**Supporting Information**

# The Antimony(III)-Bridged Heteropolyanion Sandwich Dimers $[Sb^{III}_3(A\text{-}\alpha\text{-}XW_9O_{34})_2]^{11-}$ (X = $Si^{IV}$, $Ge^{IV}$) and C-Shaped Double-Sandwich $[\{Sb^{III}_6O_2(A\text{-}PW_6O_{26})(A\text{-}\alpha\text{-}PW_9O_{34})_2\}]^{15-}$

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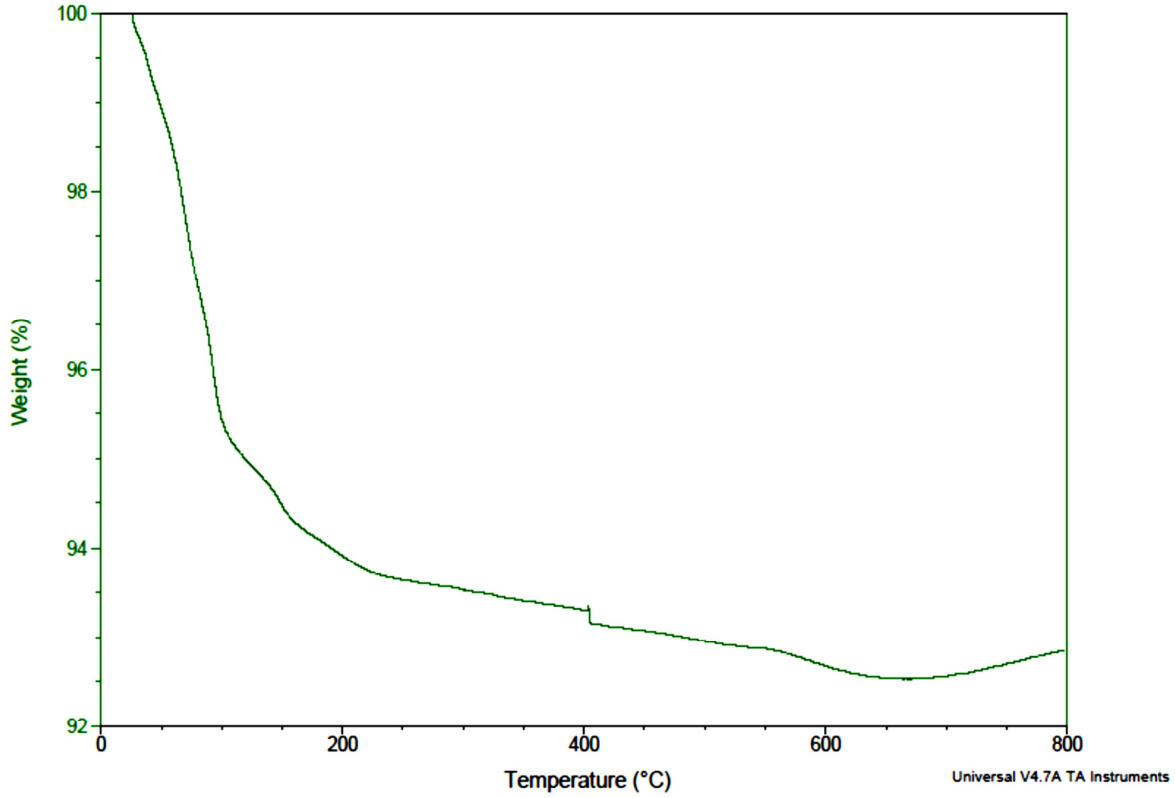


