

Supplementary Information

Stereoisomerism in polyoxometalates: structural and spectroscopic studies of bis(malate)-functionalized cluster systems

Xikui Fang, Travis M. Anderson, Yu Hou and Craig L. Hill*

Experimental:

Synthesis of $\text{K}_8\text{Na}_{10}[(\alpha\text{-P}_2\text{W}_{16}\text{O}_{59})\text{Zr}_2(\mu_3\text{-O})(\text{L-C}_4\text{O}_5\text{H}_3)]_2 \cdot 54\text{H}_2\text{O}$ (L,L-(+)-2). A 0.24 g (0.71 mmol) sample of $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is dissolved in 30 mL of deionized water, and 0.2 g (1.45 mmol) of L-malic acid is added, resulting in a slurry. The mixture is refluxed for 2 h and then cooled to room temperature. Solid $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}] \cdot 18\text{H}_2\text{O}$ (2.0 g, 0.46 mmol) is quickly added with vigorous stirring. After stirring for 30 min, KCl (0.2 g, 2.7 mmol) is added. The solution is then heated to 80 °C for 45 min before cooling to room temperature. Slow evaporation of the solution produces prismatic crystals (0.45 g, yield 21.3%, based on W) in a week. $[\alpha]_D^{20} = 1.8$ ($c = 1.0$ in H_2O). Elemental analysis: Calcd Zr, 3.62; P, 1.23; W, 58.42. Found Zr, 3.83; P, 1.31; W, 58.19. **$\text{K}_8\text{Na}_{10}[(\alpha\text{-P}_2\text{W}_{16}\text{O}_{59})\text{Zr}_2(\mu_3\text{-O})(\text{D-C}_4\text{O}_5\text{H}_3)]_2 \cdot 50\text{H}_2\text{O}$ (D,D-(-)-2)** is prepared in the similar way except that D-malic acid was used instead of L-malic acid (yield 25.4%, based on W). $[\alpha]_D^{20} = -1.6$ ($c = 1.0$ in H_2O). Elemental analysis: Calcd Zr, 3.64; P, 1.24; W, 58.84. Found Zr, 3.73; P, 1.22; W, 58.11. The number of crystal water molecules was determined by thermogravimetric analysis (TGA).

^{31}P NMR (referenced to 85% H_3PO_4): $\delta = -6.36, -6.46, -13.86$ and -13.87 ppm; ^{13}C NMR (reference to CDCl_3): $\delta = 189.15, 187.49, 182.15, 181.70, 80.71, 80.21, 43.18$ and 42.72 ppm; IR (KBr, cm^{-1}): $\tilde{\nu} = 1394(\text{m}), 1314(\text{w}), 1258(\text{w}), 1198(\text{w}), 1086(\text{s}), 1053(\text{m}), 1014(\text{m}), 941(\text{s}), 920(\text{sh}), 776(\text{s}), 629(\text{m})$.

