

3D-Transition Metal Mono-Substituted Keggin

Polyoxotungstate with an Antenna Molecule: Synthesis, Structure and Characterization

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Supplementary Materials

Thermogravimetric (TG) Analysis

Thermogravimetric analyses of compounds **1**, **2** and **3** were carried out in nitrogen atmosphere with a heating rate of 10 °C min⁻¹ in the temperature range 42-1000 °C. The TG/DTA curves of compounds **1-3** are shown in Figure S10-S12, respectively. The TG curve of compound **1** shows three distinct stages of weight loss in the temperature range 42-680 °C. The first weight loss of 3.9 % in the temperature range 42–140 °C corresponds to the release of crystallization water and is in agreement with the calculated value of 3.79 %. The successive weight loss of the second step (12 %) from 220 °C to 550 °C is in good agreement with the loss of the six protonated Im molecules (calc. 12.26 %). As expected, the coordinated Im ligand is lost at a higher temperature in a third step from 570 to 680 °C. In this third step the weight loss (3.6 %) is higher than the expected value for one Im molecule, indicating that the lost of the coordinated Im ligand is accompanied by the lost of some oxygen atoms leaving a residue of WO₃, NiO and SiO₂ of 80.5 %, is in good agreement with the calculated value of 80.59 %. The DTA curve reveals two endothermic peaks at 66 °C and 288 °C which correspond to the loss of lattice water and the protonated Im molecules,

respectively. An additional exothermic peak at 631 °C corresponds to the oxidation of the coordinated Im ligand and/or to phase transformations of the residual inorganic oxides. As expected, the thermal behaviors of **2** and **3** are very similar to that of **1**.

The IR spectra (Figures S8-S9) and XRPD patterns (Figures S13-S14) of compounds **1** and **2** after heating to 550 °C have been performed, which strongly support the TG/DTA results, and suggest that the polyanions $[\text{SiW}_{11}\text{O}_{39}\text{ZIm}]^{6-}$ ($\text{Z} = \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}}$ and Co^{II}) are remarkably stable until 550 °C.

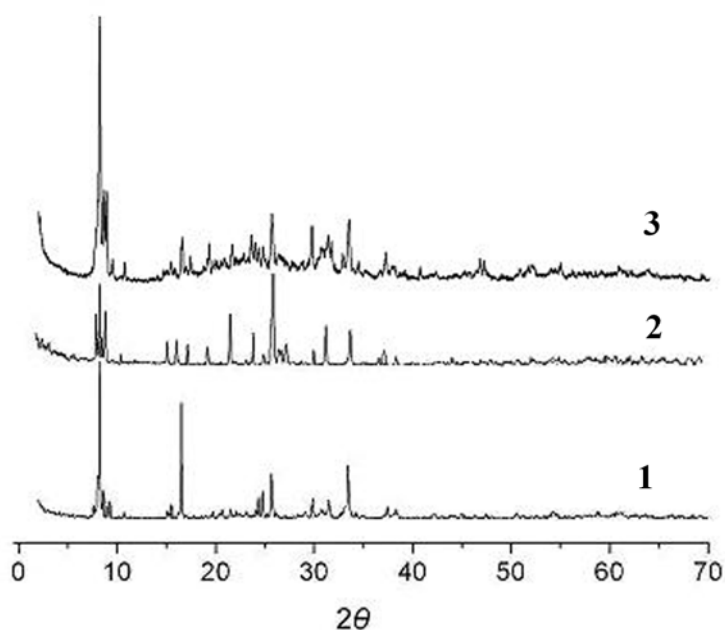


Figure S1. Experimental XRPD patterns of compound **1**, **2** and **3**.

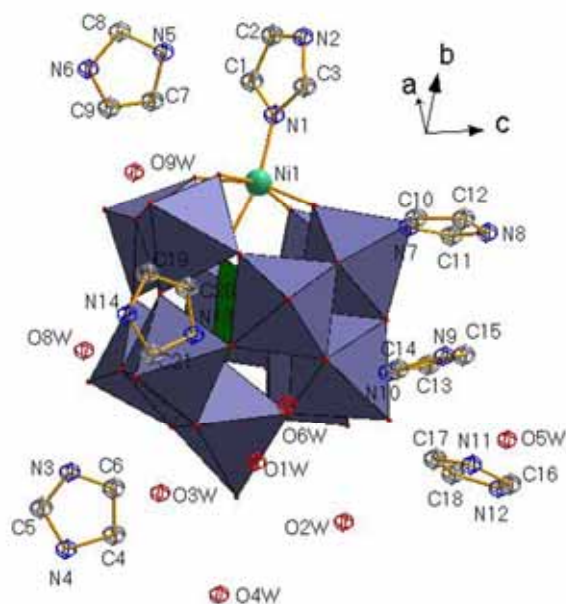


Figure S2. The molecular structure of compound **1**, showing the positions of polyanion and counteractions HIm^+ , and H_2O molecules. Hydrogen atoms are omitted for clarity.

