

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

FOR

**Multinuclear Cobalt(II)-Containing Heteropolytungstates: Structure, Magnetism, and Electrochemistry**

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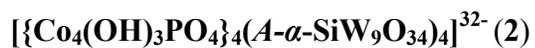
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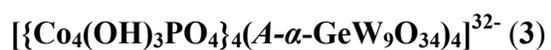
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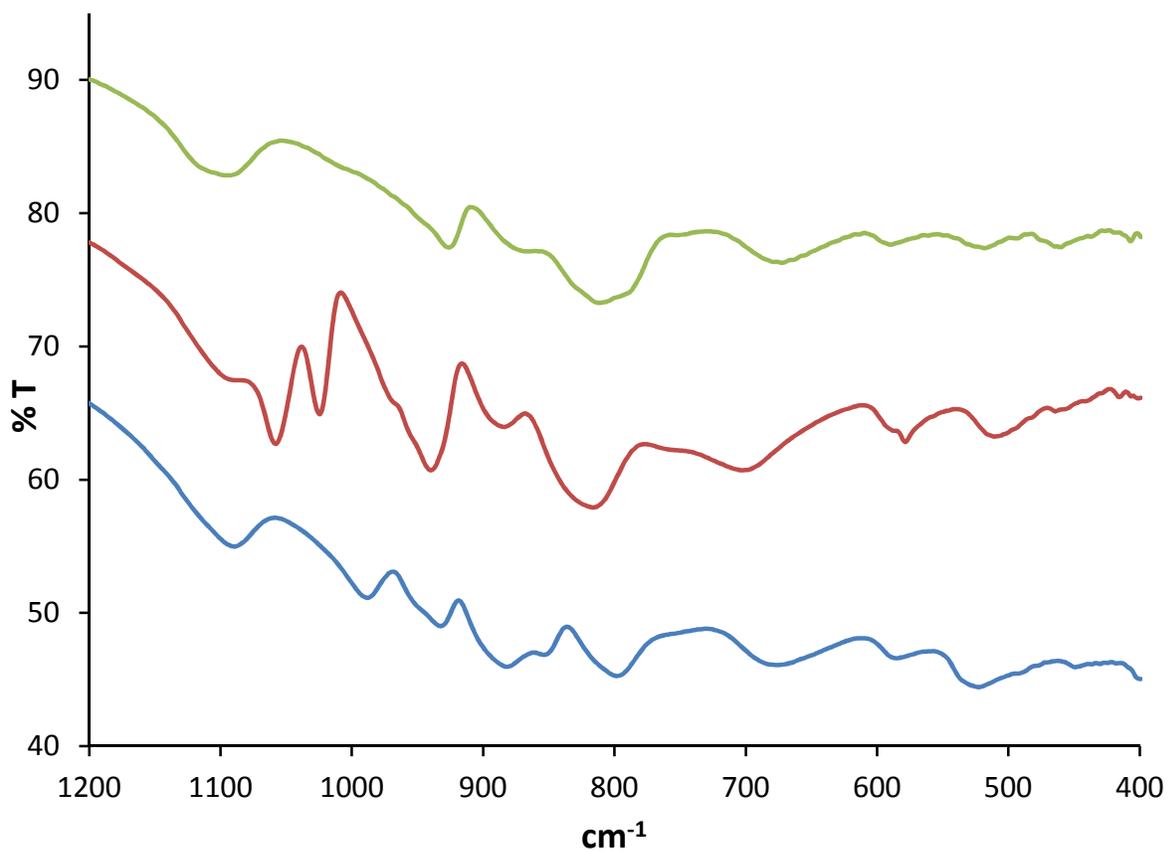
**Table S1:** Selected bond valence sum (BVS) values for **2** (upper) and **3** (lower).



