

Supporting Information

Cyclic Tungstoselenites Based on $\{\text{Se}_2\text{W}_{12}\}$ Units

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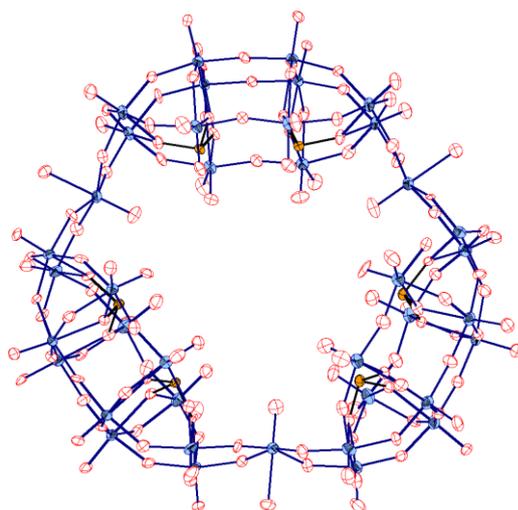


Figure S1. Thermal ellipsoid representation of $[(\text{Se}_2\text{W}_{12}\text{O}_{46}(\text{WO}(\text{H}_2\text{O}))_3)]^{24-}$ (**1**).

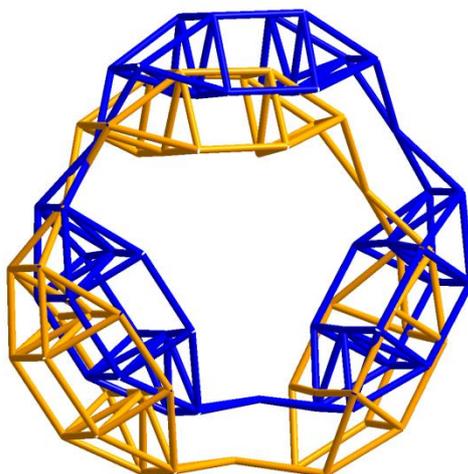


Figure S2. Solid state disorder model for the polyanions $[(\text{Se}_2\text{W}_{12}\text{O}_{46}(\text{WO}(\text{H}_2\text{O}))_3)]^{24-}$ (**1**) in **Na1**, showing only the heavy atoms W and Se.