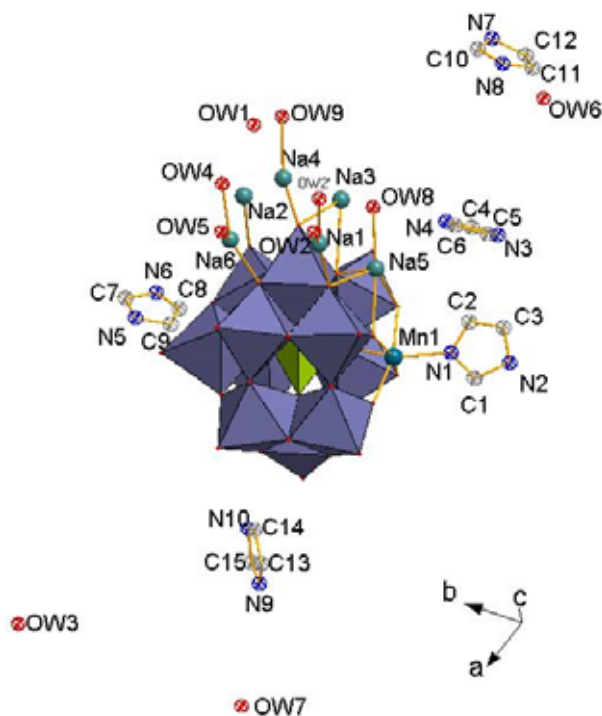


Figure S3. The molecular structure of compound **2**, showing the positions of polyanion and counteractions Na^+ , and H_2O and Im molecules. Hydrogen atoms are omitted for clarity.

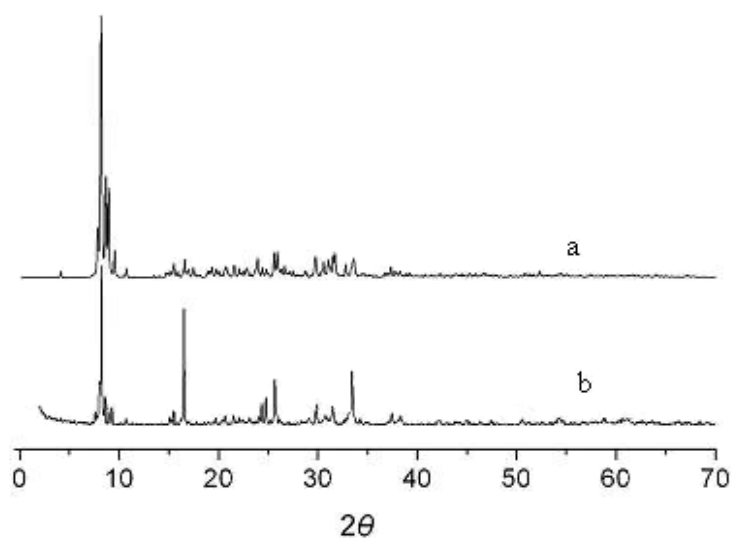


Figure S4. (a) Simulated and (b) experimental XRPD patterns of compound **1**.

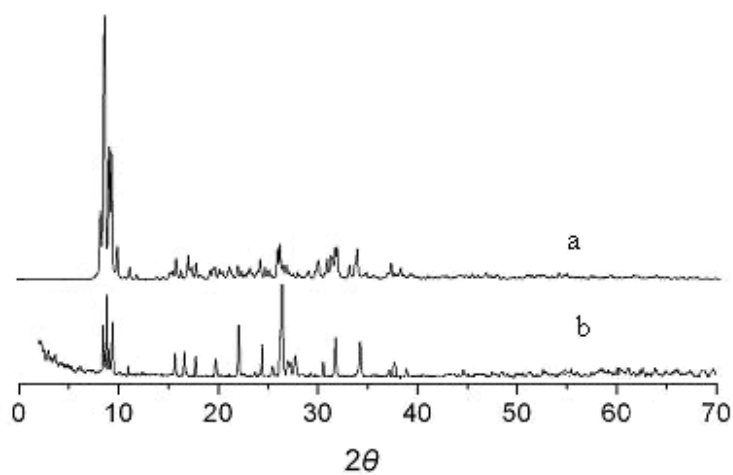


Figure S5. (a) Simulated and (b) experimental XRPD patterns of compound **2**.