**Figure S1**. Thermogram of **K-1**.

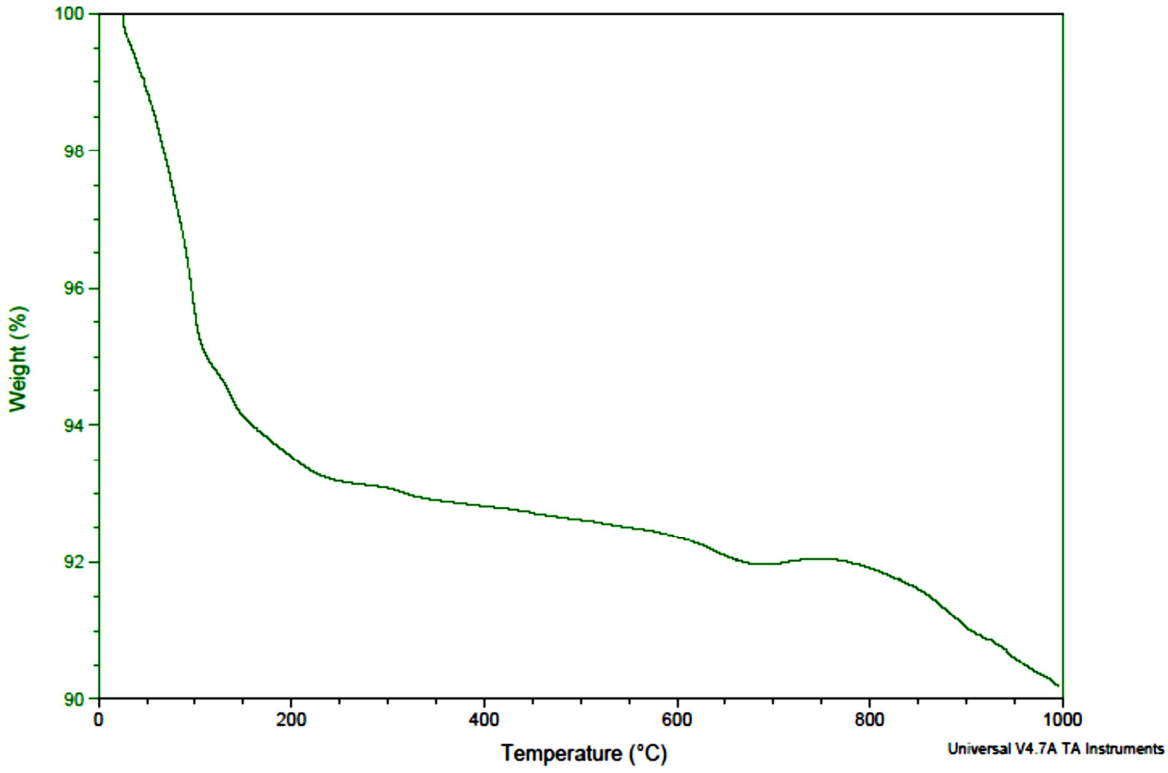


**Figure S2**. Thermogram of **K-2**.

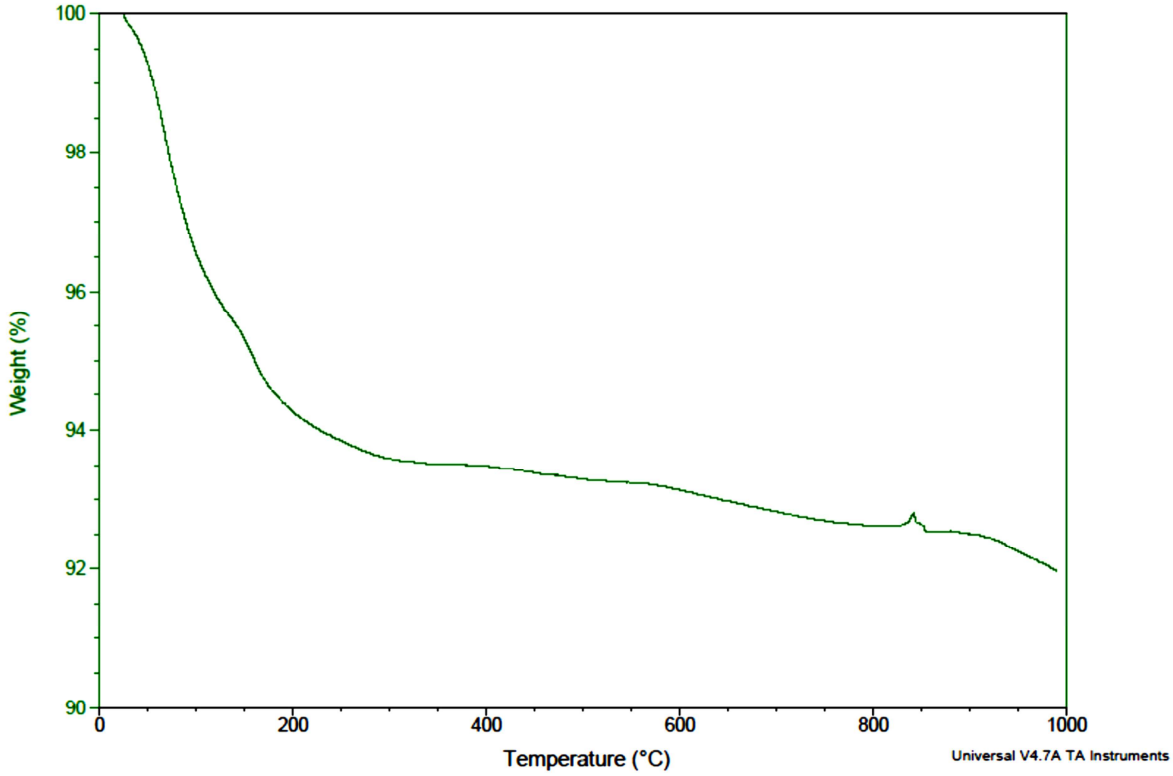


**Figure S3**. Thermogram of **KNa-3**.

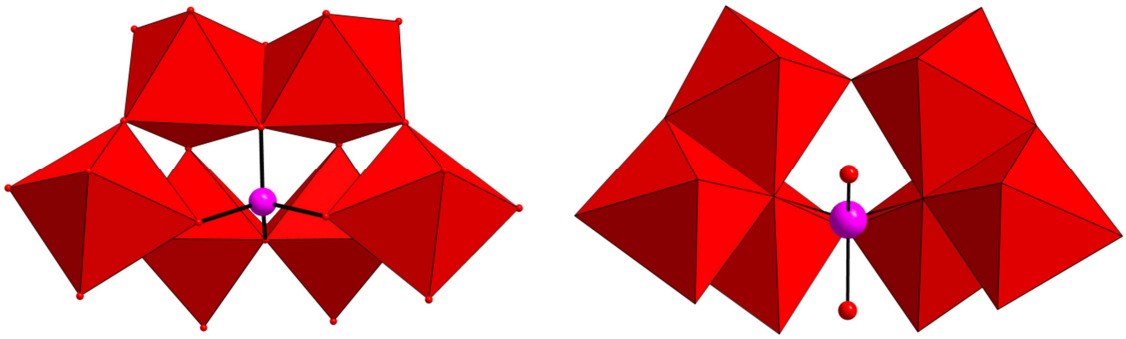

**Figure S4**. Structure of the {*A*-$\alpha$-$PW_6O_{26}$} unit in **3** (left), and {*B*-$\alpha$-$XW_6O_{26}$} unit in polyanions of the **$M_6X_3W_{24}$**-type (right), see text for details. Color legend: $WO_6$ red octahedra, P pink, and O red balls.