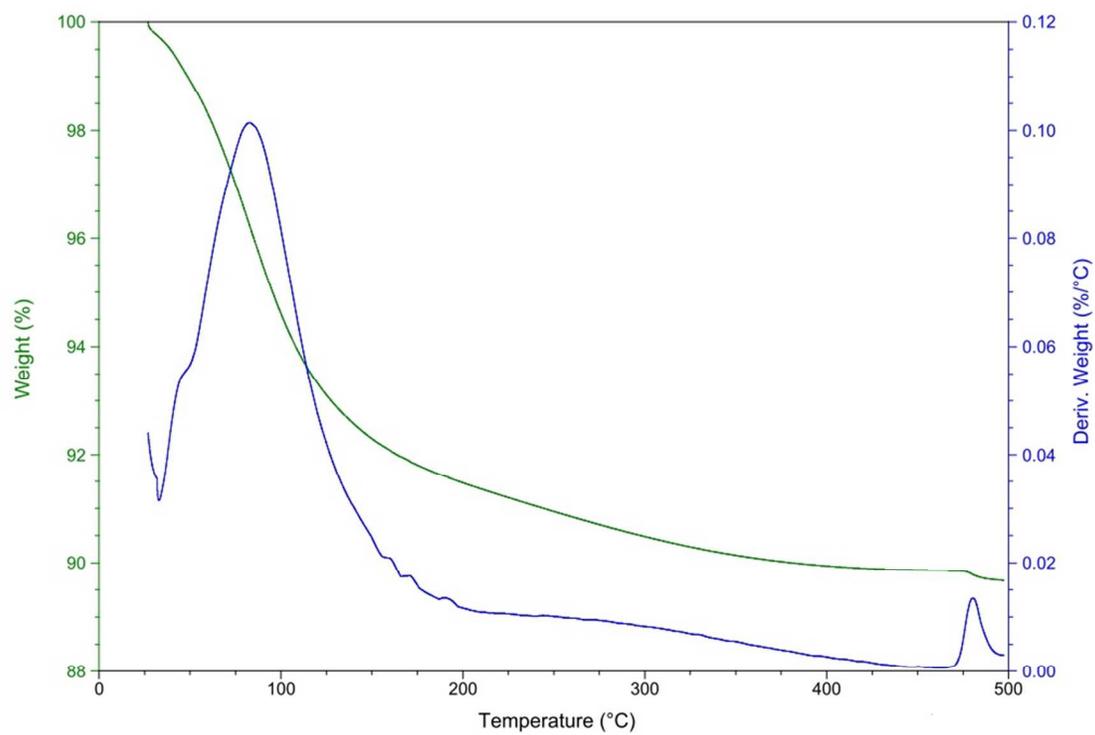
$\mu_3\text{-O}$ (3Co-O)	BVS Value	Co	BVS value
O34C	1.038	Co1	1.919
O34O	1.043	Co2	1.963
O24C	1.050	Co3	1.895
<b>O56C</b>	1.031	Co4	1.884
$\mu_2\text{-O}$ (Co-O-P)		Co5	1.929
O3P1	1.616	Co6	1.883
O1P2	1.632	<b>P</b>	
O1P1	1.789	P1	5.212
O2P1	1.616	P2	5.091
$\mu_4\text{-O}$ (3Co-O-P)			
O4P1	2.023		
O2P2	2.058		



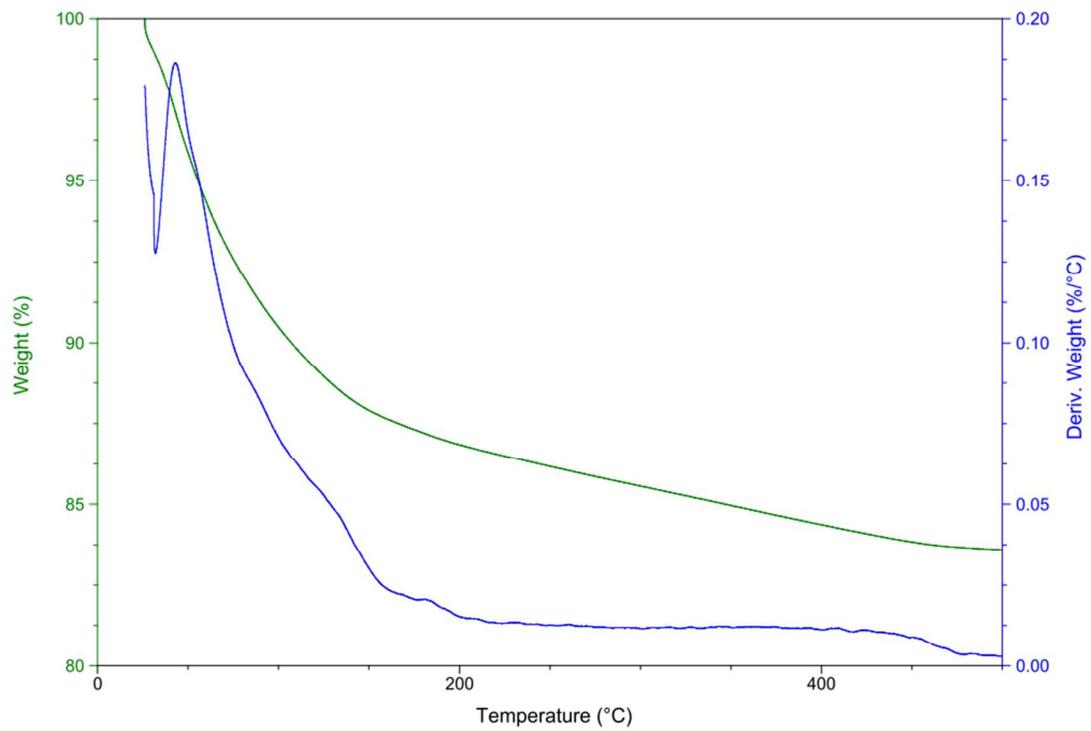
$\mu_3\text{-O}$ (3Co-O)	BVS Value	Co	BVS value
O12C	1.048	Co1	2.115
$\mu_2\text{-O}$ (Co-O-P)		Co2	1.950
O1P	1.603	<b>P</b>	
$\mu_4\text{-O}$ (3Co-O-P)		P1	4.883
O1Co	2.048		