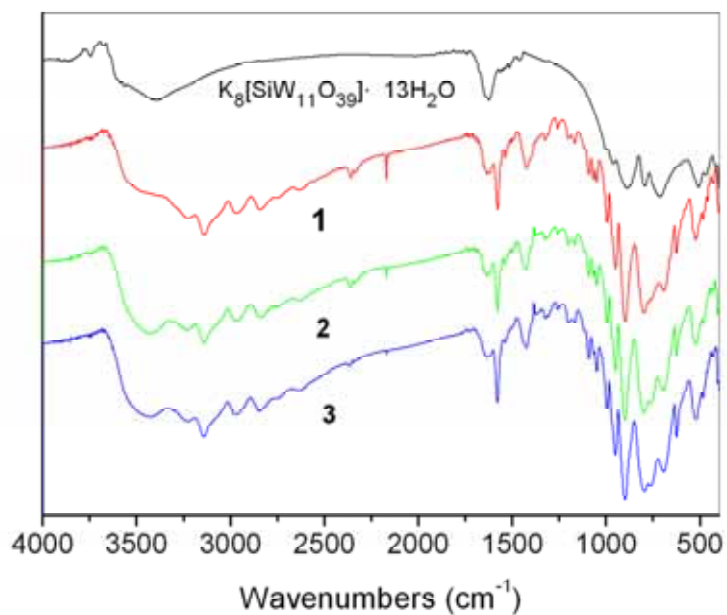


Figure S6. IR spectra for precursor, compounds **1**, **2** and **3**.

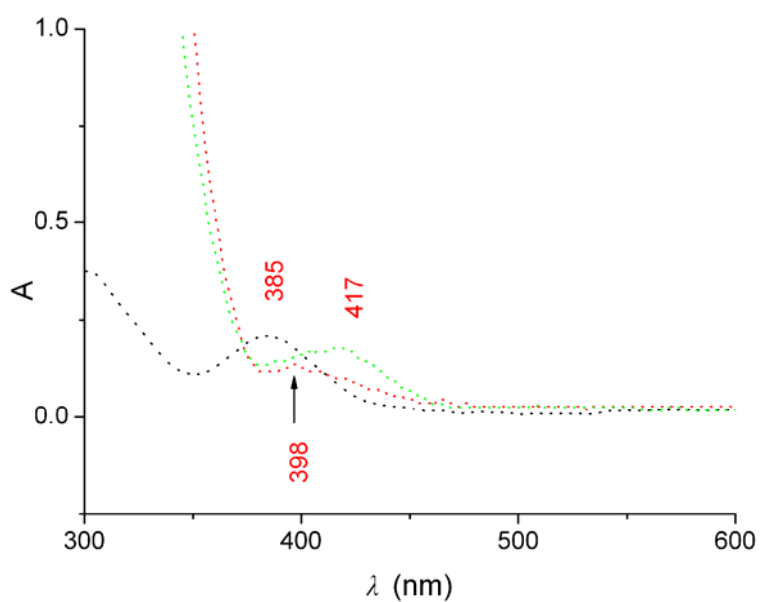


Figure S7. UV-vis spectra of the solution of compound **1** (green), $[SiW_{11}O_{39}Ni(H_2O)]^{6-}$ (red) and Ni complexes (black) in distilled water.

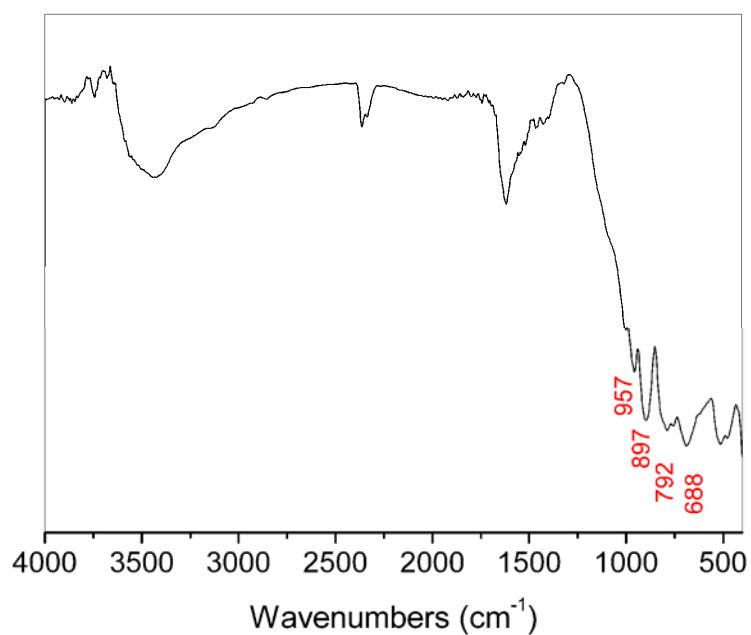


Figure S8. IR spectrum of compound **1** after heated to 550 °C.

