

SI

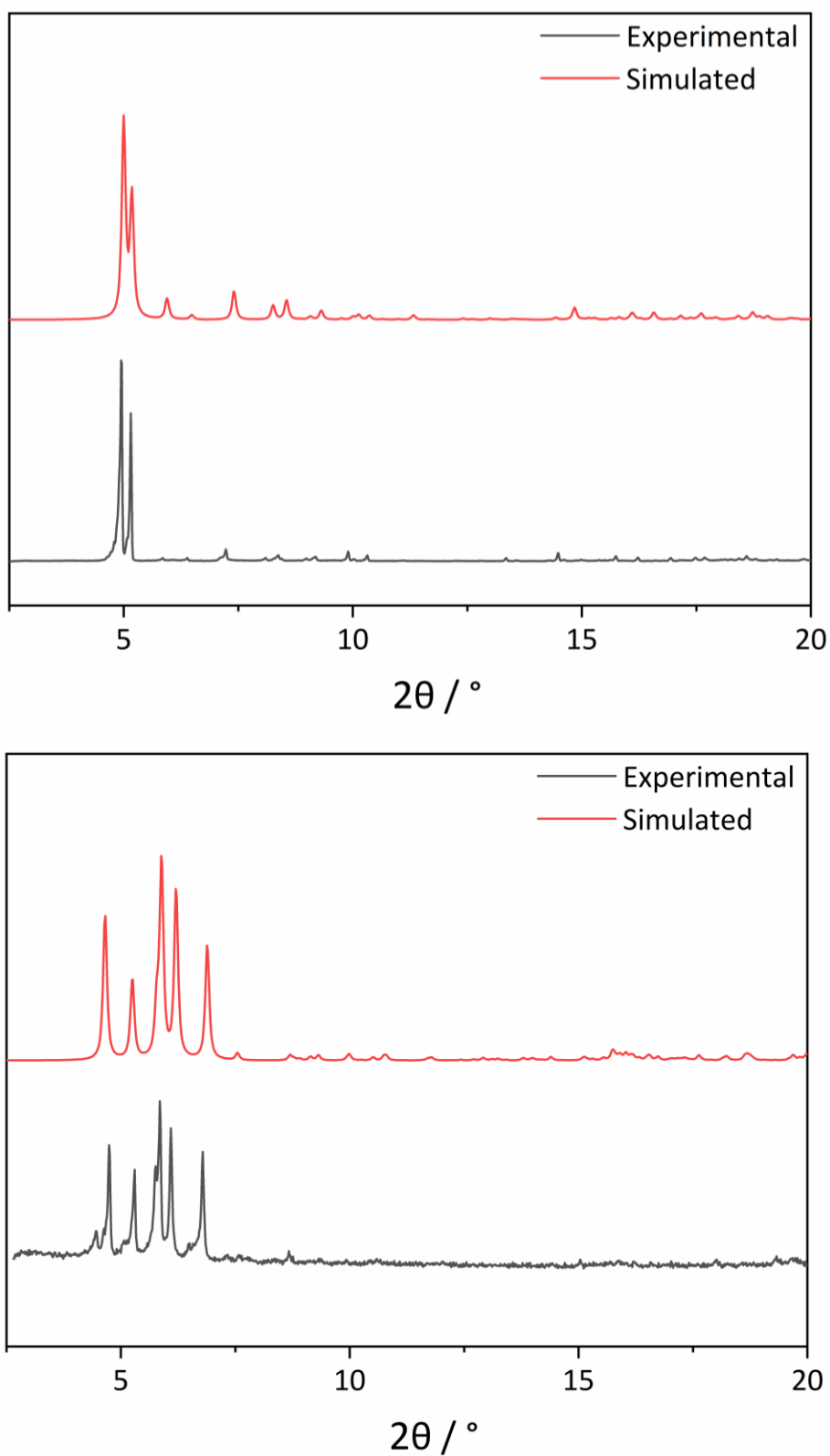


Figure S1. PXRD data for **1** (top) and **2** (bottom).

