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Characterization of Pt-containing Polyoxometalates by High Resolution Solid-State ^{195}Pt and ^{51}V NMR Spectroscopy

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1.1. Solution NMR measurements

The ^{51}V NMR spectrum of **PtV_9** was recorded on a 400 MHz JEOL ECS instrument at room temperature in H_2O / D_2O using a 5 mm tube. The resonance frequency was 105.155 MHz, and the chemical shifts are reported with respect to neat $VOCl_3$.

The ^{183}W NMR spectra were recorded in 10 mm tubes on a 400 MHz JEOL ECS instrument at room temperature and at 60 °C on a 400 MHz JEOL ECX instrument for **H_3PtW_6** with a resonance frequency of 16.688 MHz. The chemical shifts are reported with respect to 1M Na_2WO_4(aq) as a reference. For the ^{183}W NMR measurements about 1 g of **H_3PtW_6** was dissolved in 3 ml of H_2O in the presence of Li^+-loaded ion exchange resin to increase the solubility of the POM salt; then 0.5 ml of D_2O were added to the filtrate.

The ^{195}Pt NMR spectra were recorded on a 400 MHz JEOL ECX instrument at room temperature using 5 mm tubes. The resonance frequency was 85.941 MHz, and the chemical shifts are reported with respect to aqueous 1.2 M Na_2PtCl_6 solution.

Saturated solutions were used in every case.

1.2 Solid-state NMR measurements

^{195}Pt solid state MAS NMR was performed on a 300 MHz (^{1}H) Bruker DMX spectrometer (33.8% natural abundance and 0.0033 sensitivity relative to ^{1}H) at 65.46 MHz with a spinning frequency of 13 kHz, except for **$H_{2.5}PtW_6$**, which was measured at a spinning frequency of 14 kHz. Due to the poor sensitivity and low resolution, the FID needed to be acquired for about 2-3 days with 100k - 300k scans. 100k (~1day and 4 hours) scans were used for $H_2[Pt(OH)_6]$ and $K_2[Pt(OH)_6]$. 300k scans (~3 days and 13 hours) were used for **$H_{2.5}PtW_6$**. The spectra for both **$H_{2.5}PtW_6$** and **PtV_9** were acquired using 200k scans (~ 2 days and 9 hours). A 90º pulse (4 μs pulse length) with phase alternation was used to directly polarize the ^{195}Pt magnetization. The ^{195}Pt signals were then spin-locked for 60 μs with a fixed phase followed by data acquisition in order to minimize baseline distortion due to a very large spectral width used in the experiments. It was observed that using the decoupler did not significantly improve the resolution; hence no decoupler was used for the actual measurements. The precursor material $H_2[Pt(OH)_6]$ was used as a reference. All isotropic peaks were verified by changing the spinning frequency.

^{51}V MAS NMR was performed at a spinning frequency of 20 kHz using a single pulse on a Bruker 600 MHz(^{1}H) NMR spectrometer. A 0.1 M NH_4VO_3 (pH = 13) solution was used as an external reference with the downfield shifted peak set at -535.8 ppm. All isotropic peaks were verified by changing the spinning frequency.

^{195}Pt MAS spectra simulations were made using a MATLAB program by numerical calculations of the spin-Hamiltonian (CSA) under magic angle spinning. The asymmetry parameter η and the chemical shift anisotropy δ_{aniso} were varied to obtain the best fit between the simulated and the experimental spectra including all spinning sidebands. Due to the distorted baselines, the fittings were done by visual estimation. The error bars were also estimated in a similar way.

1.3 X-ray crystallography

Data for $Na_4[H_3Pt^{IV}V_9O_{28}]\cdot 19H_2O$ were collected at 100 K on a Bruker Kappa X8 APEX CCD single-crystal diffractometer equipped with a sealed Mo anode tube and graphite monochromator (λ = 0.71073 Å). The crystal was mounted on a glass fiber in epoxy glue. Absorption and data scaling corrections were applied using the SADABS program.[1] The SHELX software package (Bruker) was used to solve and refine the structures.[2] All atoms were found in subsequent difference Fourier syntheses. No H atoms were included in the model. All atoms except the oxygens of water molecules of crystallization were refined anisotropically. The relative site occupancy factors (s.o.f.) for disordered positions of sodium cations were refined in isotropic approximation and then fixed for the obtained values. The crystallographic data for 1 are summarized in Table S1. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe,

76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD - 426538.

Table S1. Crystal data and structure refinement for $Na_4[H_3Pt^{IV}V_9O_{28}]\cdot 19H_2O$.