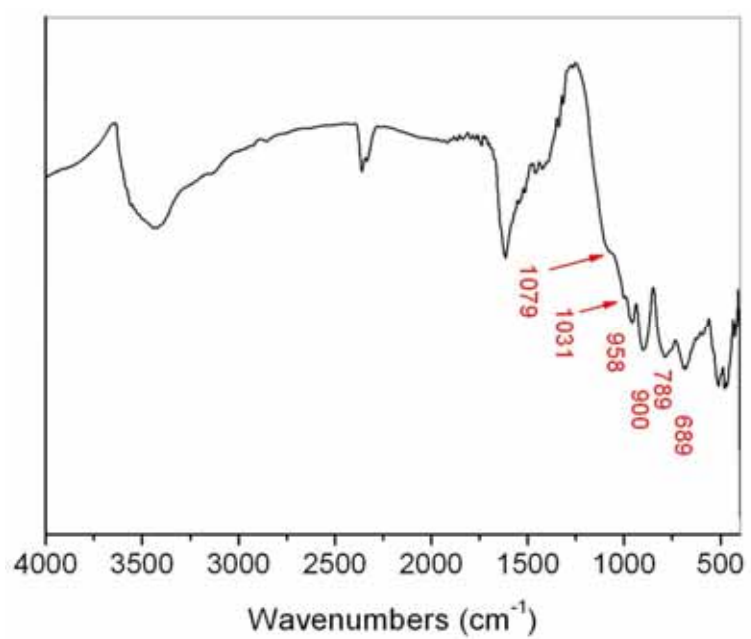


Figure S9. IR spectrum of compound **2** after heated to 550 °C.

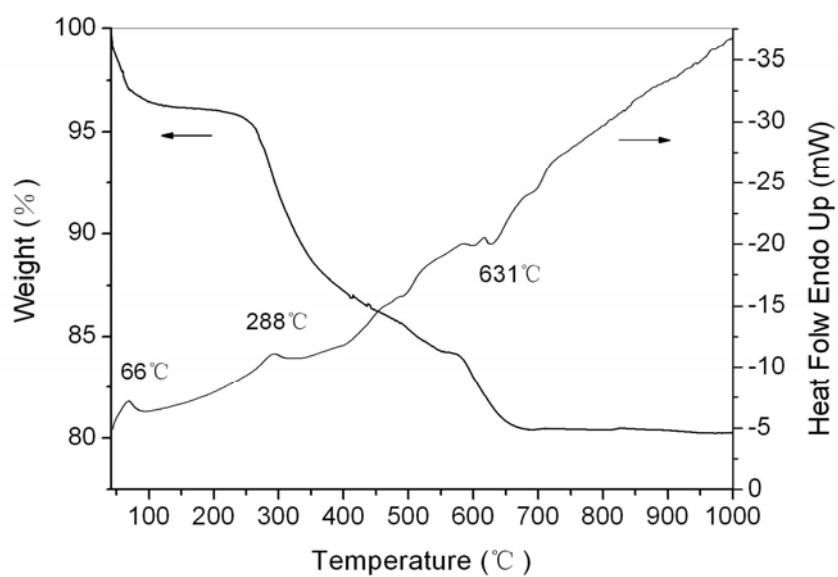


Figure S10. TG and DTA curves of compound 1.