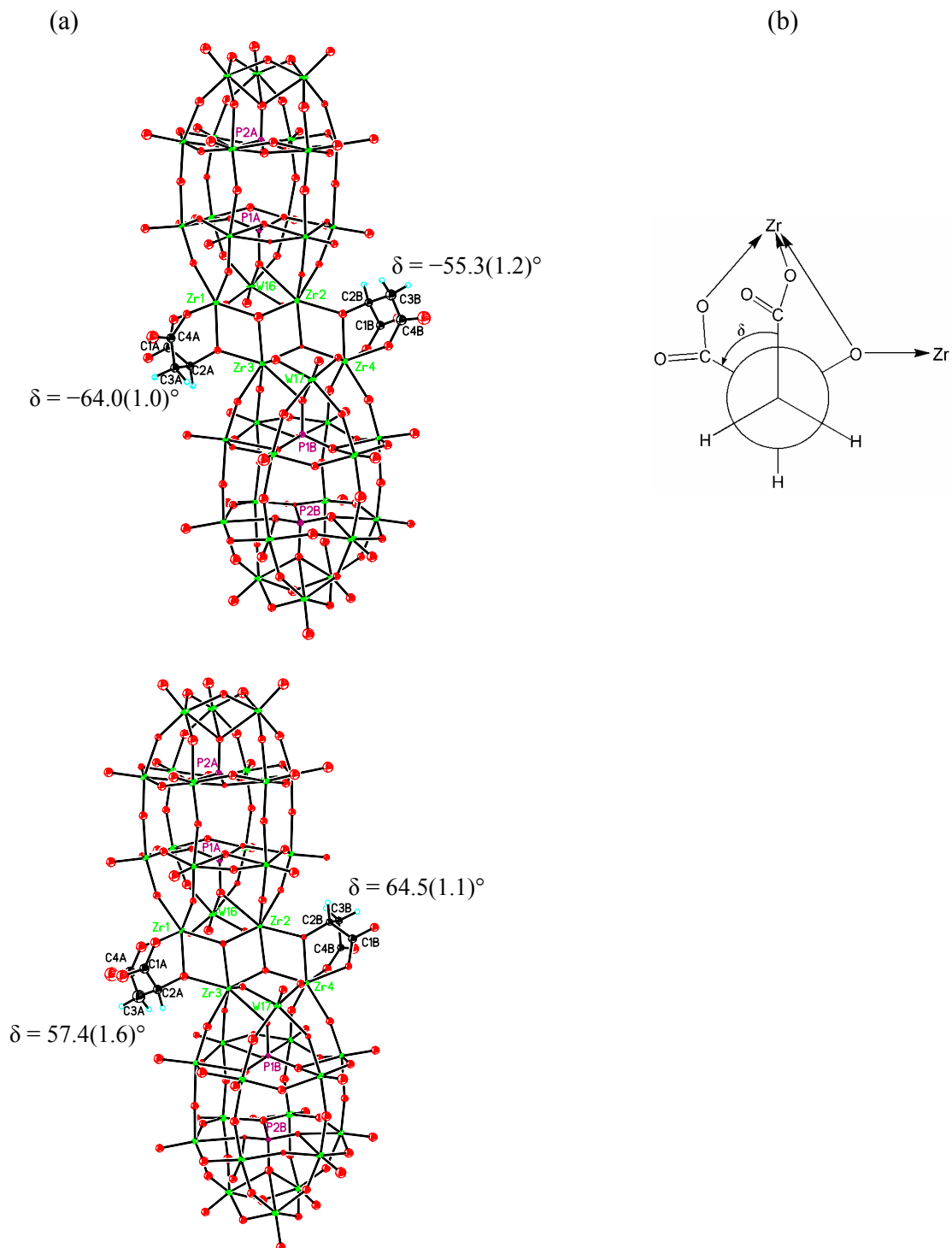


Figure S1. (a) Thermal ellipsoid plot of L,L-**2** (top) and D,D-**2** (bottom) and (b) the Newman projection of the malate ligand in L,L-**2** showing the C(1)-C(2)-C(3)-C(4) torsion angle (δ).