Empirical formula	$H_{82}Na_4O_{94}PtV_9$
Formula weight	2332.17
Temperature, K	100(2)
Wavelength	0.71073
Crystal system	Triclinic
Space group (No)	*P*-1
a, A°	12.6742(12)
b, A°	12.8294(11)
c, A°	15.1227(13)
α, °	69.032(4)
β, °	72.562(5)
γ, °	66.747(4)
Vol(A°^{3})	2073.4(3)
Z	2
Calculated density, kg/m^3	1.868
Absorption coefficient μ, mm^{-1}	2.806
F(000)	1163
Crystal size, mm	0.06 × 0.24 × 0.58
Theta range for data collection, °	3.14 – 29.57
Completeness to Θ_{max}	99.7
Index ranges	$-17 \le h \le 17$; $-17 \le k \le 17$, $-20 \le l \le 20$
Reflections collected	94886
Independent reflections	11598
R(int)	0.0502
Observed ($I > 2\sigma(I)$)	11273
Absorption correction	Semi-empirical from equivalents
T_{min} / T_{max}	0.2925 / 0.8497
Data / restraints / parameters	11598 /0 /496
Goodness-of-fit on F^2	1.071
R_1, wR_2 ($I > 2\sigma(I)$)	R_1 = 0.0468; wR_2 = 0.1374
R_1, wR_2 (all data)	R_1 = 0.0476; wR_2 = 0.1383
Largest diff. peak and hole, e·Å^{-3}	2.985 and -1.032

For comparison the unit cell parameters of $Na_5[H_2Pt^{IV}V_9O_{28}]\cdot 21H_2O$ (**PtV_9**) are: *a* = 12.540(1) Å, *b* = 13.722(1) Å, *c* = 14.884(1) Å, *α* = 116.681(5) °, *β* = 103.827(4) °, *γ* = 96.044(5) °, *V* = 2154.37 Å^3, *Z* = 2.

2. Solution NMR spectra.

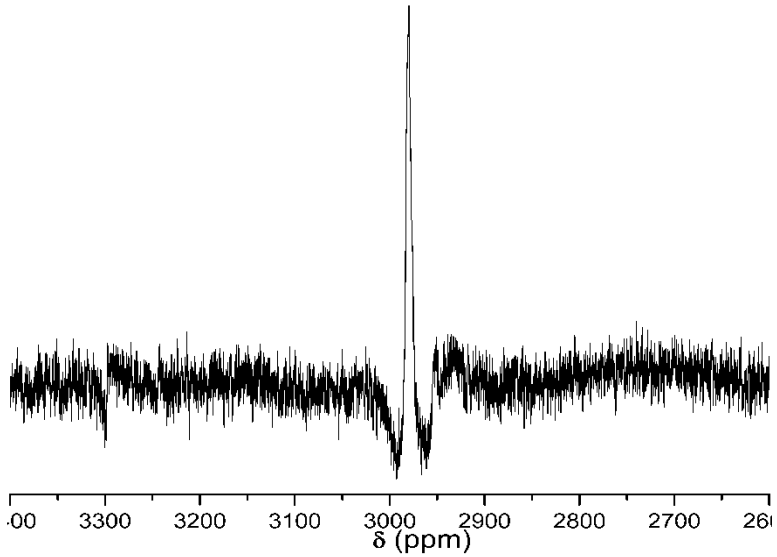

Fig. S1. Solution ^{195}Pt NMR spectrum of **H_3PtW_6** redissolved in H_2O / D_2O (room temperature).

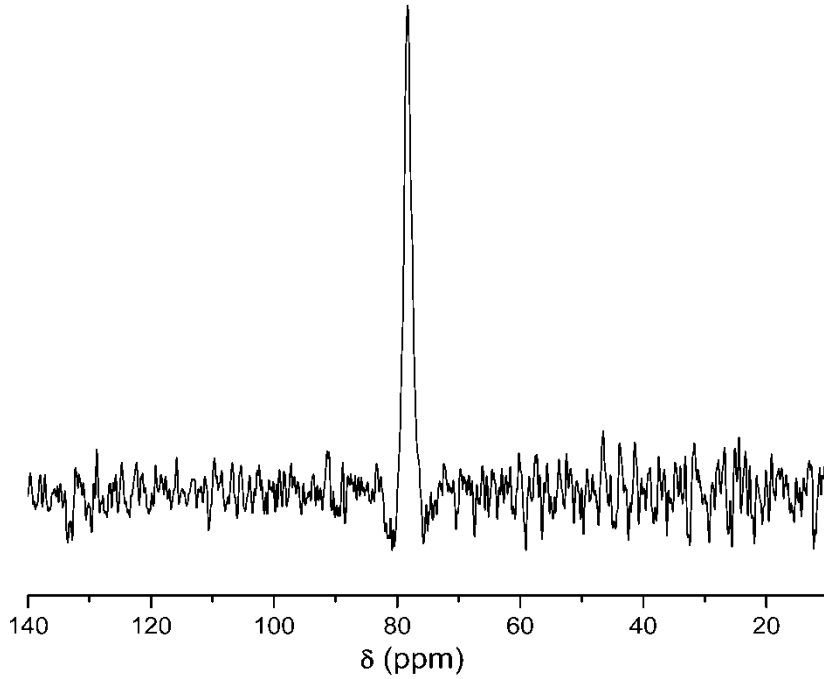

Fig. S2. Solution ^{183}W NMR spectrum of **H_3PtW_6** redissolved in H_2O / D_2O (50 °C).