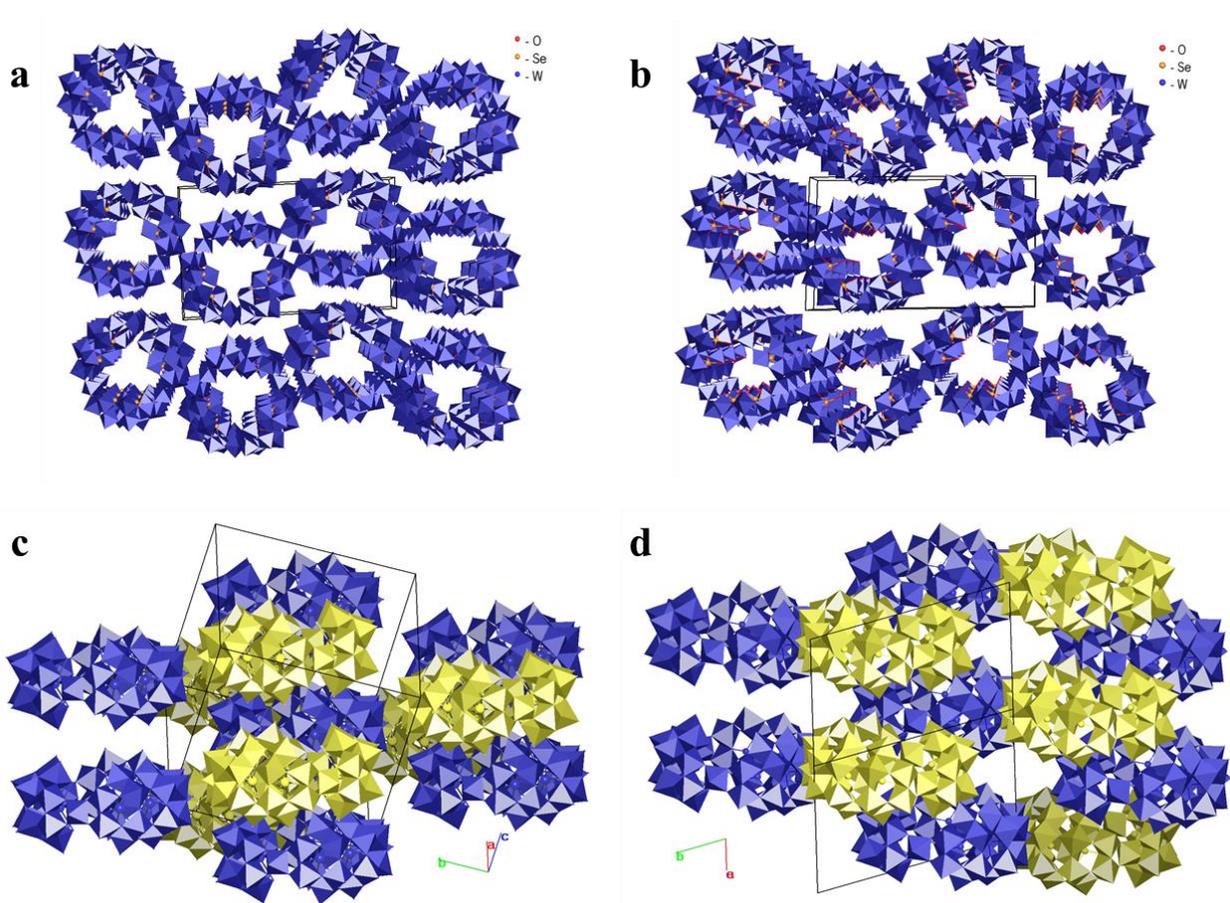


Figure S3. Crystal packing of the polyanions in **Na1** (a) and **KNa1** (b); and the hcp packing of the polyanions in **Na1** (c) and bcc in **KNa1** (d). Polyhedral view; different hexagonal layers are highlighted by blue and yellow, respectively.

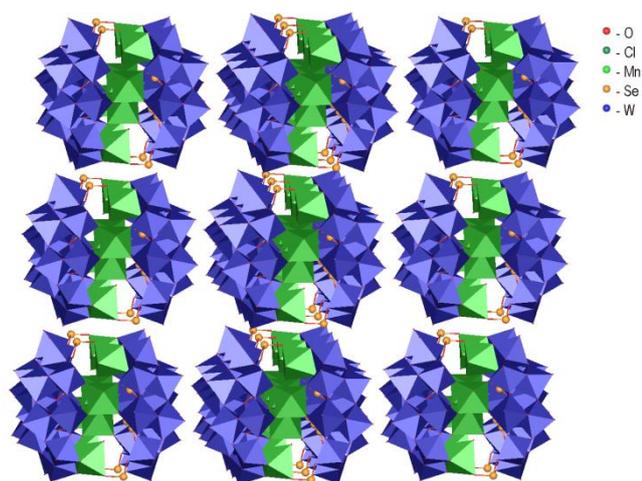


Figure S4. Crystal packing of the polyanions in Na₂'. Blue and green octahedra correspond to WO₆ and MnL₆, respectively.

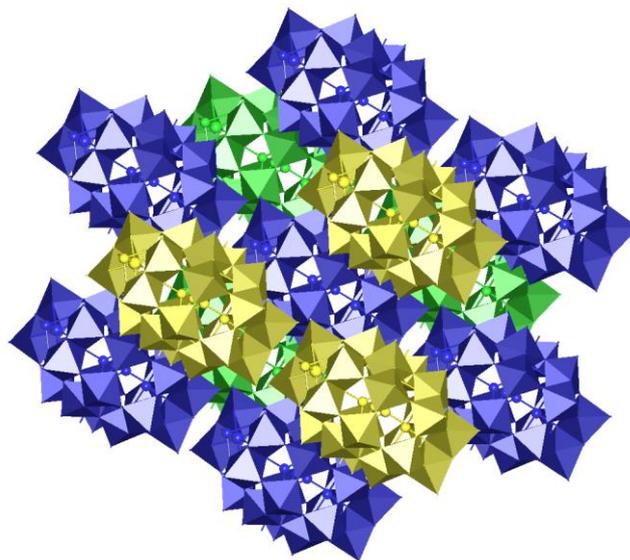


Figure S5. The distorted, three-layered, face-centered cubic (fcc) packing of the polyanion $[(\text{Se}_2\text{W}_{12}\text{O}_{46})_2\{\text{Mn}_2\text{Cl}(\text{H}_2\text{O})_2\}\{\text{Mn}(\text{H}_2\text{O})_2\}_2(\text{SeO})_2]^{13-}$ (**2**) in **Na2** (polyhedral view). The three layers are highlighted in yellow, blue, and green.