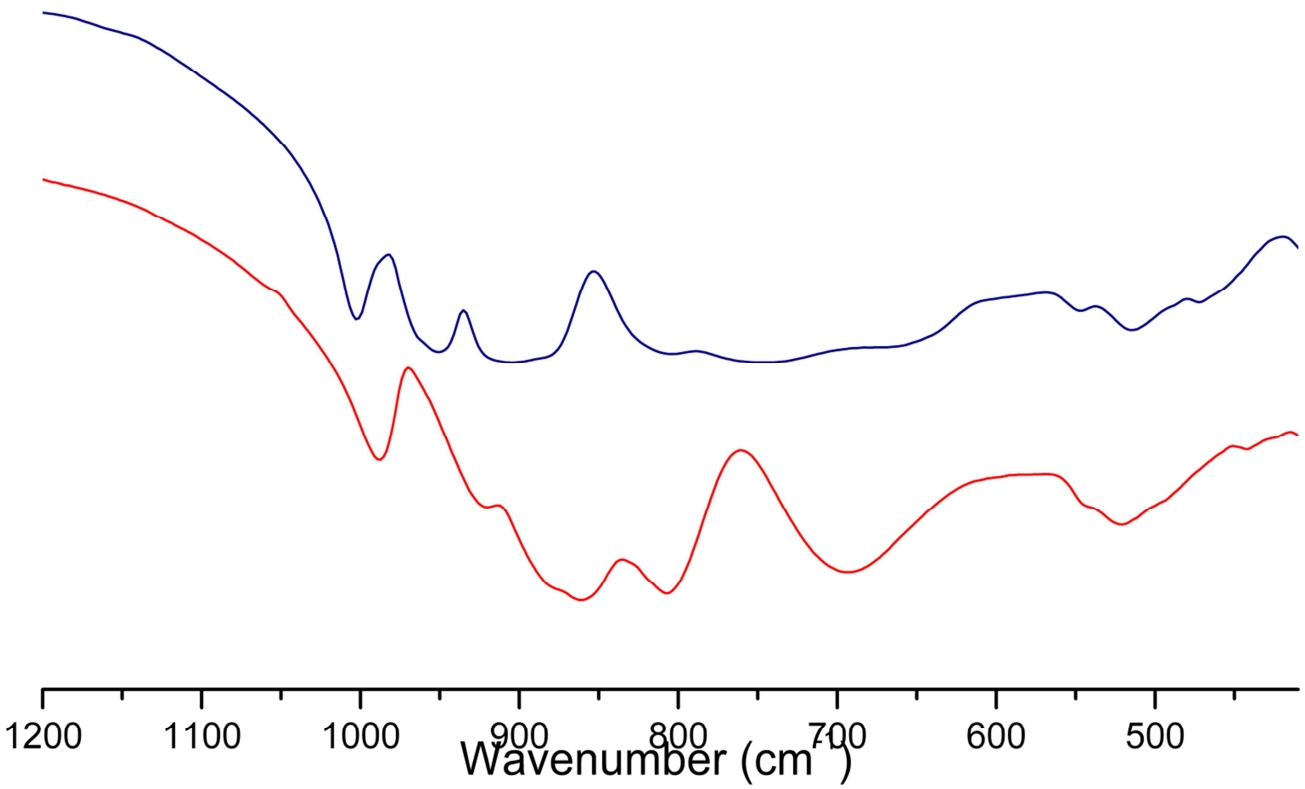


**Figure S5**. FT-IR spectra of **K-1** (blue) and $Na_9[A\text{-}\alpha\text{-}HSiW_9O_{34}]\cdot 23H_2O$ precursor (red).