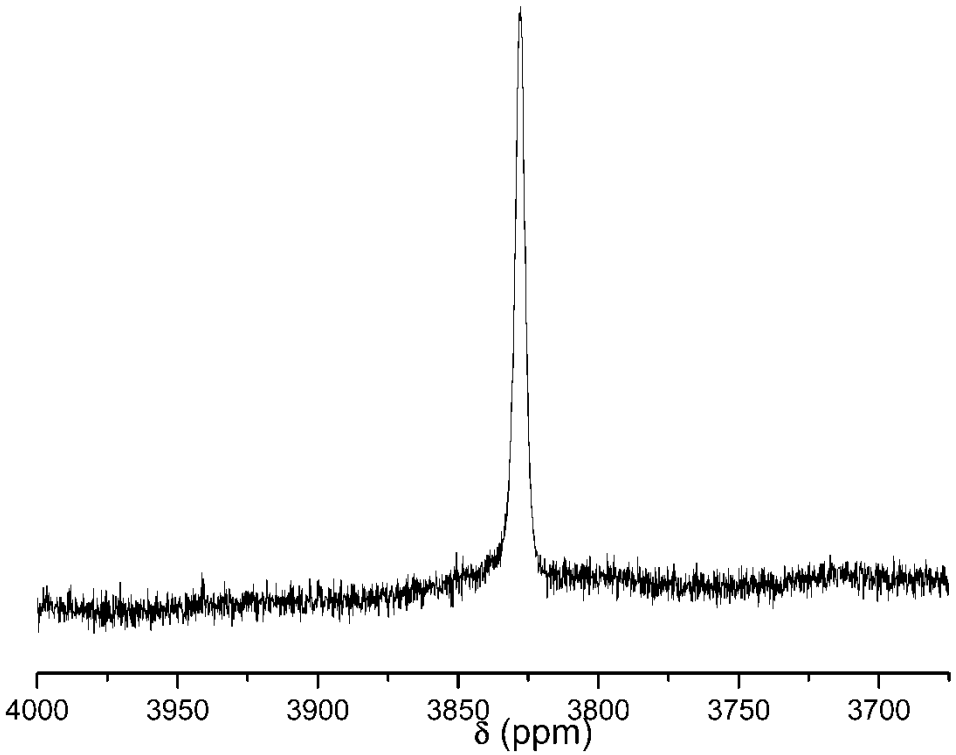

Fig. S3. Solution ^{195}Pt NMR spectrum of **PtV_9** redissolved in H_2O / D_2O (room temperature).

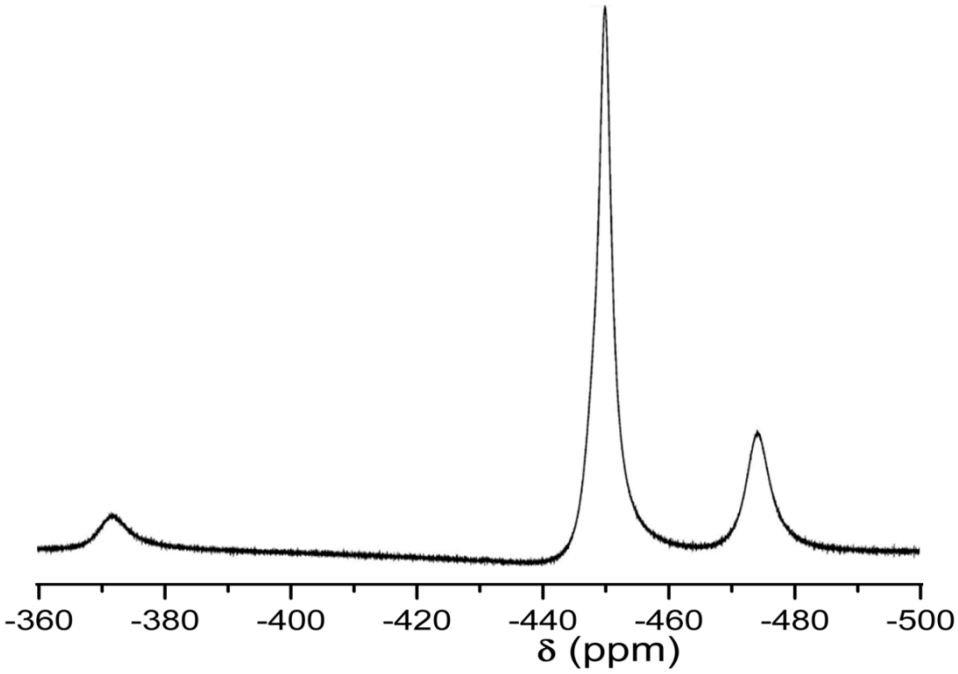

Fig. S4. Solution ^{51}V NMR spectrum of **PtV_9** redissolved in H_2O / D_2O (room temperature).

