Complex 2

Complex 2 (Figure S1) showed a $\mu_{\text{eff}}$ value of 10.9 $\mu_B$ at 300 K which is close to the expected value associated with the sum of the \{two spin 5/2 + two spin 4/2\} sites (10.86 $\mu_B$). The sample showed a gradual increase in $\mu_{\text{eff}}$ between 20 and 100 K, then the moments became almost temperature independent above 100 K. The $\chi_M$ versus temperature plot was Curie-Weiss like in shape with no distinct max. at low temperature indicative of antiferromagnetic coupling. High field magnetisation isotherms (2 to 20 K, $H = 0$ to 5 T) were measured to try to identify the ground state and are shown in Figure S2. Saturation in $M$ was not achieved at 2 K and 5 T, the $M$ value under these conditions being 8.8 N$\mu_B$; it appears that saturation might occur above fields of 5 T. From the data obtained a ground state of $S_T \sim 4$ is suggested.
The asymmetric unit of complex 4 contains half the cluster and a perchlorate counterion. The \([\text{Mn}^{II}]_2\text{Mn}^{III}_2(\text{bheapH}_2^2)(\text{MeOH})_2]\text{(ClO}_4)_2\) cluster of 4 is shown in Figure S4. The peripheral Mn\(^{III}\) ions, Mn(1), are six coordinate with distorted octahedral geometry, showing the expected Jahn-Teller elongation in the form of an elongation of the O(1) – Mn(1) – O(4) axis (2.311(2) and 2.314(2) Å respectively). The central body Mn atoms, Mn(2), are also six coordinate, exhibiting distorted trigonal prismatic geometry, although a significant interaction between Mn(2) and the face capping O(1´) atom at a distance of ~ 2.62 Å forms a seven coordinate environment (commonly observed for Mn\(^{II}\) ions). Bond length analysis and BVS calculations were used to confirm the oxidation states of Mn(1) and Mn(2). All three arms of the doubly deprotonated bheapH\(^2^-\) anions in 4 partake in bonding. Two arms link the wing-tip Mn\(^{III}\) ions (Mn(1)) to the central body Mn\(^{II}\) ions (Mn(2)) through \(\mu_2\)-bridges (via O(6) and O(7)) (Fig. S4) while the third arm, O(8), remains protonated, preferring to bond terminally to Mn(2), as does its amine nitrogen atom, N(1). Four acac\(^-\) anions are present in the structure and show two different bonding modes. While the first exhibits its traditional chelating mode (to Mn(1)), the second acac\(^-\) anion
bridges the peripheral Mn$^{III}$ ions (Mn(1)) to the central body Mn$^{II}$ ions (Mn(2)) via a $\mu_2$-bridge from one of its oxygen atoms, O(5), while the second oxygen, O(4), bonds terminally to Mn(2) (Fig. S4). The coordination geometries at the wing-tip Mn positions (Mn(1)) are completed by terminal MeOH molecules. The ClO$_4^-$ counter ions are hydrogen bonded to the protonated arm of the bheapH$^+$ ligand (O(8)...O(10) 2.759 Å). There are no hydrogen bonds between neighbouring clusters.