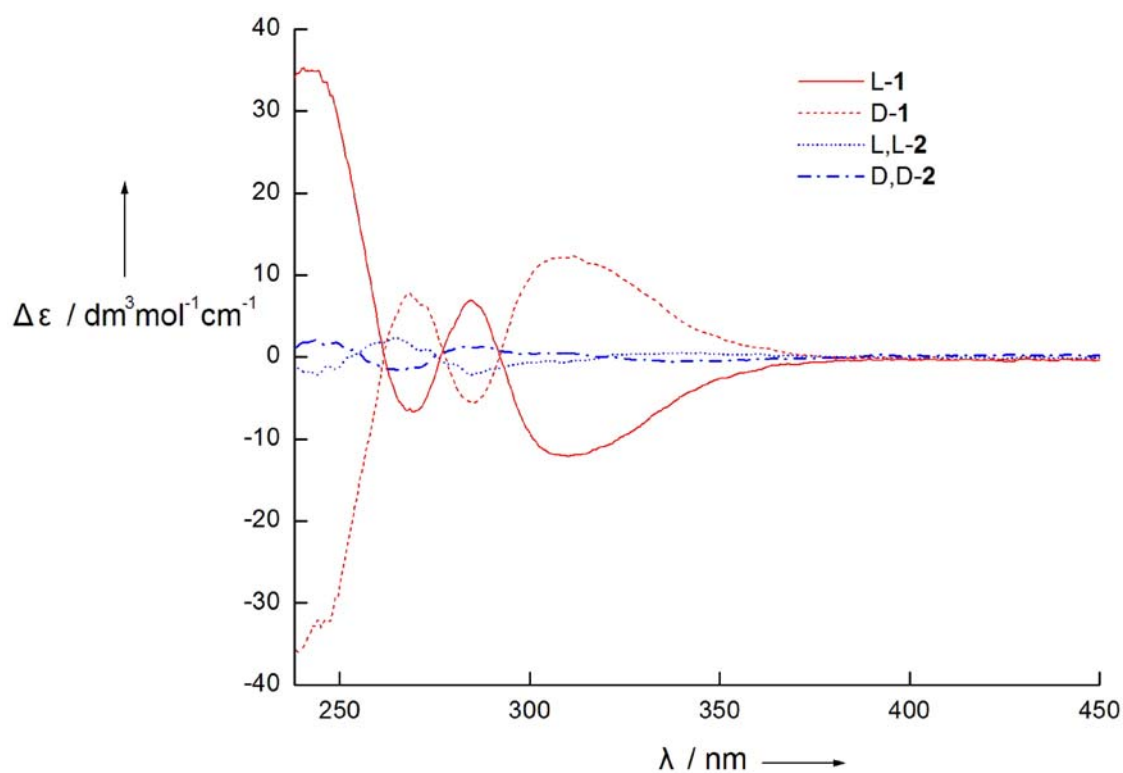


Figure S2. Comparison of the circular dichroism (CD) spectra of L-**1**, D-**1** and L,L-**2**, D,D-**2**, demonstrating that the Cotton effects observed here originate from the metal oxide moieties (the CD data for L-**1** and D-**1** are taken from reference 8).

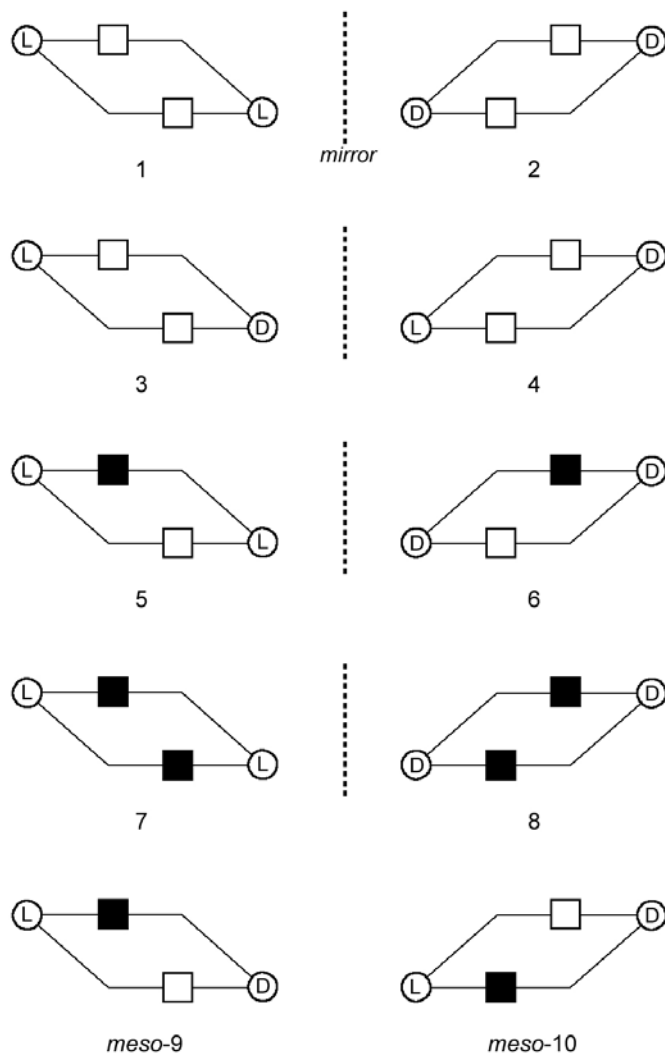


Figure S3. Anticipated isomers of **2**. In principle, there are 10 stereoisomers for **2**: 4 enantiomeric pairs (diagrams 1 to 8) and 2 *meso* forms (diagrams 9 and 10). Only four isomers (5, 6, 9 and 10) are considered possible since all of the others put the two $[\text{P}_2\text{W}_{16}\text{O}_{59}]^{12-}$ units into a *cisoid* arrangement with respect to the Zr_4 plane, which is energetically unfavorable due to the internal steric effects.

The parallelogram represents the $[\text{Zr}_4\text{O}_4]^{8+}$ unit, whereas labeled open circles represent L and D-malate ligands. The two $[\alpha\text{-P}_2\text{W}_{16}\text{O}_{59}]^{12-}$ units are in a *transoid* arrangement with respect to the Zr_4 parallelogram plane, with the inward-oriented unit represented by a filled square and the outward counterpart represented by an open square.