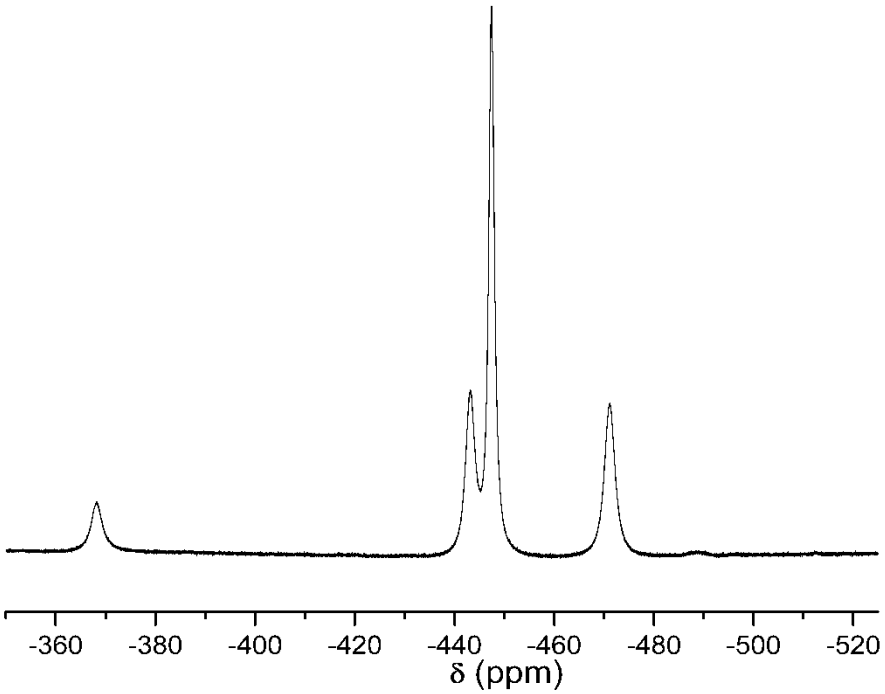

Fig. S5. Solution ^{51}V NMR spectrum of PtV_9 redissolved in H_2O / D_2O (60 °C).

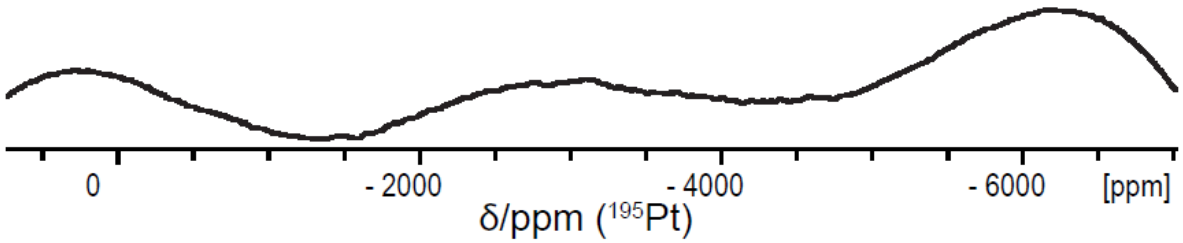

Fig. S6. $^{195}Pt^{II}$ solid-state MAS NMR of $Cs_3[PW_{11}O_{39}\{Pt^{II}(NH_3)_2\}_2]\cdot 6H_2O$. No signal was discernible.

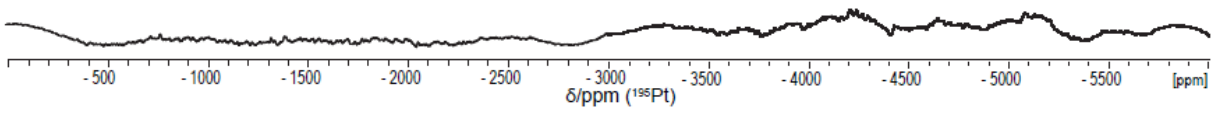

Fig. S7. $^{195}Pt^{II}$ solid-state MAS NMR of $K_2[PtCl_4]$; no signal was observed.

3. Comparison of crystal packing of $[H_xPt^{IV}V_9O_{28}]^{(7-x)-}$ polyanions in the structures of $Na_5[H_2Pt^{IV}V_9O_{28}]\cdot 21H_2O$ (PtV_9) and $Na_4[H_3Pt^{IV}V_9O_{28}]\cdot 19H_2O$.