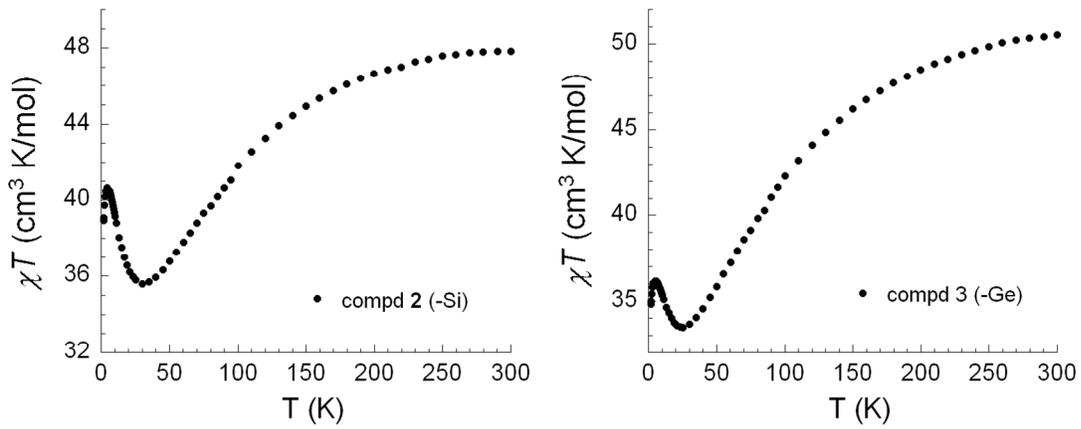
**Figure S1.** Infrared spectra of **KNa-3** (green), **RbNa-1** (red), and **Na-2** (blue).



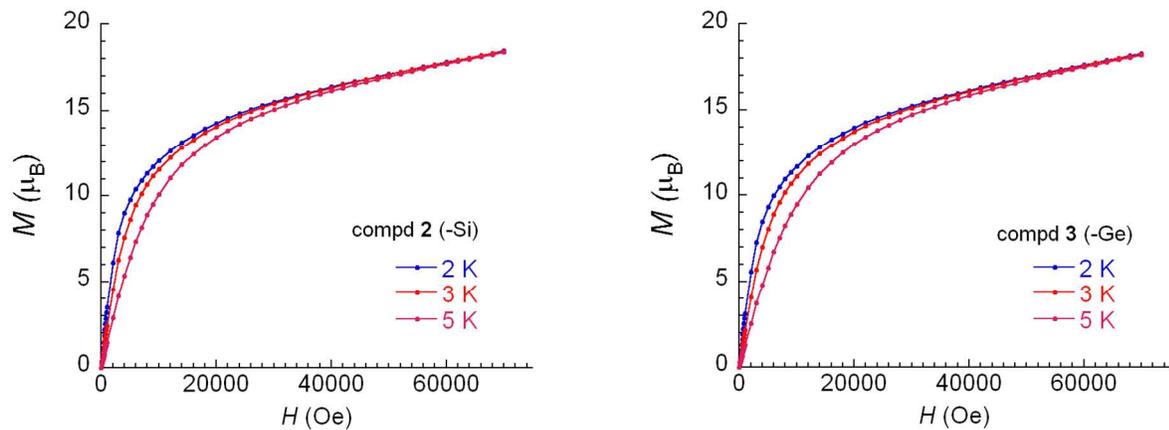
**Figure S2.** Thermogram of Na-2.