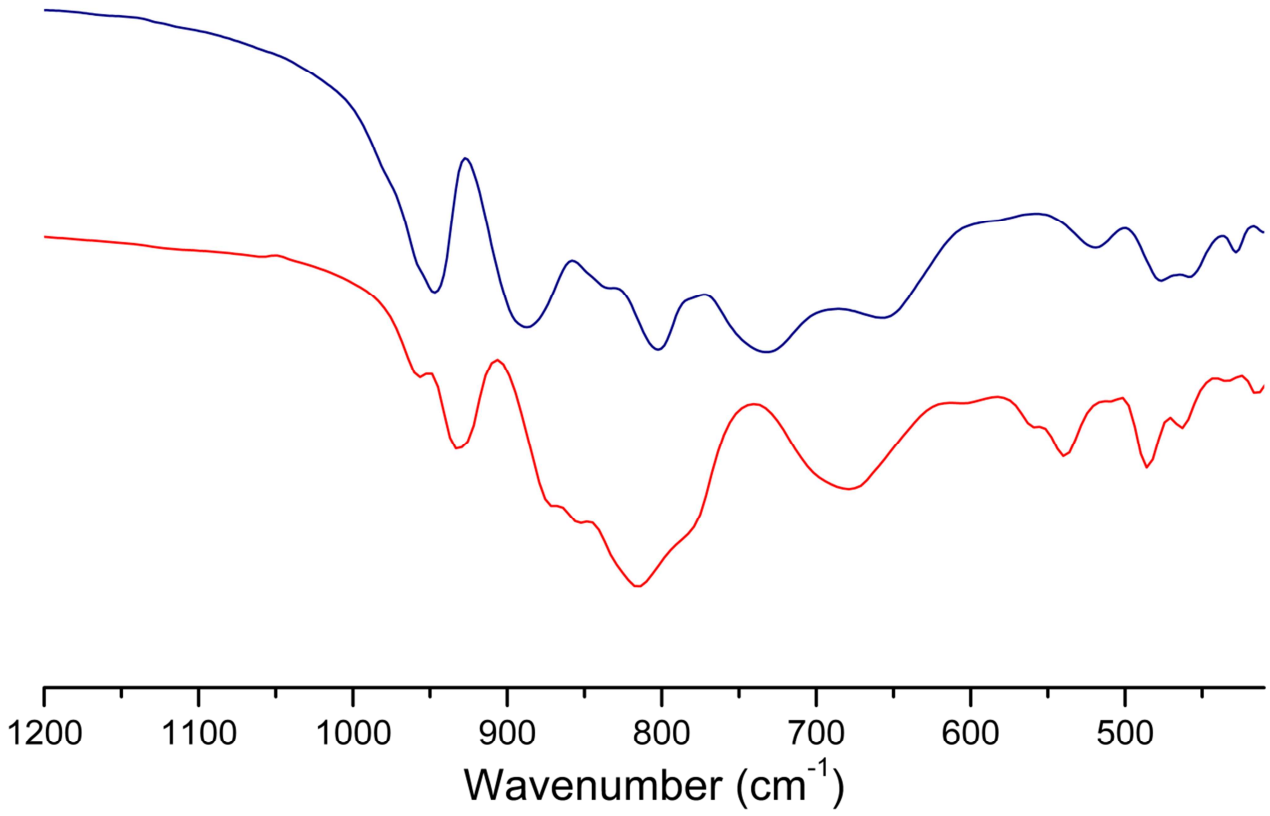


**Figure S6**. FT-IR spectra of **K-2 (**blue) and $Na_9[A\text{-}\alpha\text{-}HGeW_9O_{34}]\cdot 23H_2O$ precursor (red).

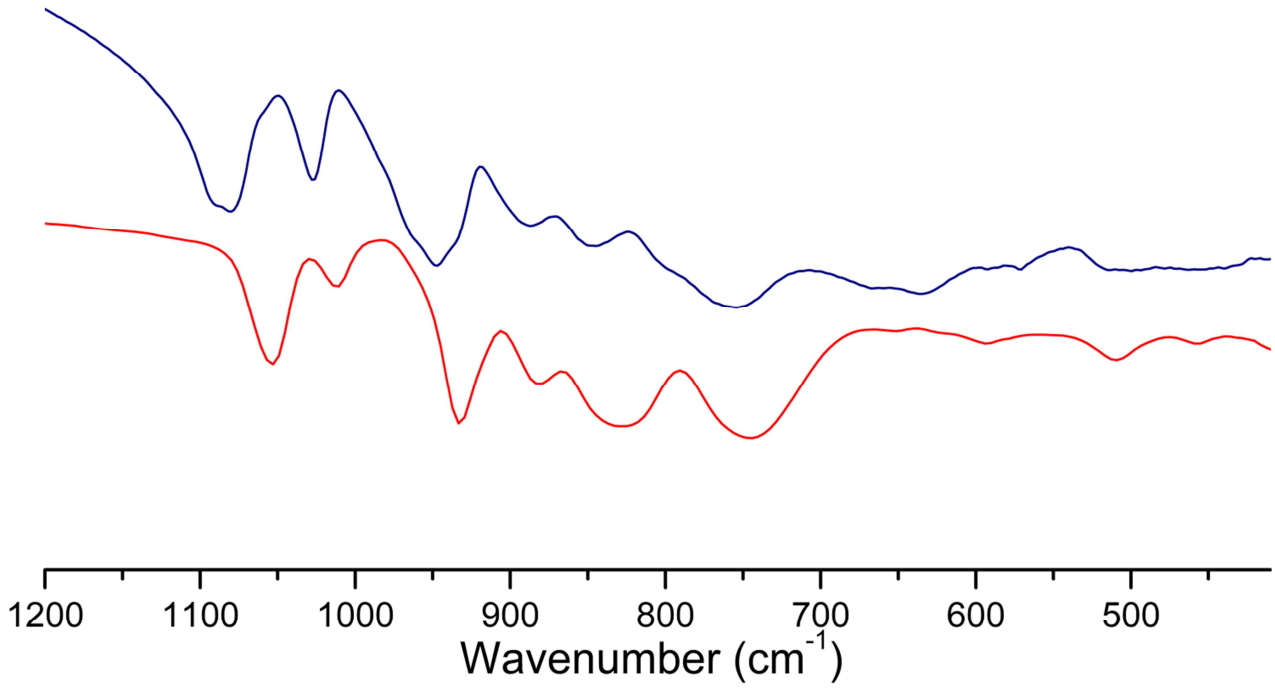


**Figure S7**. FT-IR spectrum of **KNa-3** (blue) and $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ precursor (red).