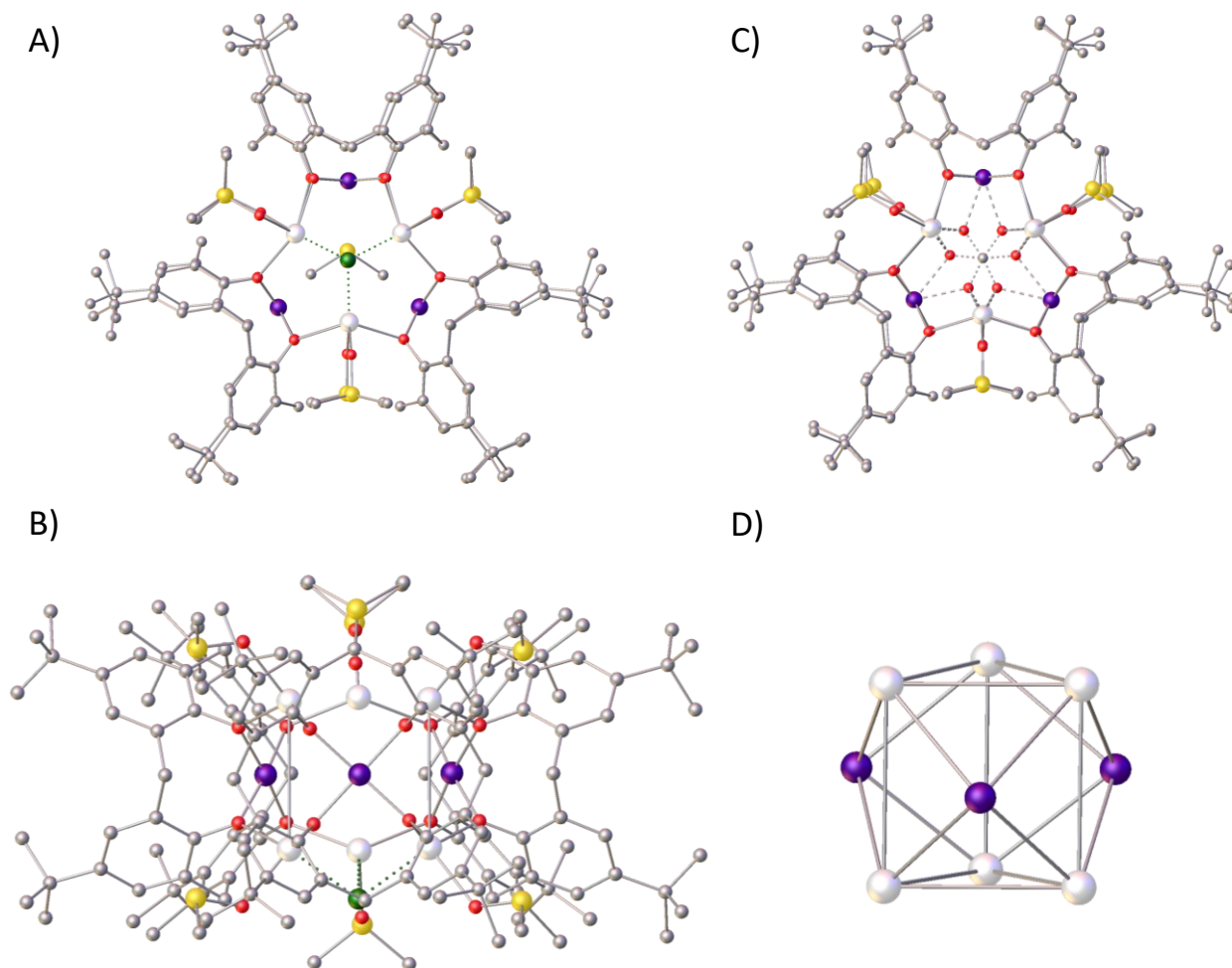


Figure S2. A) The molecular structure of complex **1** viewed down the *c*-axis of the cell. H atoms, solvent molecules and the disordered carbonate ion are omitted for clarity. B) The molecular structure of complex **1** viewed down the *b*-axis of the cell. H atoms, solvent molecules and the disordered carbonate ion are omitted for clarity. C) The molecular structure of complex **1** viewed down the *c*-axis of the cell, with the disordered carbonate ion included and the capping dmsu, Cl ion, H atoms and solvent molecules removed. D) Metallic skeleton of **1** highlighting the tricapped trigonal prism. Colour code: Mn^{III} = dark purple, Na = white, O = red, C = grey, S = yellow, Cl = green.