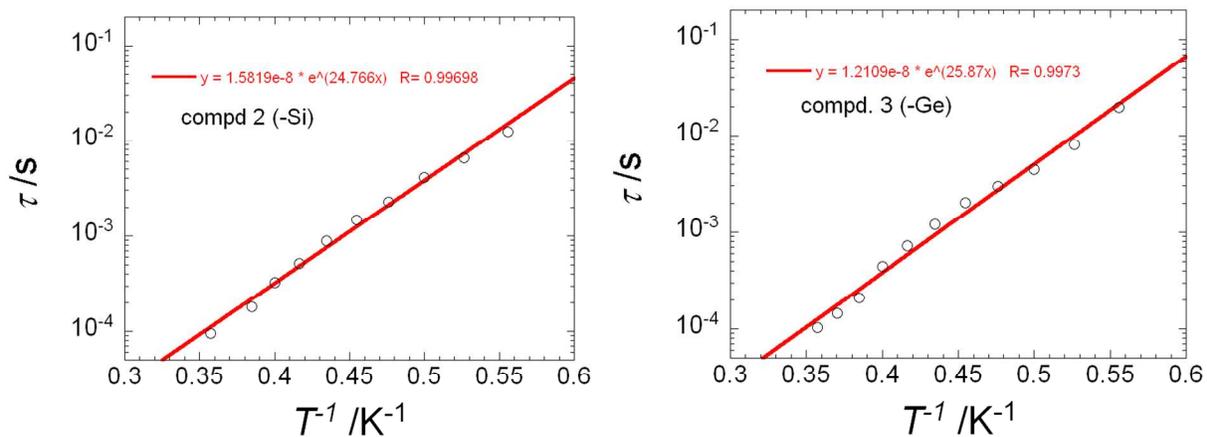
**Figure S3.** Thermogram of KNa-3.



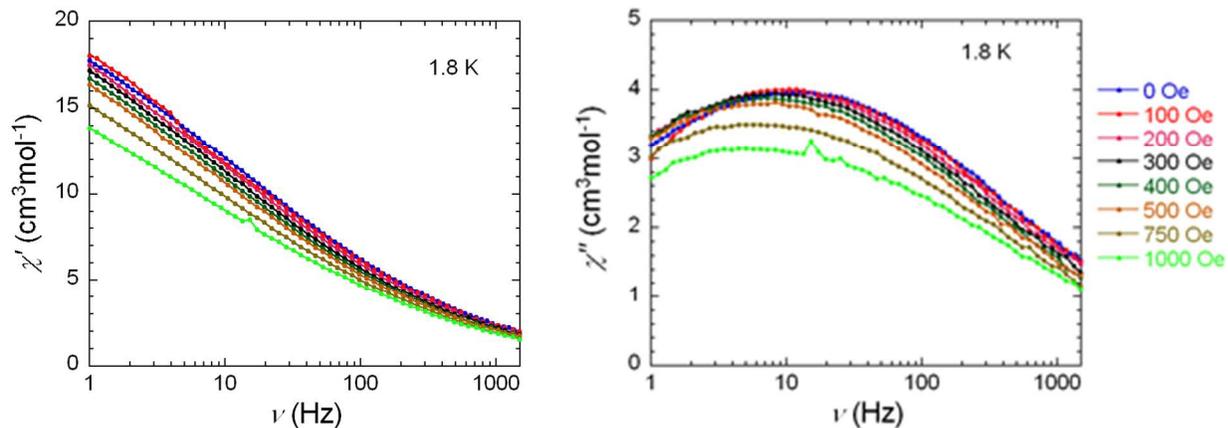
**Figure S4.** The plots of  $\chi T$  vs T for **Na-2** (left) and **KNa-3** (right).