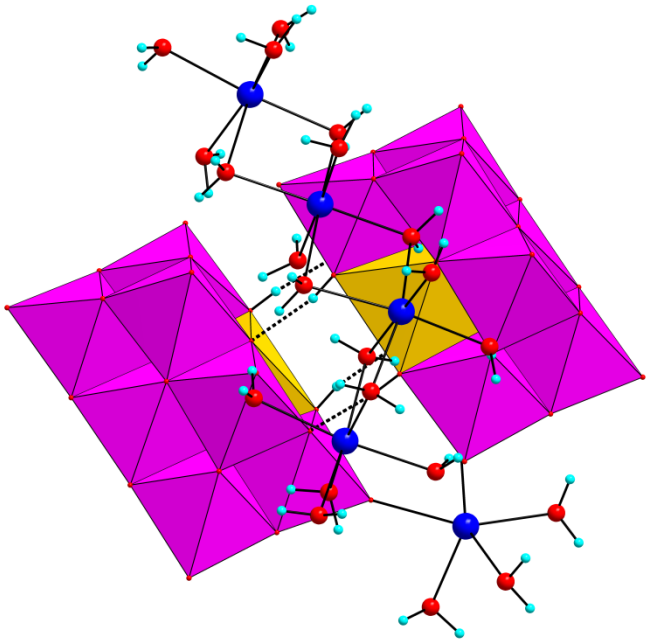

Fig. S8. Hydrogen-bonded dimers of $[H_2Pt^{IV}V_9O_{28}]^{5-}$ polyanions in the structure of **PtV_9** and the surrounding counter cations. Color legend: VO_6 and PtO_6 pink and yellow octahedra, respectively; O red, Na blue, inferred H turquoise balls. The hydrogen bonds are shown as dotted lines.

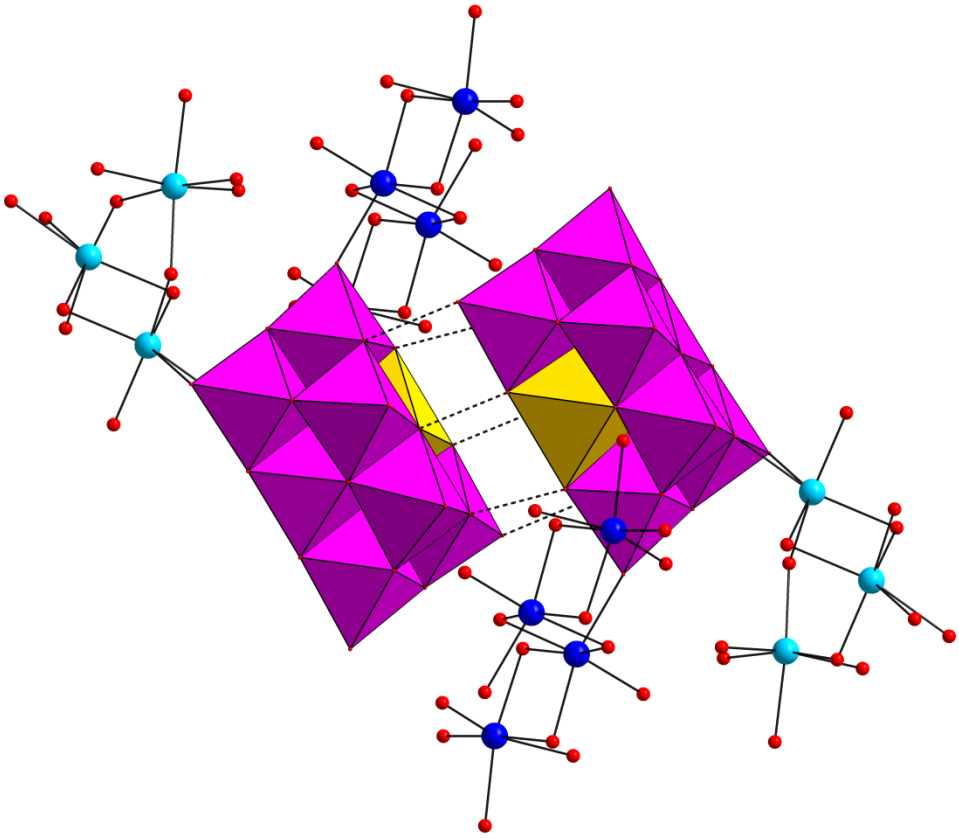

Fig. S9. Hydrogen bonded dimers of $[H_3Pt^{IV}V_9O_{28}]^{4-}$ polyanions in the structure of $Na_4[H_3Pt^{IV}V_9O_{28}]\cdot 19H_2O$ and the surrounding counter cations. Color legend as in Fig. S8. Disordered Na^+ counter cations with site occupancy of 50 % are shown as light-blue balls.