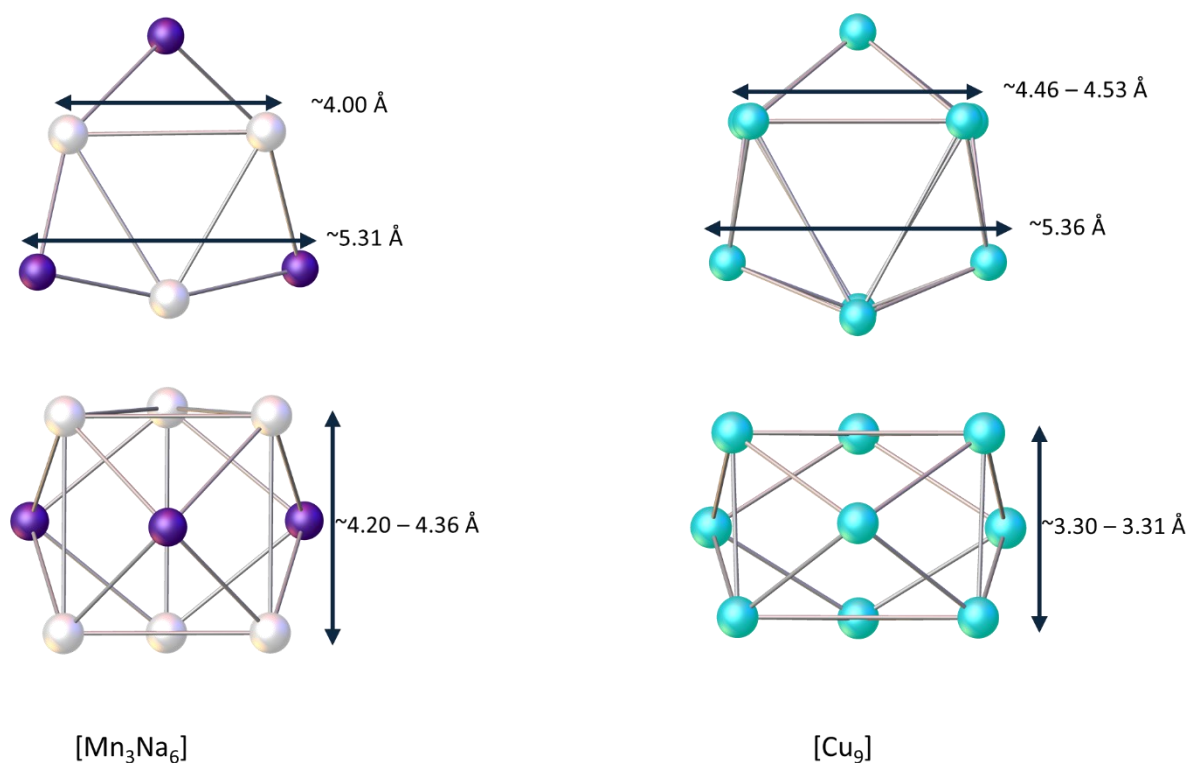


Figure S3. Comparison of the metallic skeleton of **1** (left) with $[\text{Cu}_9]$ (right). Colour code: Mn^{III} = dark purple, Na = white, Cu^{II} = turquoise. Figures not to scale.