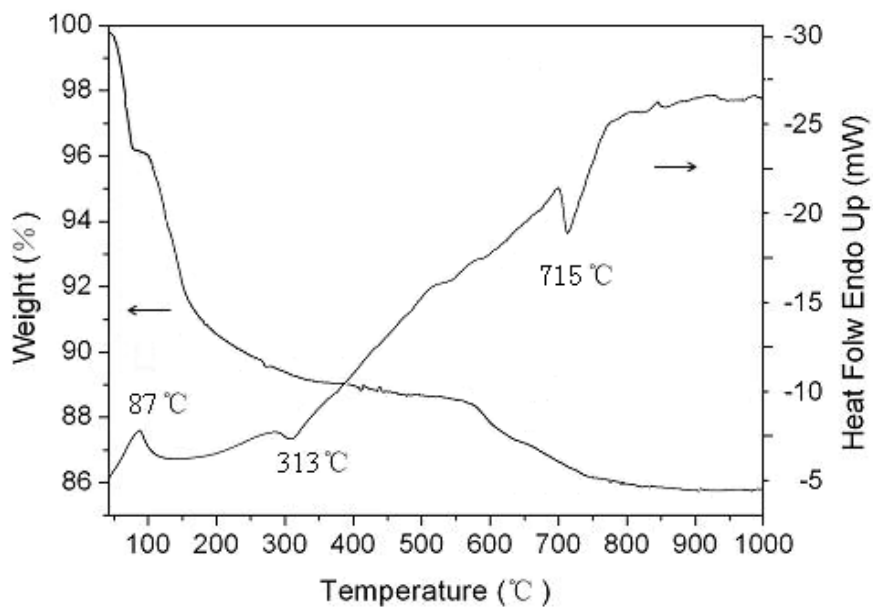


Figure S11. TG and DTA curves of compound 2.

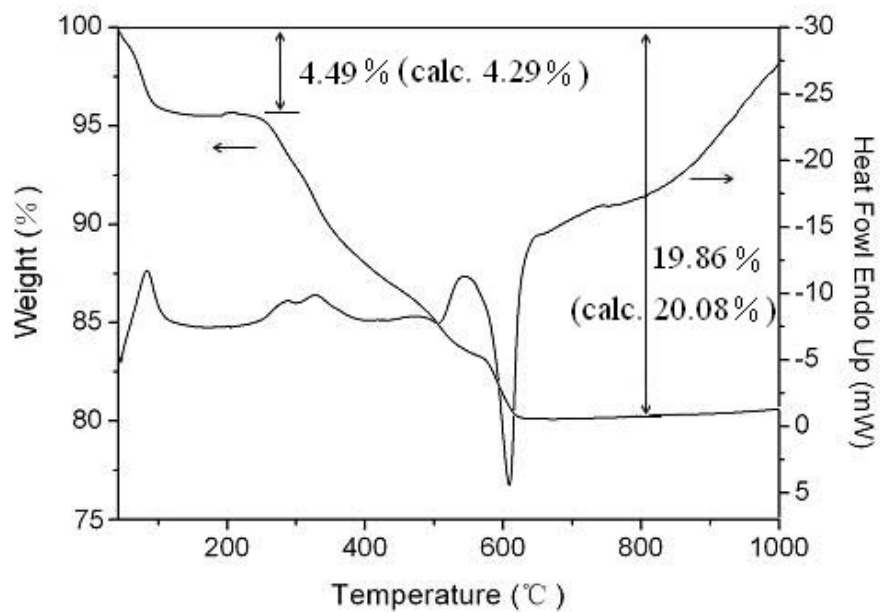


Figure S12. TG and DTA curves of compound 3.

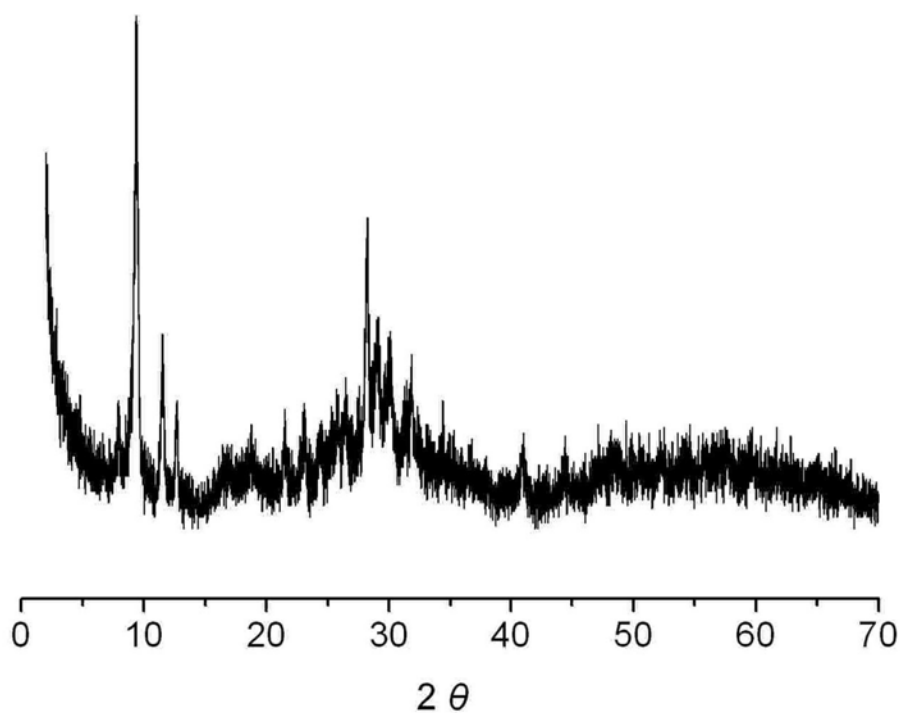


Figure S13. Experimental XRPD patterns of compound 1 after heated to 550 °C.

