

Syntheses

[Mn₆O₂(Ph-sao)₆(prop)₂(MeCN)₂]·5.27 MeCN (1·5.27MeCN).** Mn(ClO₄)₂·6H₂O (360 mg, 1.0 mmol), Ph-saoH₂ (261 mg, 1.0 mmol) and Naprop (192 mg, 2 mmol) were left upon stirring in MeCN (25 mL) for ~ 5 h to form a black solution. After filtration the solution was left to evaporate slowly and black X-ray quality crystals were formed during ~ 3 days. The crystals were collected by filtration, washed with Et₂O (2 x 4 mL), and dried in vacuo; yield, ~45%. Elemental Anal. Calcd (found) for **1**: C 56.91 (56.83), H 3.80 (3.72), N 6.03 (6.14).**

[Mn₆O₂(Ph-sao)₆(prop)₂(EtOH)₄] (2**).** Mn(ClO₄)₂·6H₂O (360 mg, 1.0 mmol), Ph-saoH₂ (261 mg, 1.0 mmol) and Naprop (192 mg, 2 mmol) were left upon stirring in EtOH (25 mL) for ~ 3 h to form a black solution. After filtration the solution was left to evaporate slowly and black X-ray quality crystals were formed during ~ 2 days. The crystals were collected by filtration, washed with Et₂O (2 x 5 mL), and dried in vacuo; yield, ~40%. Elemental Anal. Calcd (found) for **2**: C 56.40 (56.49), H 4.53 (4.39), N 4.29 (4.21).

[Mn₆O₂(Ph-sao)₆(O₂C-ada)₂(MeOH)₄] (3**).** Mn(ClO₄)₂·6H₂O (360 mg, 1.0 mmol), Ph-saoH₂ (261 mg, 1.0 mmol) and NaO₂C-ada (404 mg, 2 mmol) were dissolved upon stirring in MeOH (25 mL) to form a colourless solution. To this solution were added slowly 20 drops of a 1.0 M aqueous solution of NEt₄OH to afford a black solution which was left to stir for 1h. After filtration the solution was layered with Et₂O (40 mL) and black X-ray quality crystals were formed during ~ 3 days. The crystals were collected by filtration, washed with Et₂O (2 x 5 mL), and dried in vacuo; yield, ~35%. Elemental Anal. Calcd (found) for **3**: C 59.04 (59.64), H 4.76 (4.62), N 3.97 (4.17).

[Mn₆O₂(Ph-sao)₆(piv)₂(EtOH)₄]·0.5Et₂O (4·0.5Et₂O).** Mn(ClO₄)₂·6H₂O (360 mg, 1.0 mmol), Ph-saoH₂ (261 mg, 1.0 mmol) and Napiv (250 mg, 2 mmol) were dissolved upon stirring in EtOH (25 mL) to form a pale yellow solution. To this solution were added slowly 15 drops of a 1.0 M aqueous solution of NEt₄OH to afford a black solution which was left to stir for 45'. After filtration the solution was layered with Et₂O (40 mL) and black X-ray quality crystals were formed during ~ 4 days. The crystals were collected by filtration, washed with Et₂O (2 x 5 mL), and dried in vacuo;**

yield, ~45%. Elemental Anal. Calcd (found) for **4**: C 57.21 (57.34), H 4.80 (4.67), N 4.17 (4.29).