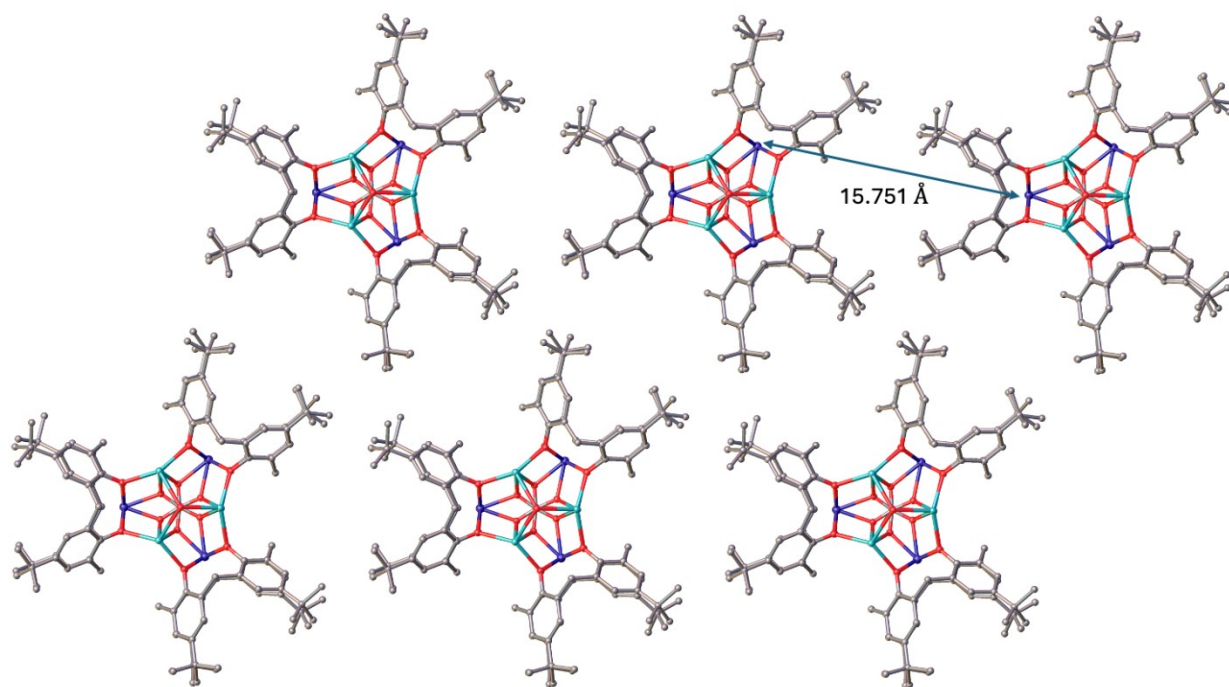


Figure S4. View of the *ab* plane in the extended structure of **1** with closest inter-cluster Mn...Mn distance highlighted. Ligated solvent molecules, Cl anions, H atoms and MeCN of crystallisation have been omitted for clarity. Disordered ^tBu groups are shown in just one position.