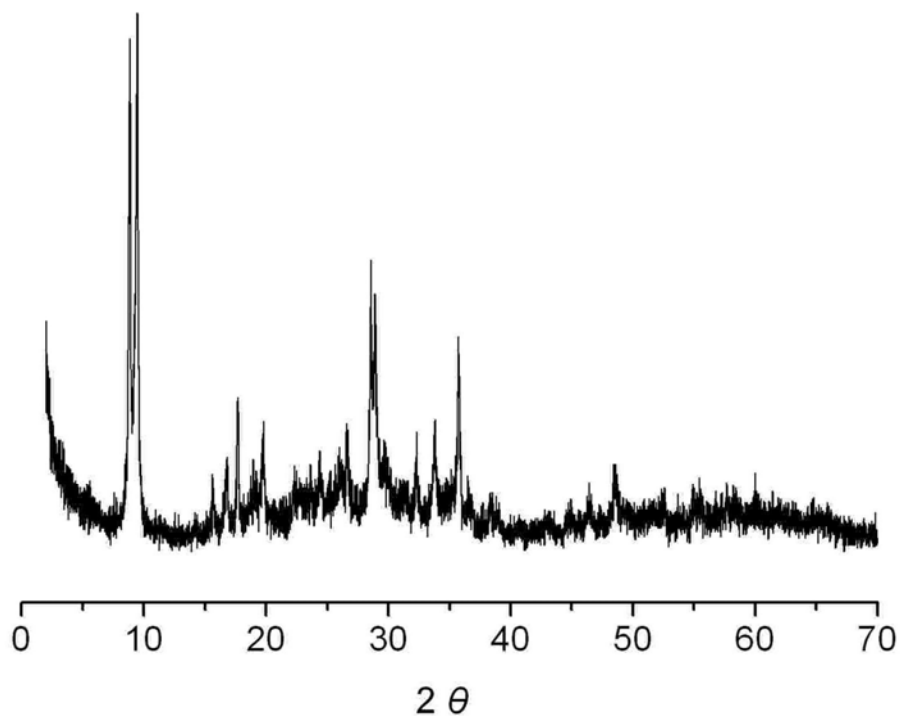


Figure S14. Experimental XRPD patterns of compound **2** after heated to 550 °C.

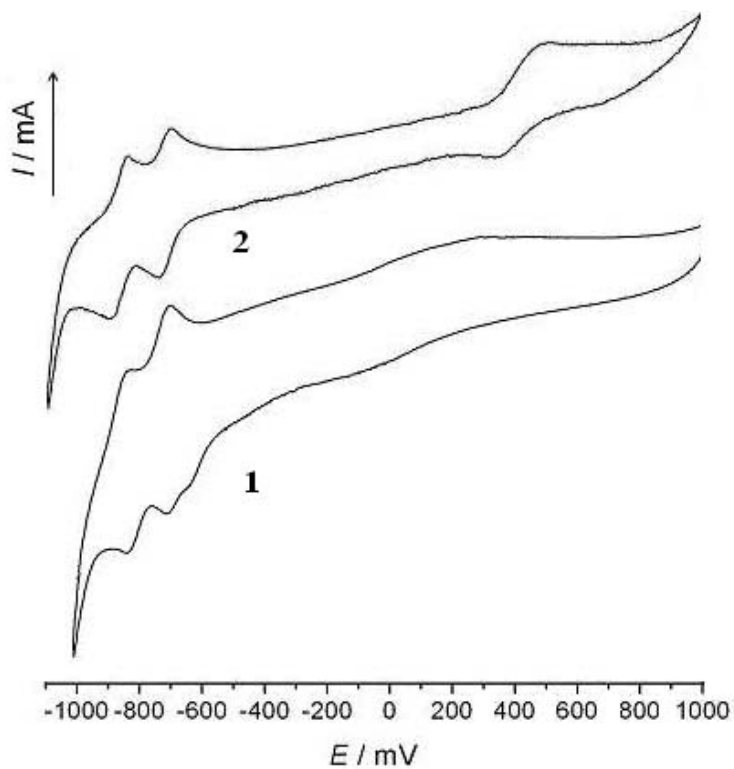


Figure S15. Cyclic voltammograms of compounds **1** and **2** (glassy-carbon working electrode, scan-rate 50mV s^{-1} , 0.5 M KAc/HAc buffer solution, pH 4.7).