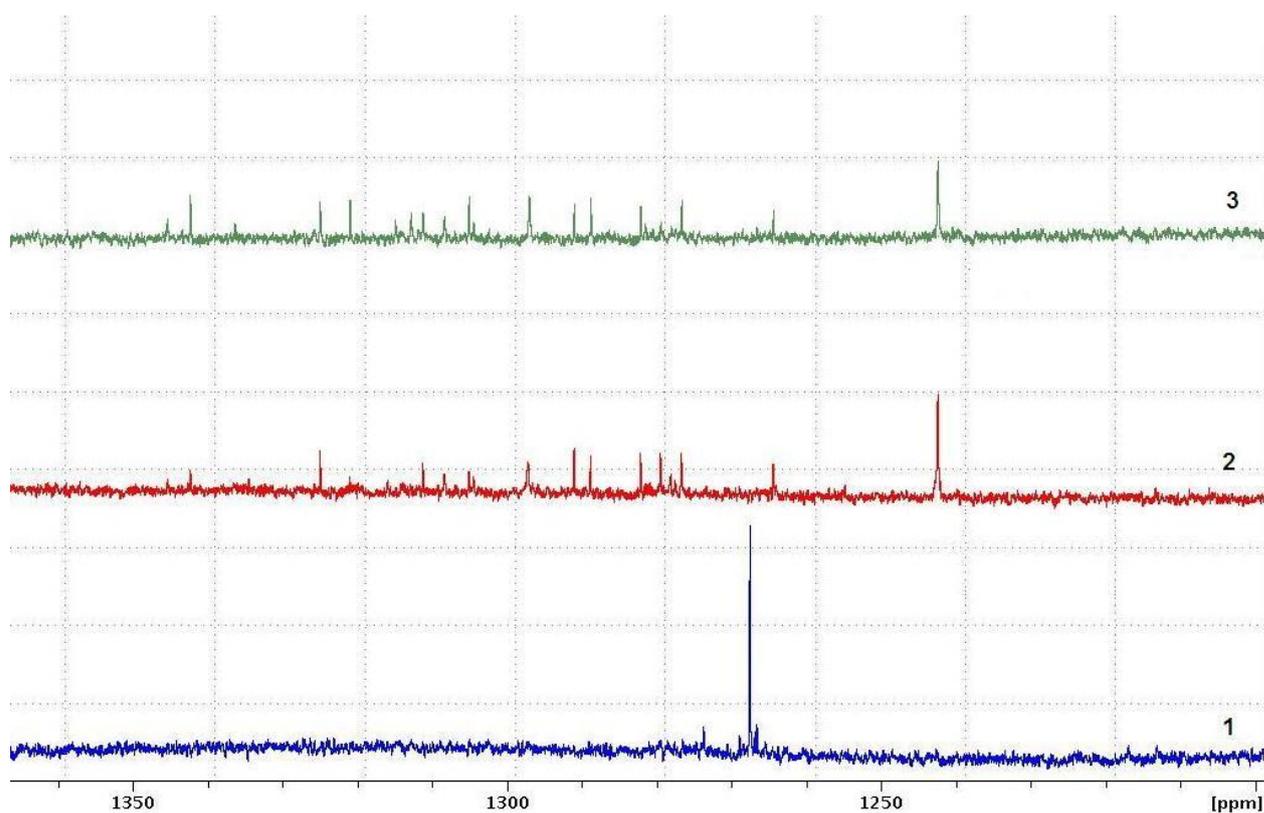


Figure S6. ^{77}Se NMR of $\text{Na}_{24}[\text{H}_6\text{Se}_6\text{W}_{39}\text{O}_{144}] \cdot 74\text{H}_2\text{O}$ (**Na1**) dissolved in D_2O using a 5 mm tube: 1 - spectrum recorded immediately after dissolution; 2 - spectrum recorded 4 h after dissolution; 3 - spectrum recorded 16 h after dissolution.