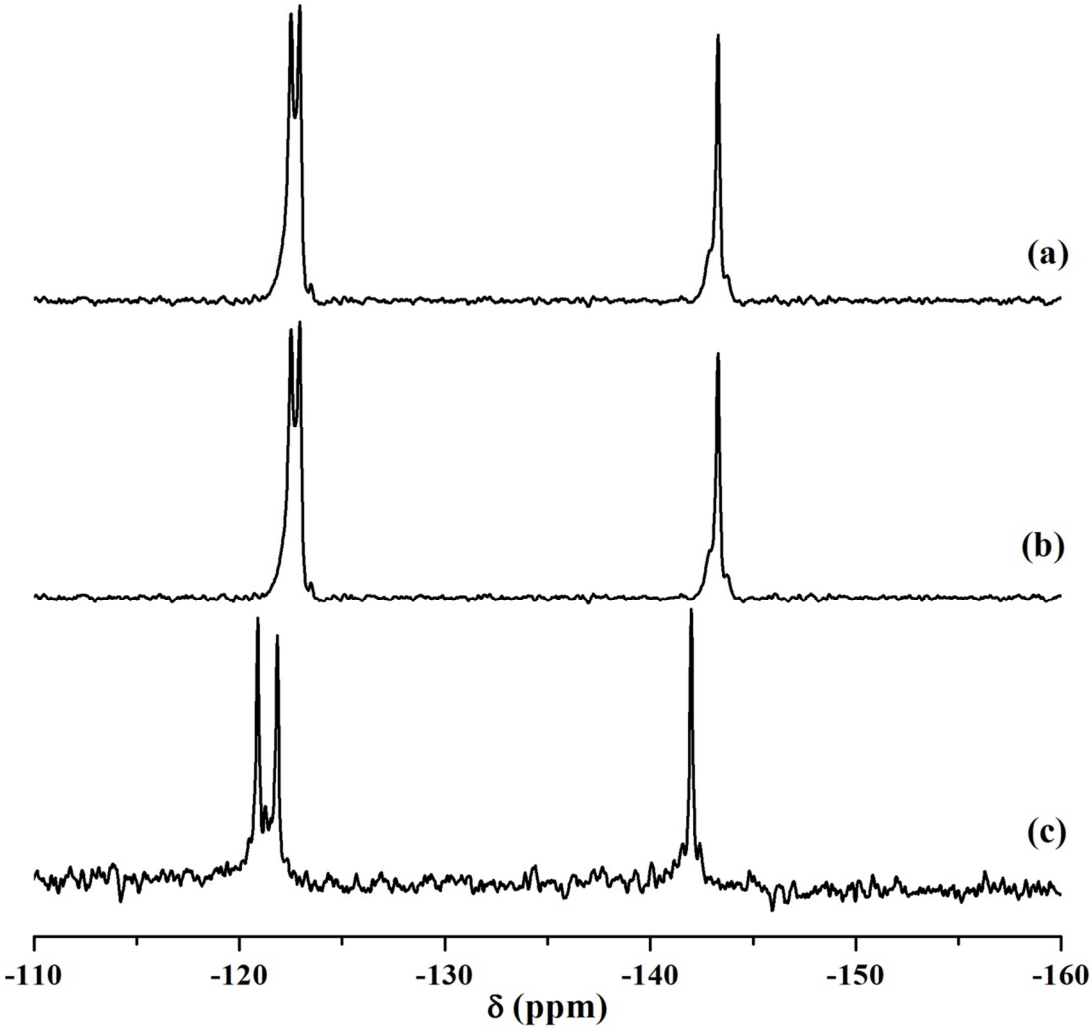


**Figure S8**. Room temperature $^{183}$W NMR spectra of **K-1** redissolved (a) in water, pH 7.0, (b) in 1M LIOAc, pH 4.9, and (c) in 1M KOAc, pH 4.9.

