.35$. Sample **j** was prepared according to procedure B.

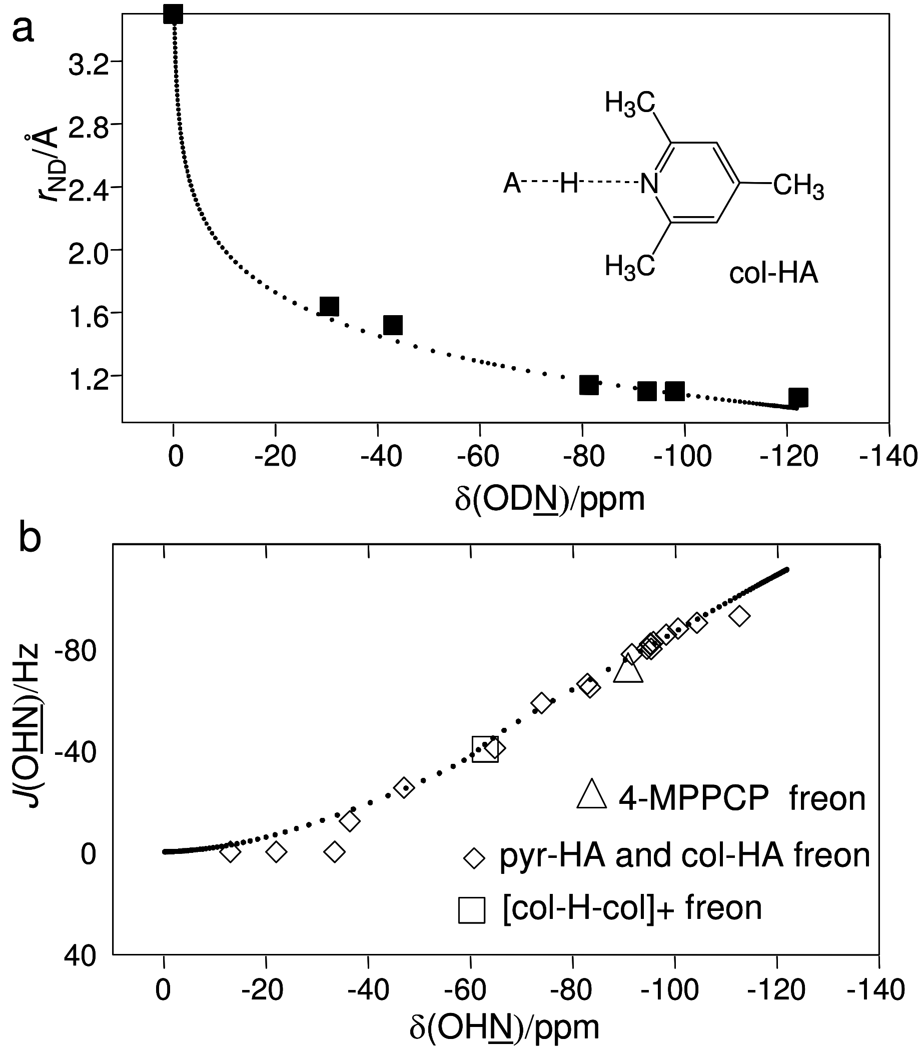

Figure S7. (a) Correlation of ND - distances obtained for polycrystalline collidine-acid complexes by dipolar solid state NMR with the corresponding isotropic ^{15}N chemical shifts δ(OH$\underline{\mathrm{N}}$).[6] (b) Correlation between the ^{1}H-^{15}N scalar couplings J(O$\underline{\mathrm{HN}}$) and the ^{15}N chemical shifts of pyridine-acid and collidine-acid complexes in CDF$_3$/CDF$_2$Cl at low temperatures. Adapted from Ref 7.

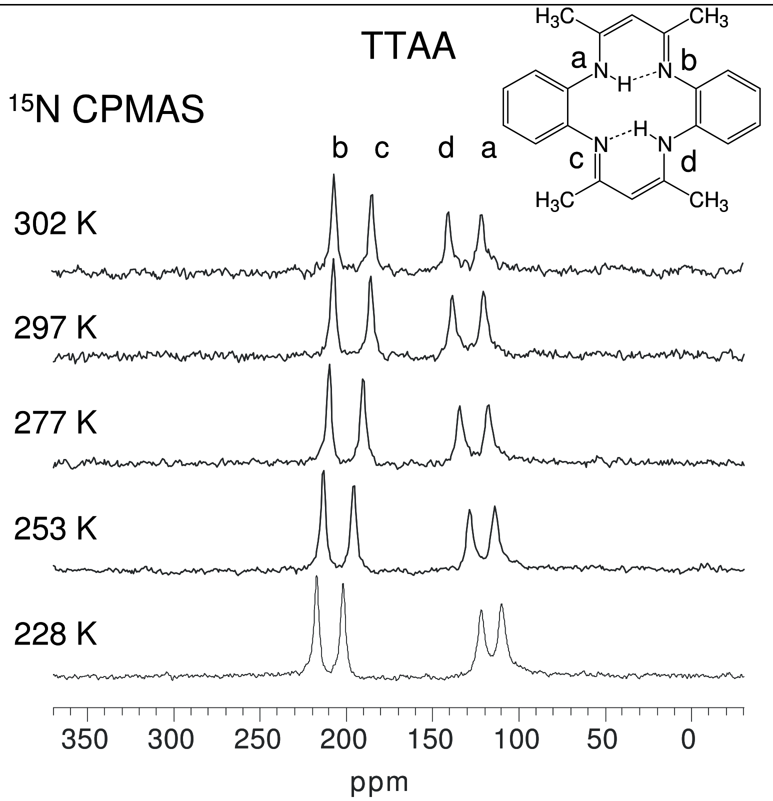

Figure S8. ^{15}N CPMAS NMR spectra of 95% enriched TTAA[1] at 60.8 MHz as a function of temperature; all spectra were measured without proton decoupling, 5 ms cross-polarization time, 100 scans on average, 10 kHz rotation frequency.

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