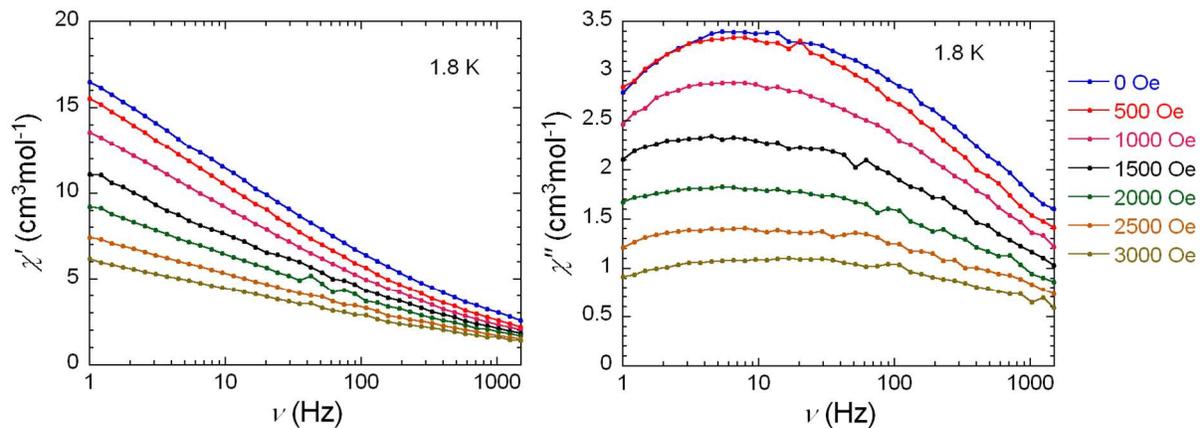
**Figure S5:** The plots of  $M$  vs  $H$  for **Na-2** (left) and **KNa-3** (right).



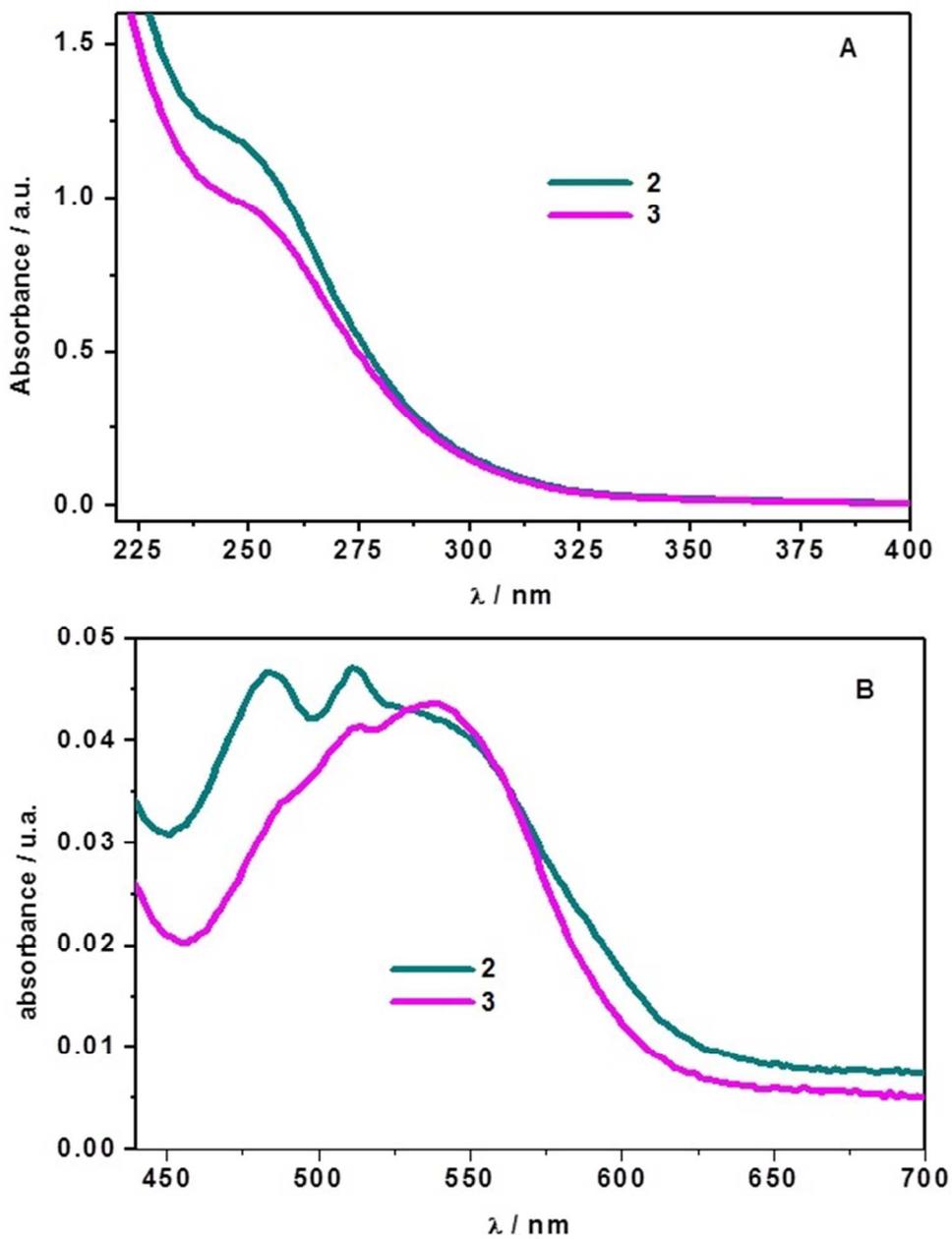
**Figure S6.** The relaxation time as a function of  $1/T$  for **Na-2** (left) and **KNa-3** (right).