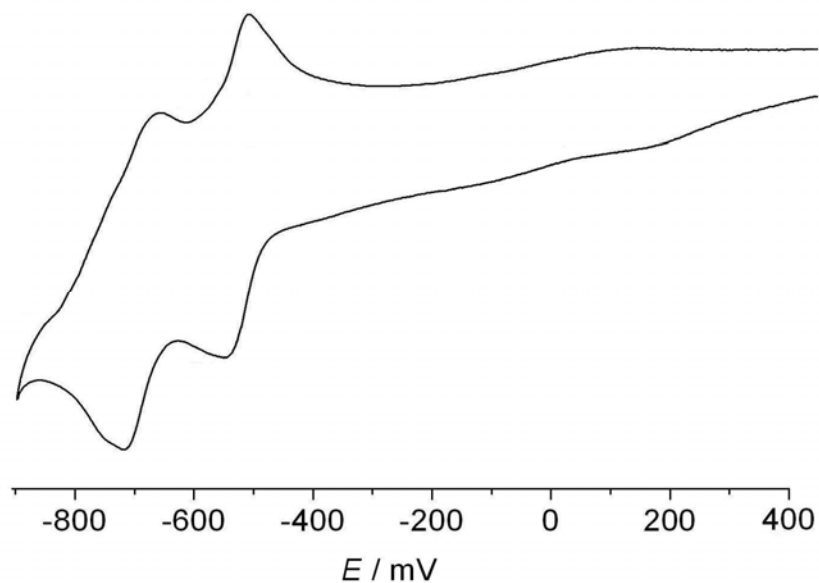


Figure S16. Cyclic voltammogram of compound $[\text{SiW}_{11}\text{O}_{39}\text{Ni}(\text{H}_2\text{O})]^{6-}$ (glassy-carbon working electrode, scan-rate 50mV s^{-1} , 0.5 M KAc/HAc buffer solution, pH 4.7).

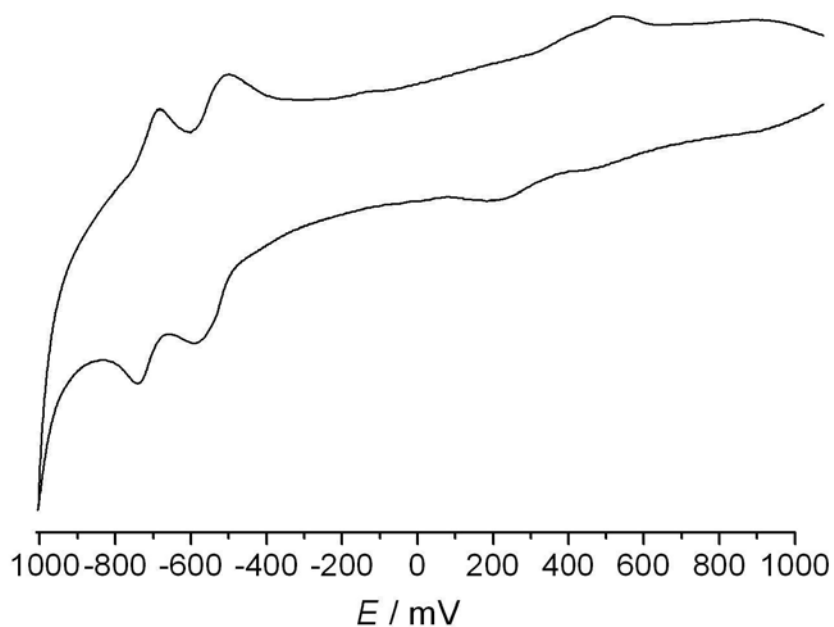


Figure S17. Cyclic voltammogram of compound $[\text{SiW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})]^{6-}$ (glassy-carbon working electrode, scan-rate 50mV s^{-1} , 0.5 M KAc/HAc buffer solution, pH 4.7).