4. Experimental *vs* simulated ^{195}Pt solid-state MAS NMR spectra.

Figures

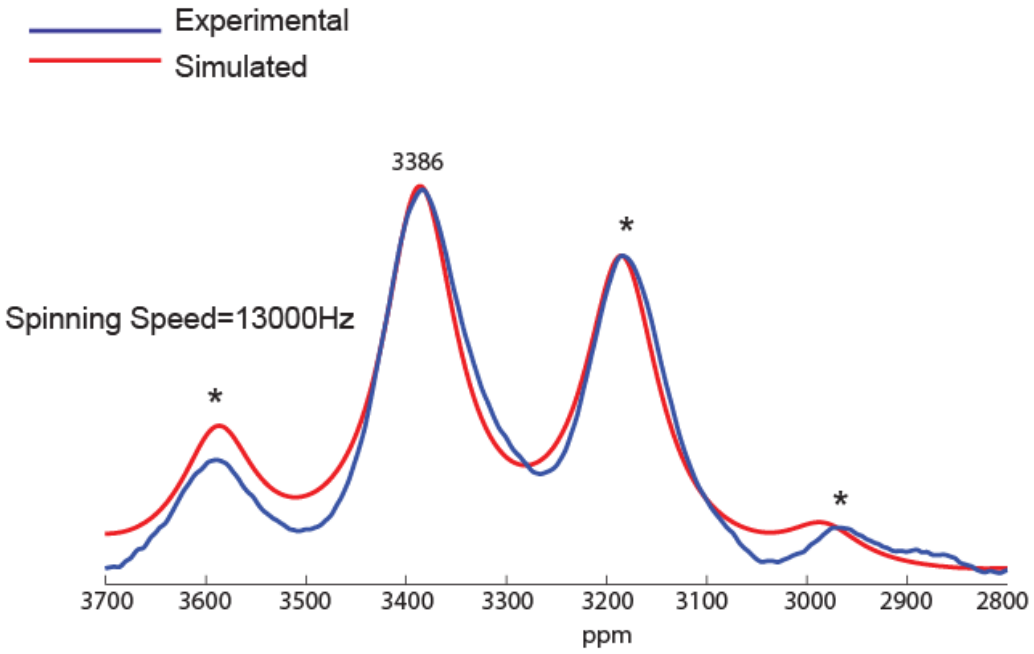

Fig. S10. Experimental (blue) and simulated (red) $^{195}Pt^{IV}$ solid-state MAS NMR spectra of $H_2[Pt(OH)_6]$. * represents spinning side bands in this and the following figures.

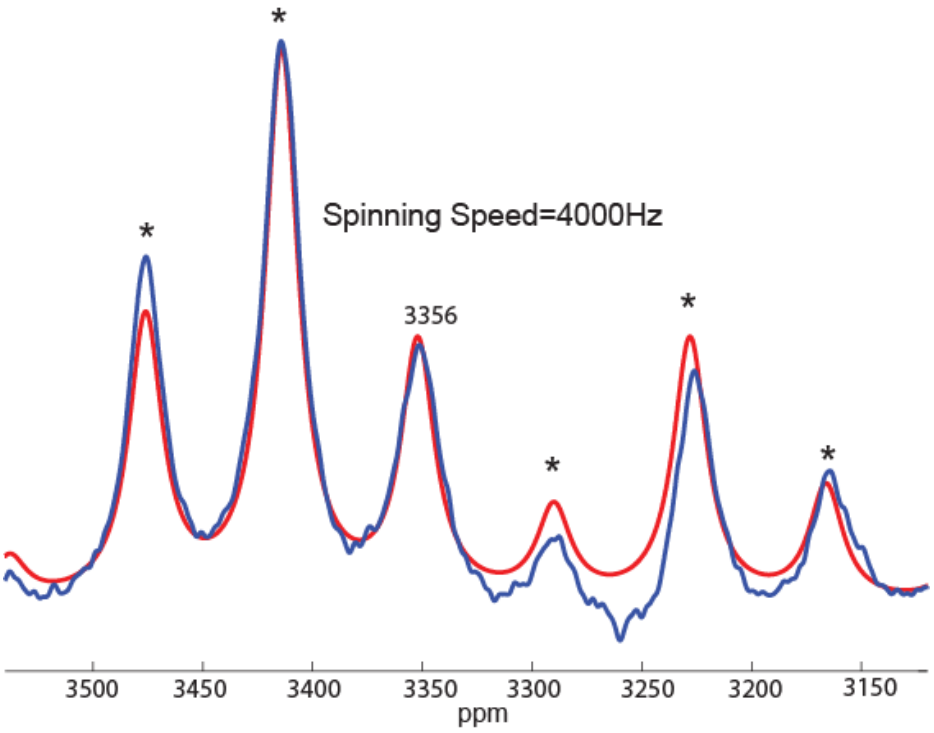

Fig. S11. Experimental (blue) and simulated (red) $^{195}Pt^{IV}$ solid-state MAS NMR spectra of $K_2[Pt(OH)_6]$.