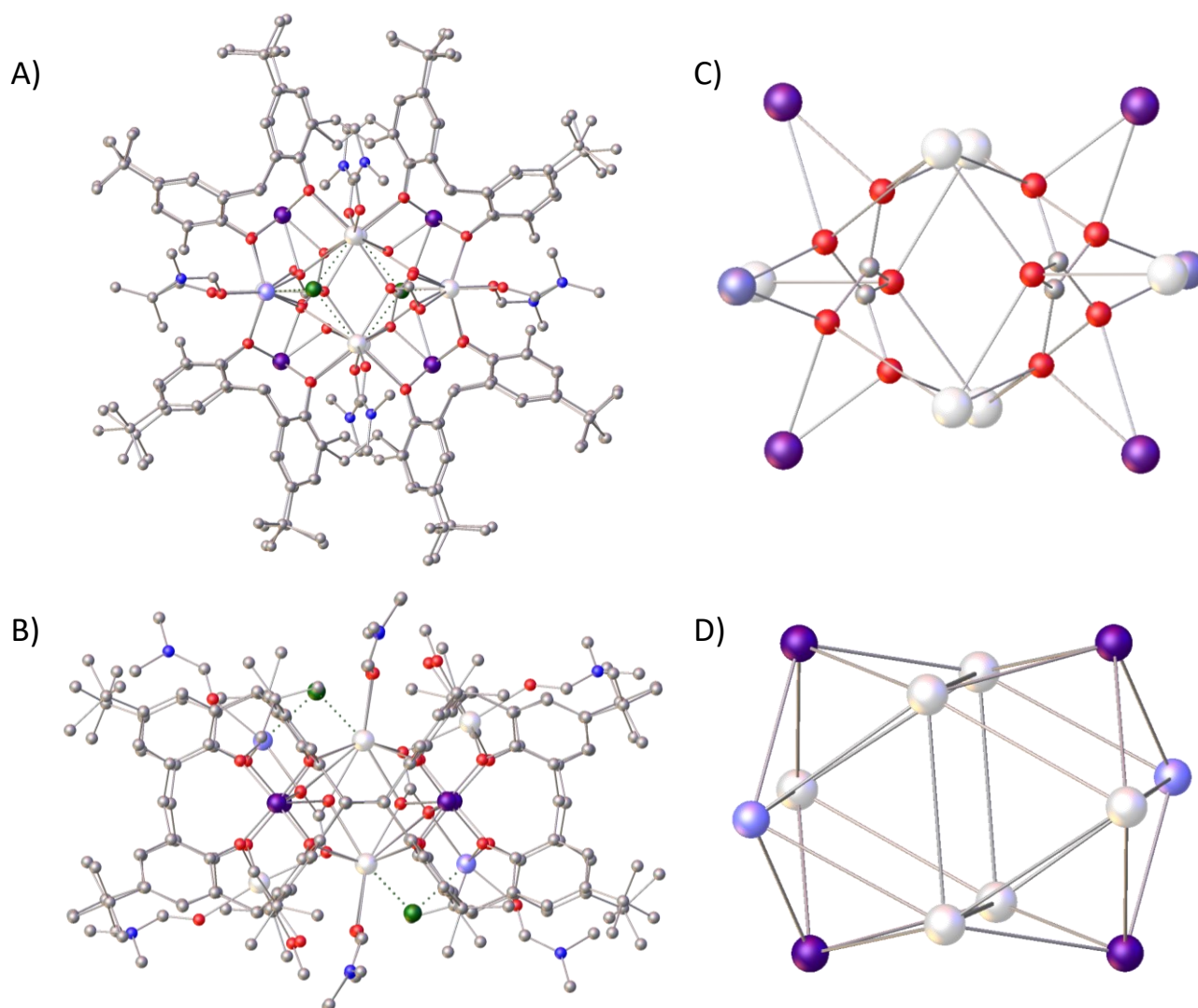


Figure S5. A)-B) Orthogonal views of the structure of **2**. C) View of the bonding of the disordered carbonate ions in **2**. D) Metallic skeleton of **2**. Colour code: Mn^{III} = dark purple, Mn^{II} = light purple, Na = white, O = red, C = grey, N = blue, Cl = green.

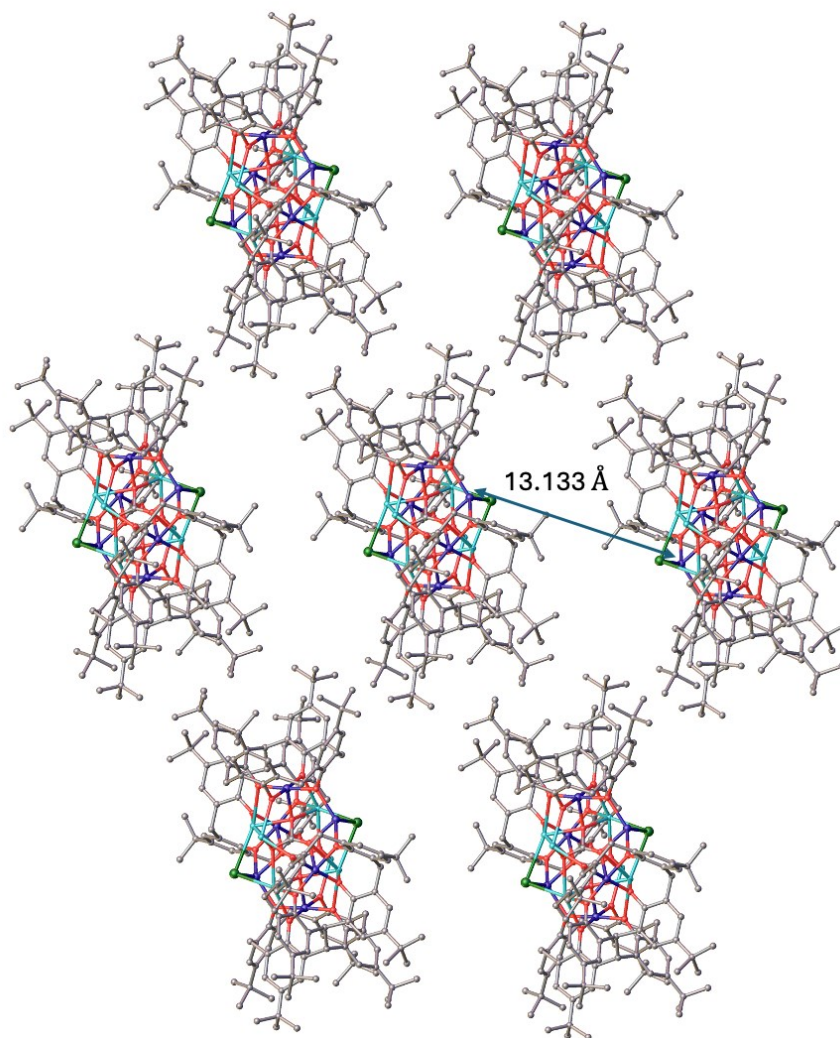


Figure S6. View along the *b* axis showing layers in the *ab* plane in the extended structure of **2** with closest inter-cluster Mn···Mn distance highlighted. Ligated solvent, H atoms and co-crystallised solvent molecules have been omitted for clarity. Disorder related to ^tBu, methylene bridging, and carbonate anions in the cluster core is shown in only one position.