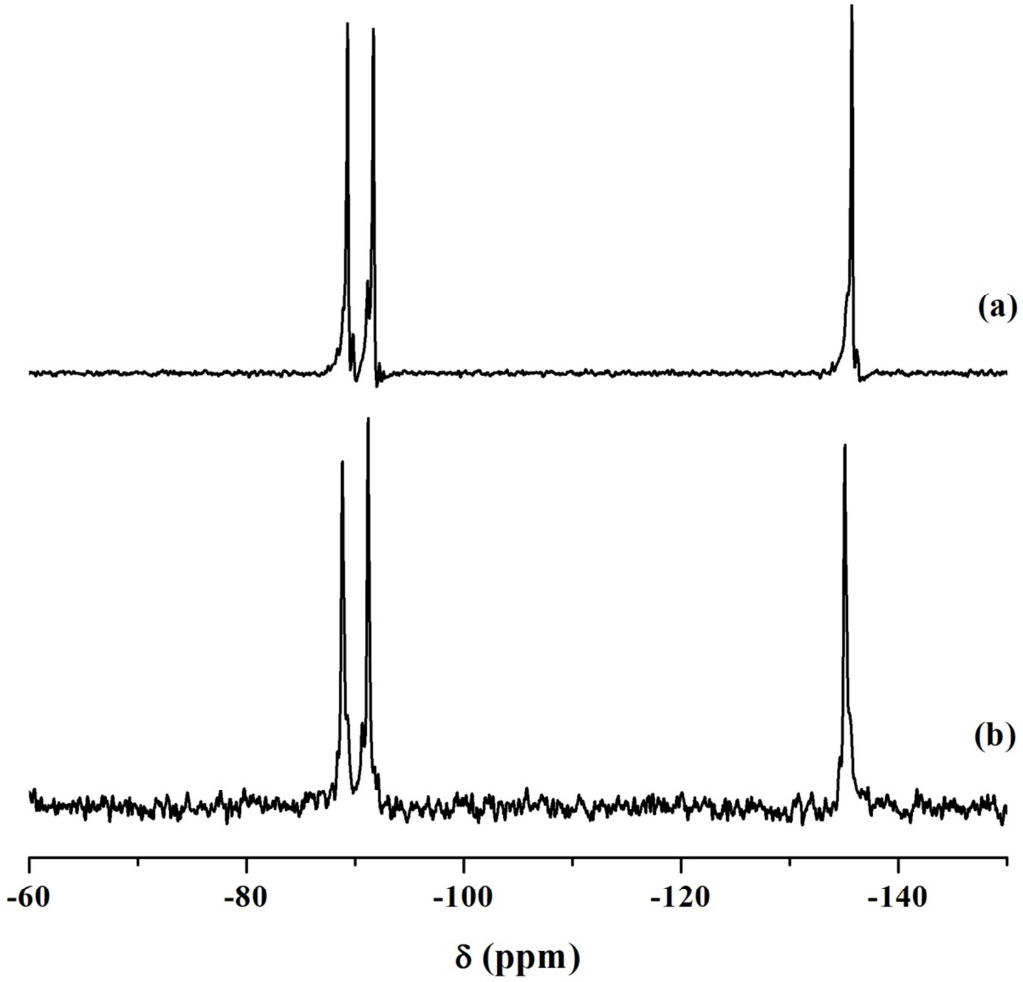


**Figure S9.** Room temperature $^{183}$WNMR spectra of **K-2** redissolved (a) in water, pH 7.0 and (b) in 1M KOAc, pH 4.9.