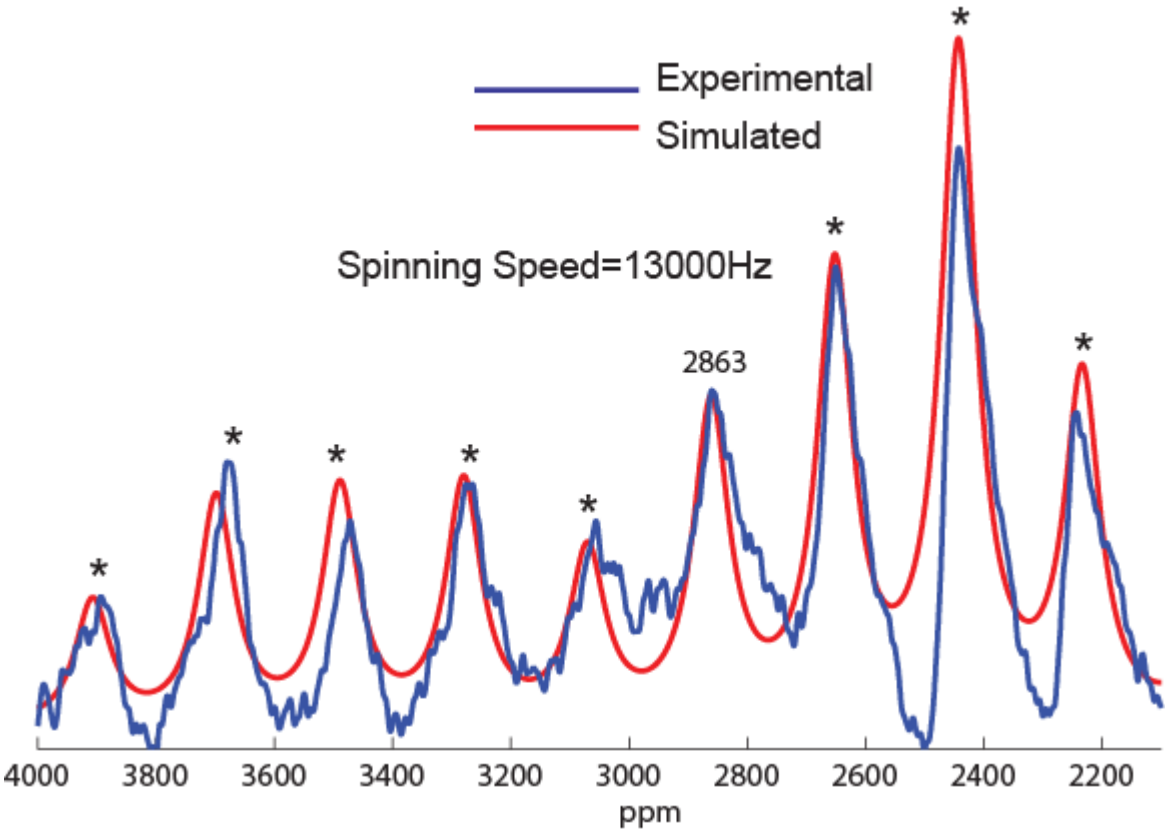

Fig. S12. Experimental and simulated $^{195}Pt^{IV}$ solid-state MAS NMR spectra of $H_{2.5}PtW_6$.

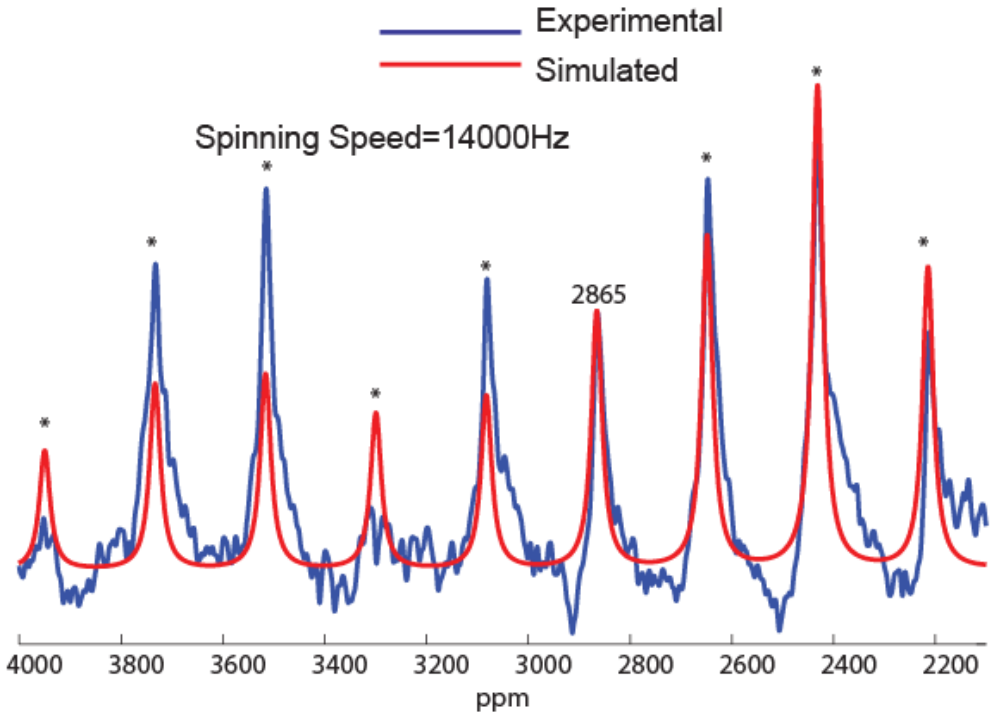

Fig. S13. Experimental and simulated $^{195}Pt^{IV}$ solid-state MAS NMR spectra of H_3PtW_6.