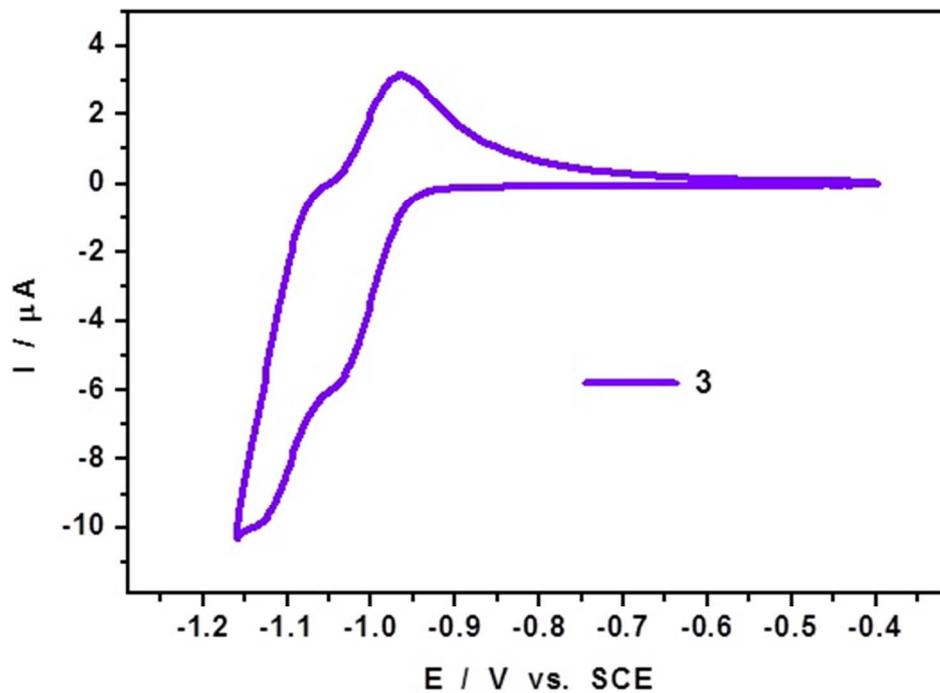
**Figure S7.** Frequency dependence of the in-phase (left) and the out-of-phase (right) components of the ac susceptibility at 1.8 K for **Na-2** under different dc field.



**Figure S8.** Frequency dependence of the in-phase (left) and the out-of-phase (right) components of the ac susceptibility at 1.8 K for **KNa-3** under different dc field.



**Figure S9.** Absorption spectra of **2** and **3** recorded in a pH 7 (1M CH<sub>3</sub>COOLi + CH<sub>3</sub>COOH) medium with a 0.2 cm optical path quartz cuvette. (A) Spectra of the W<sup>VI</sup> centers. (B) Spectra of the Co<sup>II</sup> centers. The polyanion concentration was  $5 \times 10^{-4}$  M.



**Figure S10.** Cyclic voltammograms of the two first  $\text{W}^{\text{VI}}$ -waves of **3** ( $10^{-4}$  M) run in a pH 7 (1M  $\text{CH}_3\text{COOLi}$  +  $\text{CH}_3\text{COOH}$ ) medium. The scan rate was  $10 \text{ mVs}^{-1}$  and the reference electrode was saturated calomel electrode (SCE).