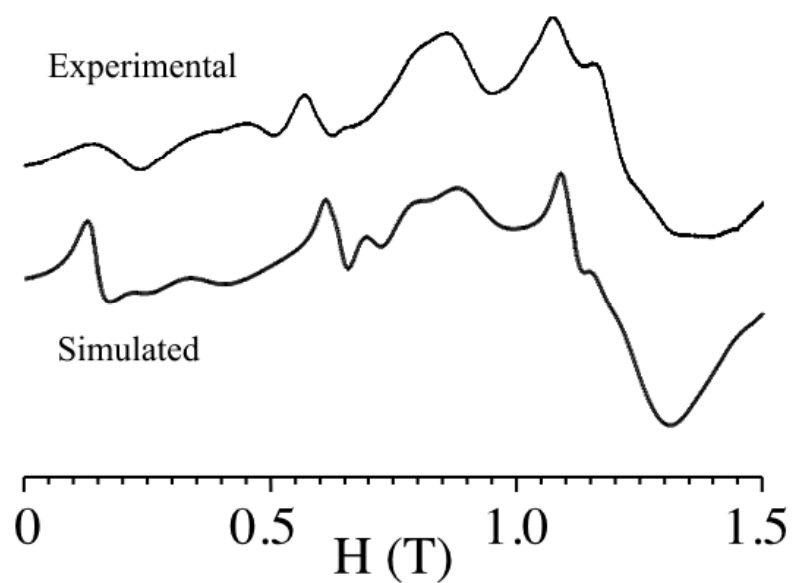


Figure S18. Experimental and simulated EPR spectra at 15 K of compound **2**.

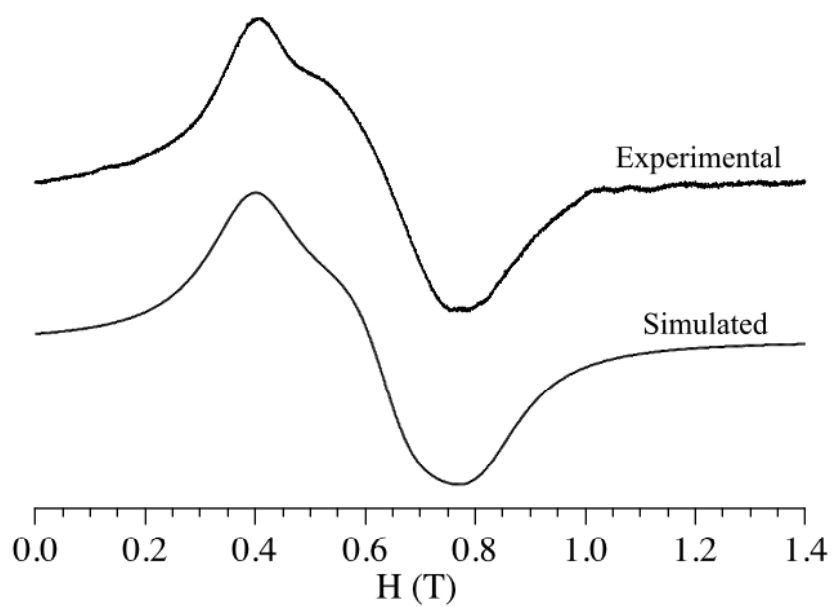


Figure S19. Experimental and simulated EPR spectra at 50 K of compound **3**.

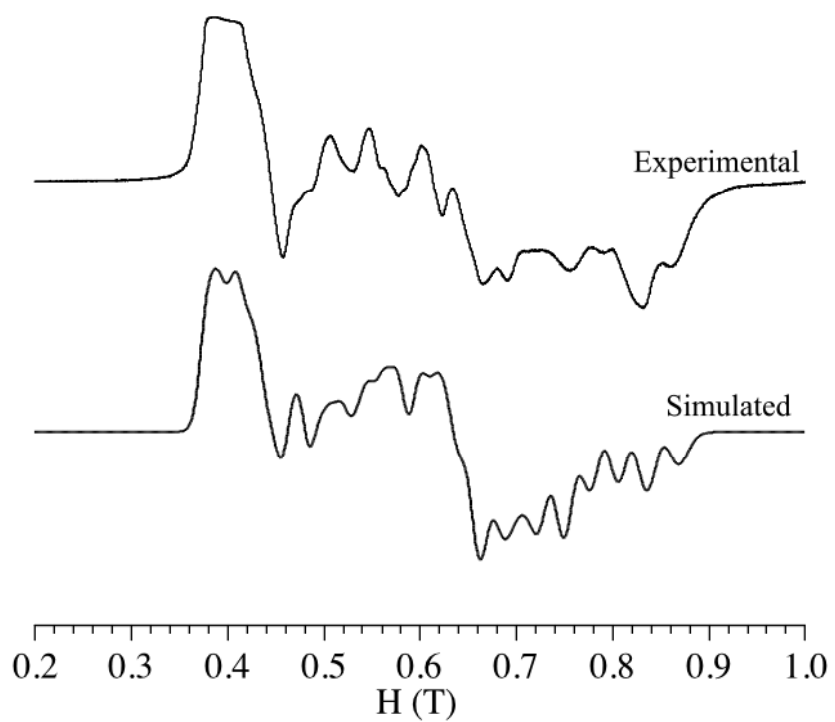


Figure S20. Experimental and simulated EPR spectra at 5 K of compound **3**.