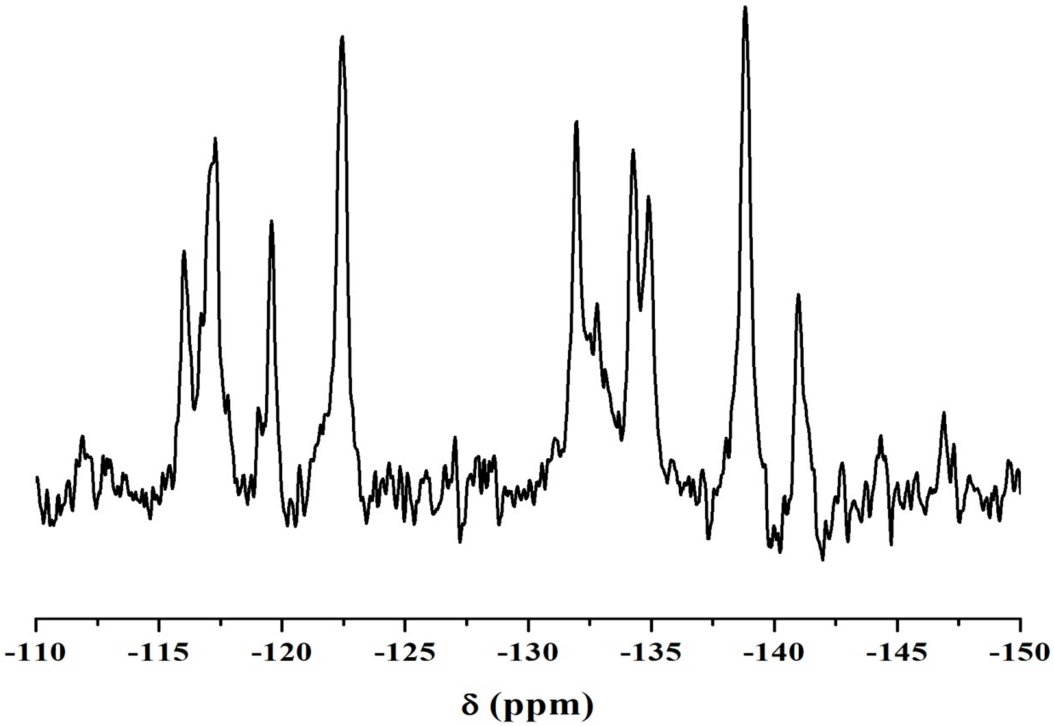


**Figure S10.** Room temperature $^{183}$W NMR spectrum of **KNa-3** redissolved in water.

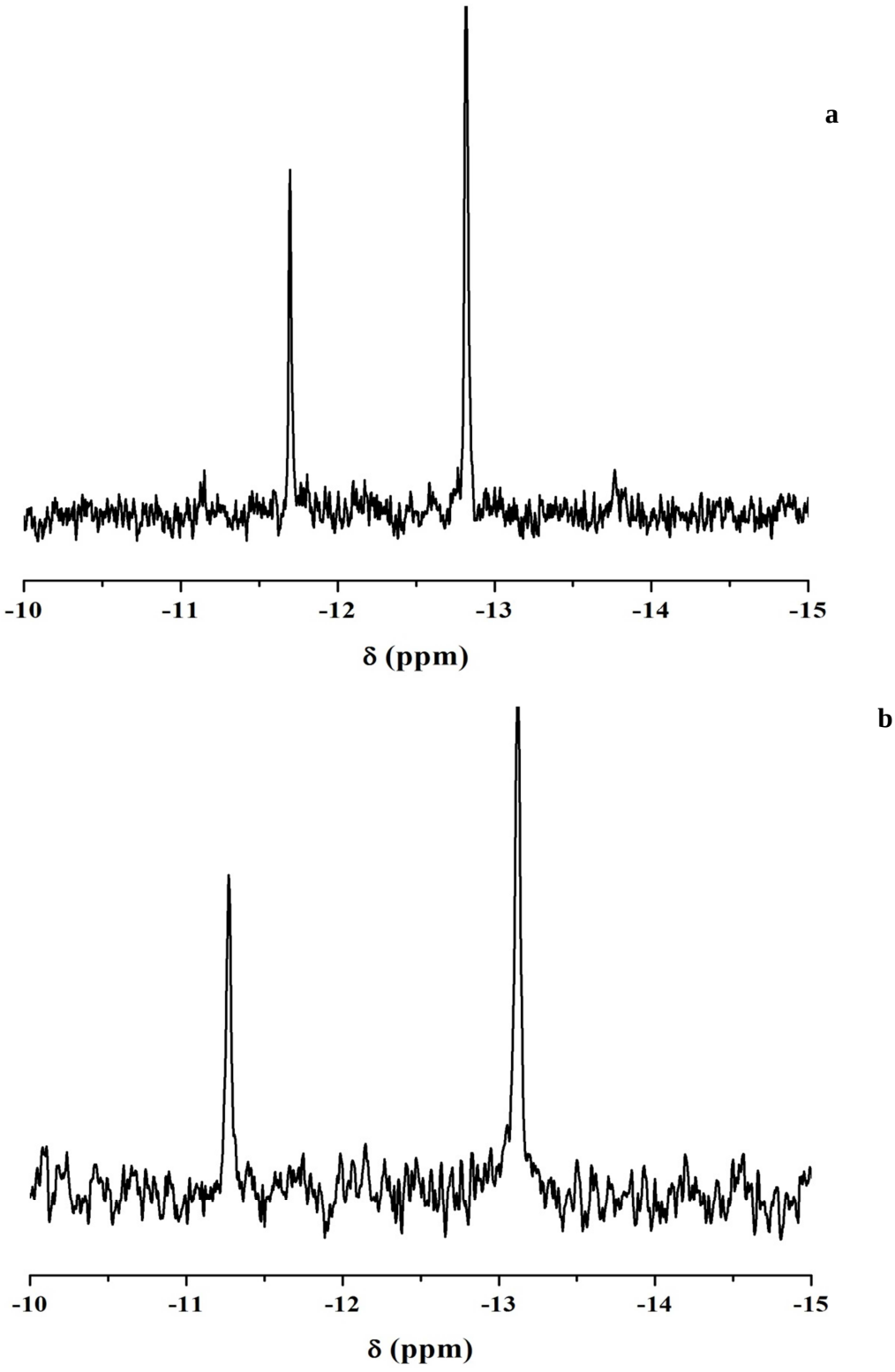


**Figure S11.** Room temperature $^{31}$P NMR spectra of **KNa-3** (a) and **K-3** (b) redissolved in water.