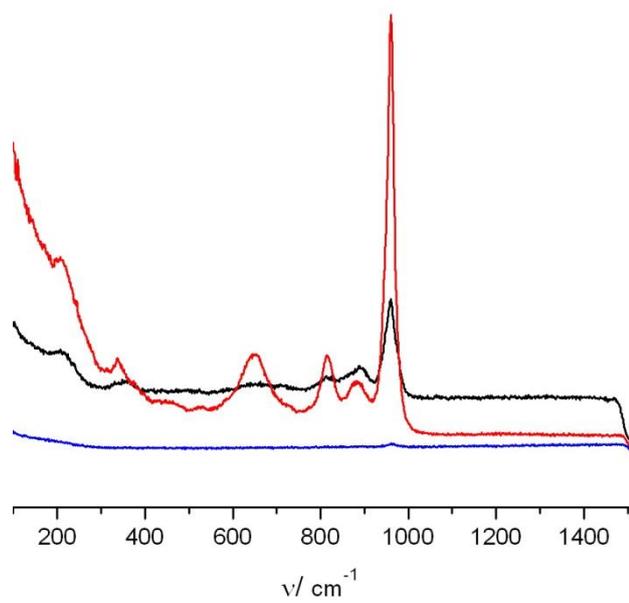


Figure S7. Raman spectra of **Na1**: reaction mixture (black), dry **Na1** (red), and aqueous solution of **Na1** (blue).

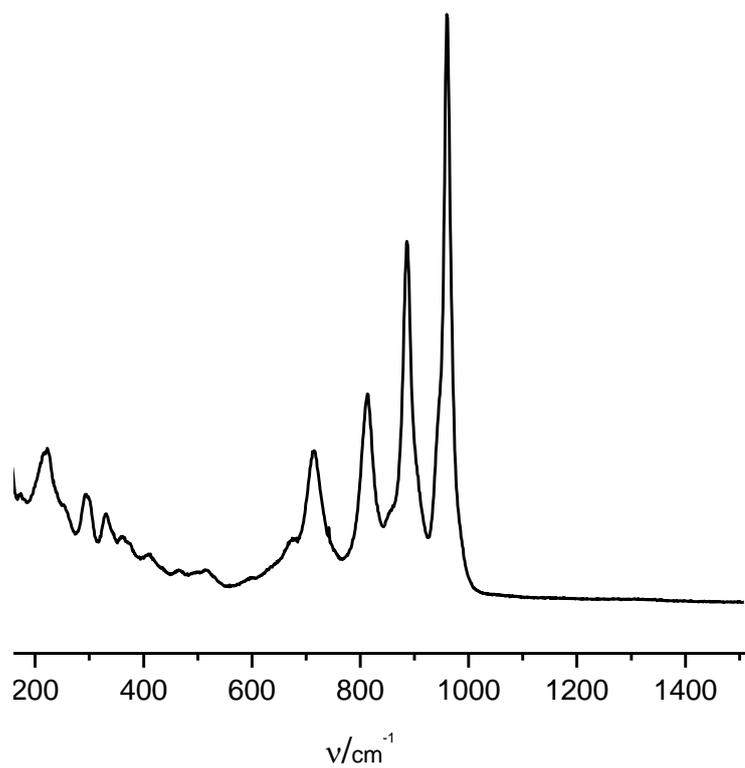


Figure S8. Raman spectrum of Na₂.