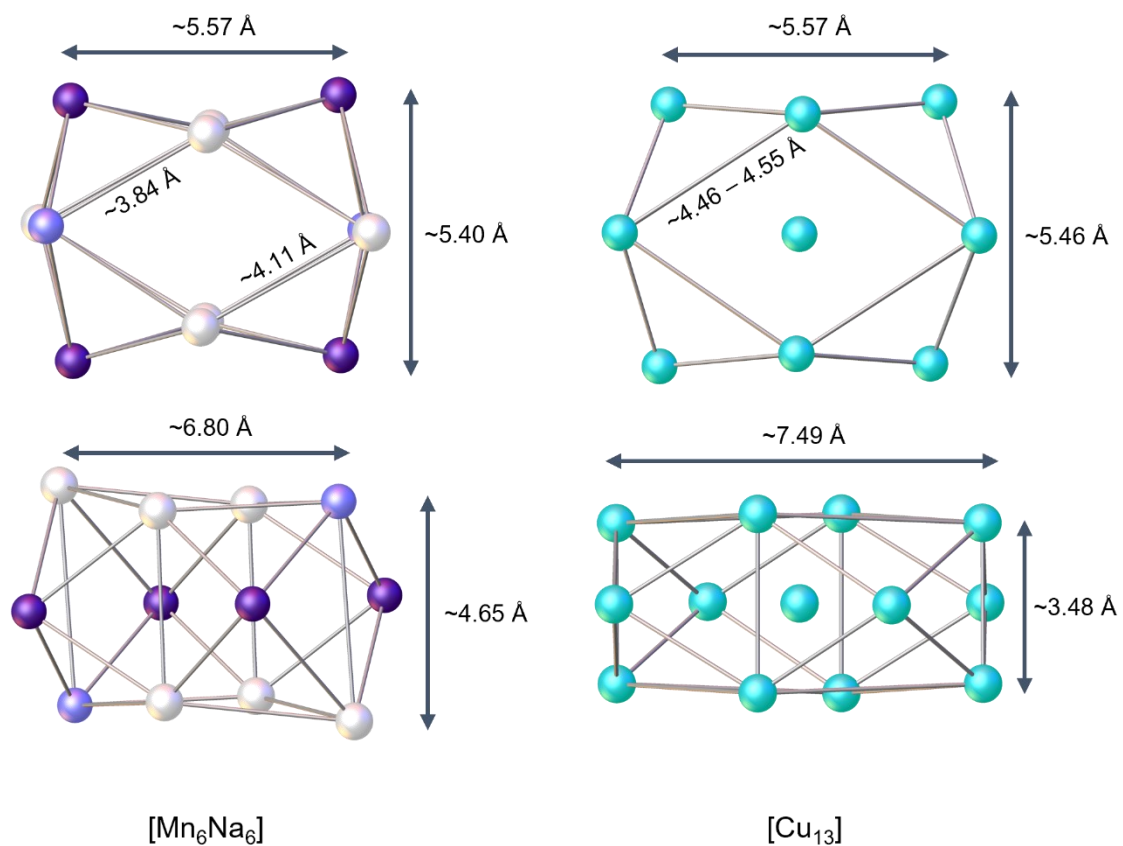


Figure S7. Comparison of the metallic skeletons of **2** (left) and [Cu₁₃] (right). Colour code: Mn^{III} = dark purple, Mn^{II} = pale purple, Na = white, Cu^{II} = turquoise.

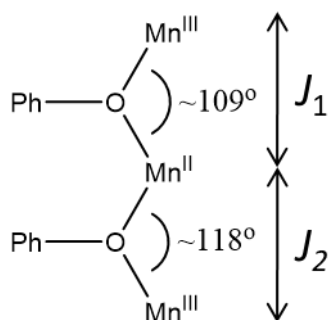


Figure S8. Model of the magnetic exchange interaction scheme used to simultaneously fit the susceptibility and magnetisation data for compound **2**.