SUPPLEMENTAL MATERIAL

Solid-state Structural Characterization of a Rigid Framework of Lacunary Heteropolyniobates

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Figure 1S: The high speed ^1H MAS NMR spectrum (—) and double-quantum (DQ) filtered ^1H MAS NMR spectra (- - -) of (**1**). All of the solid-state ^1H MAS NMR experiments were performed on a Bruker Avance 600 NMR instrument operating at 600.13 MHz, unless otherwise specified. Spectra were obtained using a 2.5 mm double resonance MAS probe spinning at 30 kHz. The high spinning speed is known to cause additional heating of the sample, and from a separate calibration study using $\text{Pb}(\text{NO}_3)_2$ it is known that for a 30 kHz spinning speed, the unregulated sample temperature is $\sim 45^\circ\text{C}$. The relative intensities reported were obtained from deconvolution of the entire spinning sideband manifold on the single pulse Bloch spectra. The solid-state 1D double quantum (DQ) filtered experiments utilized the chemical shift anisotropy (CSA) and offset compensated back-to-back (BABA) multiple pulse train for the excitation and reconversion of multiple quantum coherences as detailed in [S1]. The $0 \rightarrow \pm 2 \rightarrow 0 \rightarrow 1$ coherence pathway was selected using a 64 step phase cycle using an excitation/reconversion lengths of $133\ \mu\text{s}$ ($4\ \tau_R$), and a dephasing delay of $\tau_0 = 5\ \mu\text{s}$.

[S1]. Alam, T. M.; Tischendorf, B. C.; Brow, R. K. , *Solid State Nucl. Magn. Reson.* **2005**, 27, 99.

Figure 2S: The $^1\text{H} \rightarrow ^{31}\text{P}$ CP build-up curves for the ^{31}P resonances observed at +1.4 (●) and +6.1 (▲) ppm in the ^{31}P CP-MAS spectrum of (**1**). Variable-contact $^1\text{H} \rightarrow ^{31}\text{P}$ CP-MAS spectra were collected on a Bruker Avance 600 utilizing a 4 mm double resonance CP-MAS probe operating at 600.1 and 242.9 MHz for ^1H and ^{31}P , respectively. The CP-MAS pulse sequence used a square contact pulse and TPPM ^1H decoupling during acquisition of the free induction decay. The MAS speed was 10 kHz and a recycle delay of 10 s was implemented in all CP-MAS experiments. The CP build-up curves were fit as described in [S2, S3]. The observed CP build-up behavior is consistent with the assignment of the resonances at +1.4 and +6.1 to central and decorating PO_4 groups, respectively.

[S2]. Walter, T. H.; Turner, G. L.; Oldfield, E. J. *Magn. Reson.*, **1988**, 76, 106.

[S3]. Kolodziejewski, W.; Klinowski, J. *J. Phys. Chem. B.*, **1997**, 101, 3937.