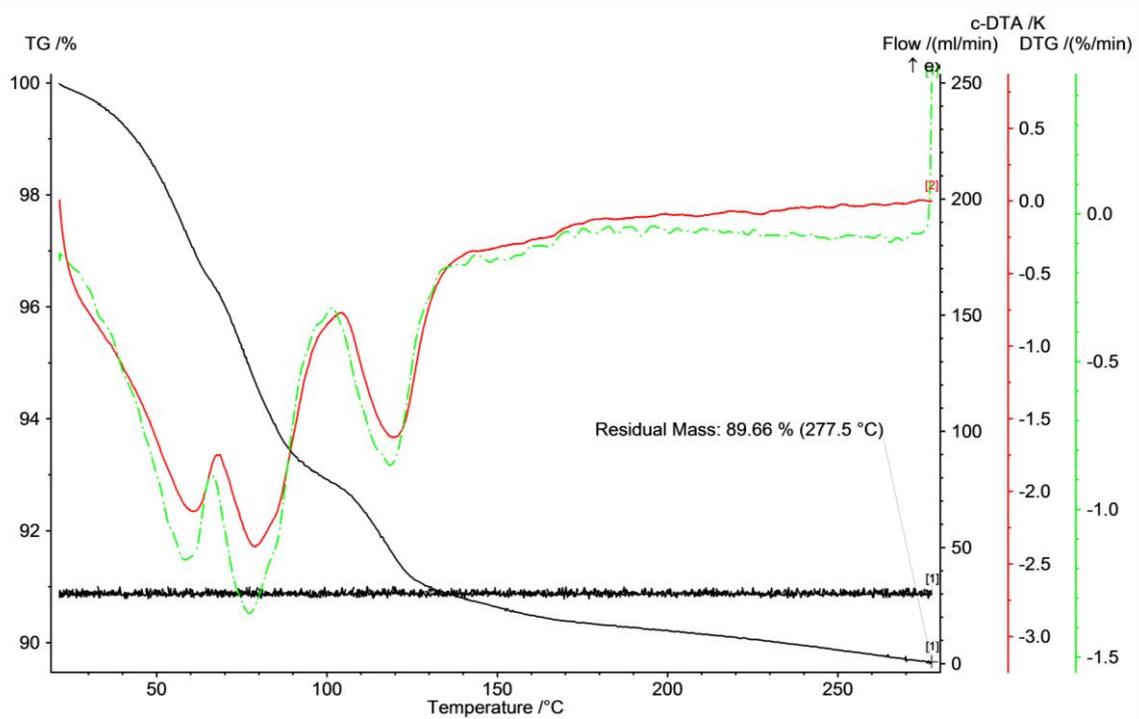


Figure S9. Thermogram of Na1.

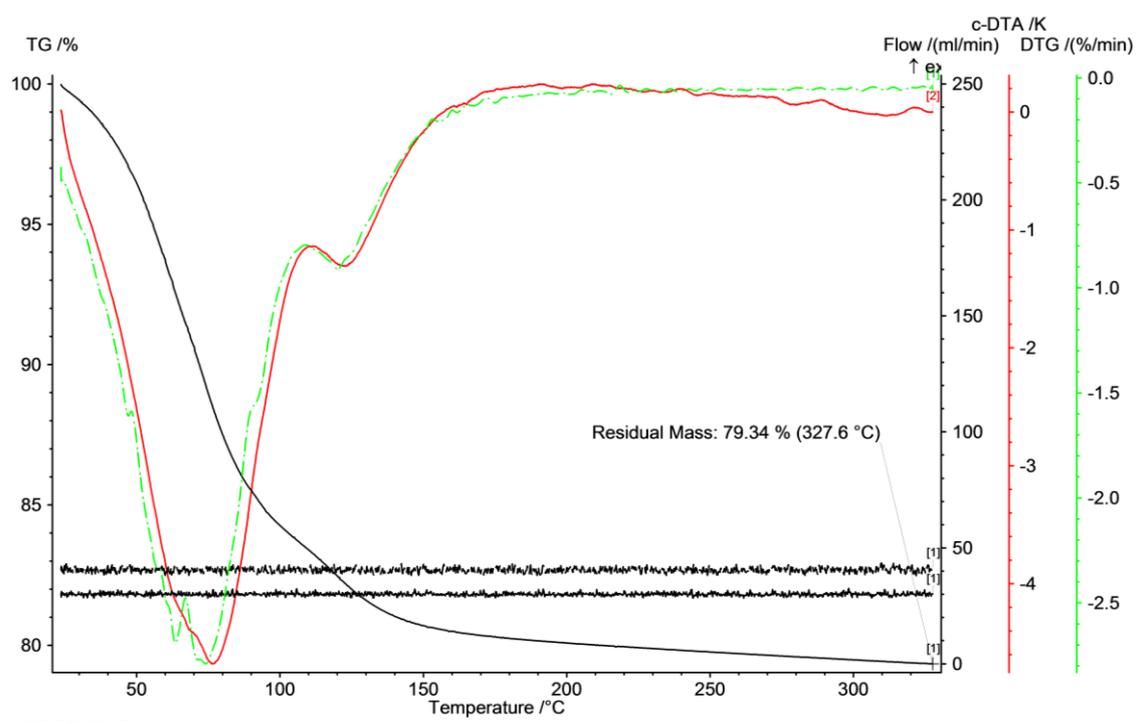


Figure S10. Thermogram of Na₂.