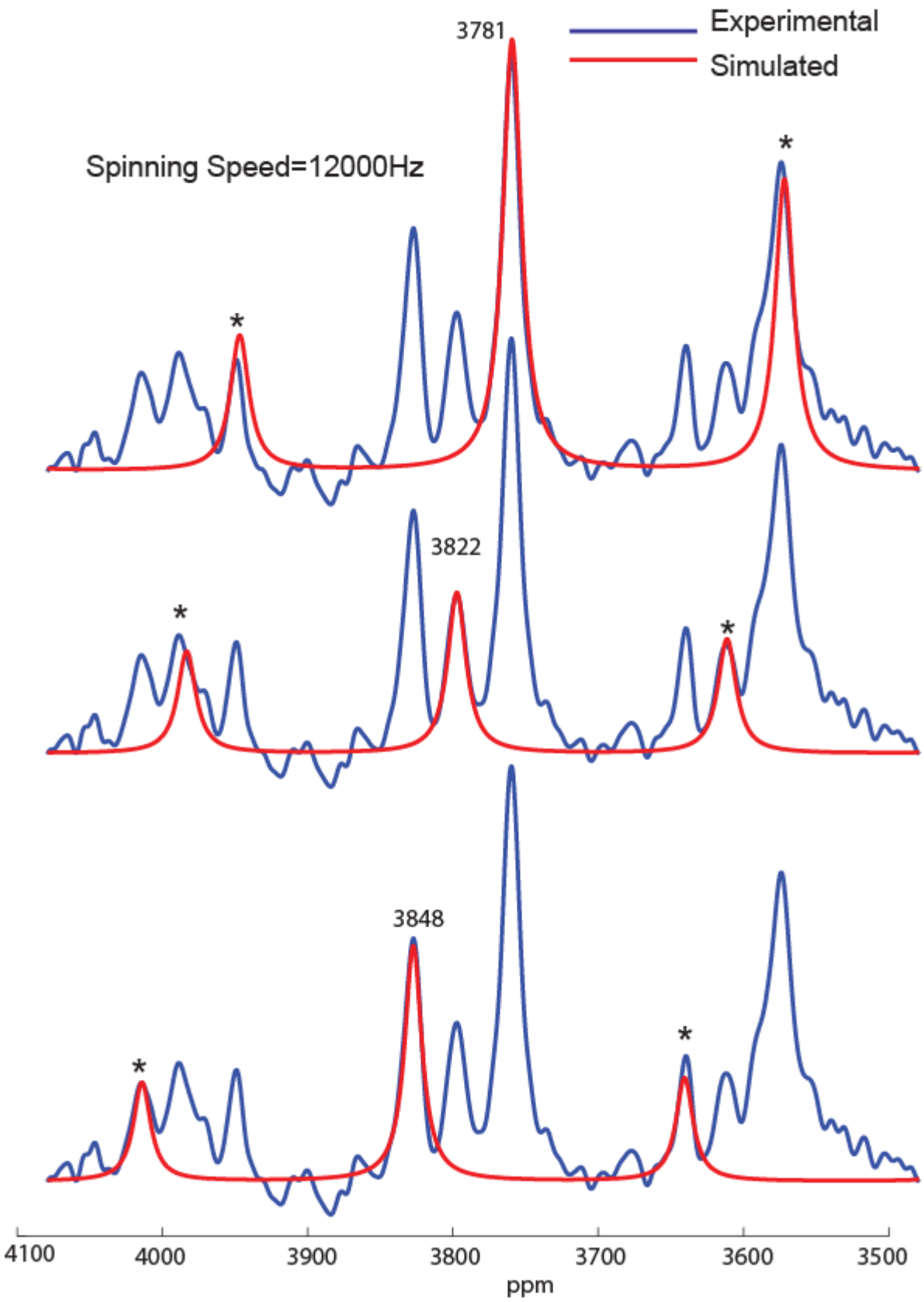

Fig. S14. Experimental and simulated $^{195}Pt^{IV}$ solid-state MAS NMR spectra of PtV_9.

5. References

1. G. M. Sheldrick, *SADABS, Program for empirical X-ray absorption correction*, Bruker-Nonius, 1990.

2. G. M. Sheldrick, *Acta Crystallogr.* 2007, ***A64***, 112-122.