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**A Family of 3D Coordination Polymers Composed of Mn<sub>19</sub> Magnetic Units\*\****Eleni E. Moushi, Theocharis C. Stamatatos, Wolfgang Wernsdorfer, Vassilios Nastopoulos, George Christou,\* and Anastasios J. Tasiopoulos\**

The current intense interest in polynuclear clusters stems not only from their aesthetically pleasing structures, magnetic interactions, and magnetostructural correlations, but also from the discovery that some function as nanoscale magnetic particles, or single-molecule magnets (SMMs).<sup>[1]</sup> Below their blocking temperature ( $T_B$ ), such molecules behave as magnets and exhibit hysteresis in scans of magnetization versus dc field. This behavior results from the combination of a large ground spin state ( $S$ ) with a large and negative (easy-axis type) magnetoanisotropy. SMMs have several potential applications, including high-density information storage, in which each bit of information is stored as the magnetization orientation of an individual molecule, and quantum computation, in which the molecules can serve as qubits.

Although there are many known species displaying SMM behavior,<sup>[1–5]</sup> most of which are manganese–carboxylate complexes,<sup>[3–5]</sup> there is a continuing need for new SMMs. One of the most successful synthetic approaches to new polynuclear clusters involves the use of chelating ligands containing alkoxide functions, since these are good bridging groups and, thus, favor the formation of polynuclear products.<sup>[4]</sup> Recently, we have been investigating the use of 1,3-propanediol (H<sub>2</sub>pd) and 2-methyl-1,3-propanediol (H<sub>2</sub>mpd) in manganese–carboxylate chemistry. Herein, we report the syntheses, crystal structures, and magnetic properties of two new 3D coordination polymers based on [Mn<sub>19</sub>Na(μ<sub>4</sub>-O)<sub>9</sub>(μ<sub>3</sub>-

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O)( $\mu_3$ -OH) $_3$ (O $_2$ CMe) $_9$ (pd) $_9$ (H $_2$ O) $_3$ ][OH] (**1**) and [Mn $_{19}$ Na( $\mu_4$ -O) $_9$ ( $\mu_3$ -O)( $\mu_3$ -OH) $_3$ (O $_2$ CMe) $_9$ (mpd) $_9$ (H $_2$ O) $_3$ ][OH] (**2**) repeating units. Compounds {**1**·0.5 MeCN·6 H $_2$ O} $_{\infty}$  and {**2**·6 H $_2$ O} $_{\infty}$ , which are the first manganese complexes with the ligands H $_2$ pd and H $_2$ mpd, have open-framework structures with nanometer-sized channels and, in addition, behave as SMMs.<sup>[5]</sup>

The reaction of [Mn $_3$ O(O $_2$ CMe) $_6$ (py) $_3$ ]·py (py = pyridine), H $_2$ pd, and NaClO $_4$  in a 1:5:2 molar ratio in MeCN led to the isolation of {**1**·0.5 MeCN·6 H $_2$ O} $_{\infty}$  in 23% yield after several weeks (single crystals could be obtained as {**1**·3 H $_2$ O} $_{\infty}$ ). When the same reaction was repeated with H $_2$ mpd instead of H $_2$ pd, with the reactants in a 1:5:1 molar ratio, {**2**·6 H $_2$ O} $_{\infty}$  was isolated in 25% yield (single crystals could be obtained as {**2**·3 H $_2$ O} $_{\infty}$ ). As the crystal structures and magnetic properties of **1** and **2** are strikingly similar, only those of **1** will be described; structural figures and plots of dc and ac magnetic-susceptibility data for **2** are provided in the Supporting Information.

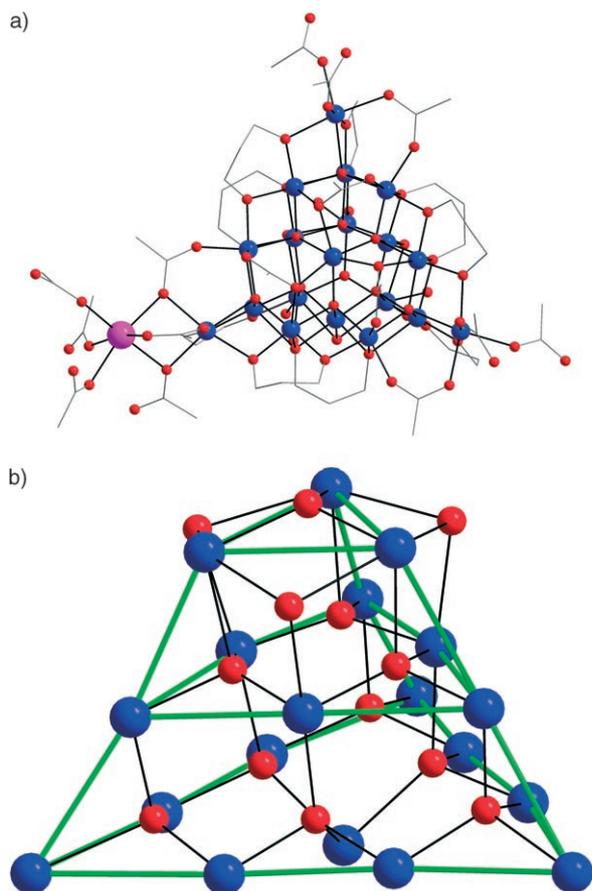
The crystal structure of {**1**·3 H $_2$ O} $_{\infty}$ , in the cubic space group  $P2_13$ ,<sup>[6]</sup> reveals that **1** (Figure 1a) is a mixed-valent complex, containing seven Mn<sup>II</sup> ions and twelve Mn<sup>III</sup> ions, as determined by bond-valence calculations,<sup>[7]</sup> charge considerations, and inspection of the metric parameters. The man-

ganese–oxygen core of **1** (Figure 1b) consists of three equilateral triangles stacked one above the other. The basal triangle contains ten manganese ions, nine on its edges, and the tenth near its center, whereas the middle and apex triangles contain six and three manganese ions, respectively, all of which lie on their edges. The manganese ions of the core are held together by nine  $\mu_4$ -O $^{2-}$ , one  $\mu_3$ -O $^{2-}$ , and three  $\mu_3$ -OH $^-$  ions,<sup>[8]</sup> resulting in an overall triangular-pyramidal-frustum topology (Figure 1b). The peripheral ligation of **1** is completed by nine bridging pd $^{2-}$  ligands, nine bridging O $_2$ CMe $^-$  ligands, and three terminal H $_2$ O molecules.

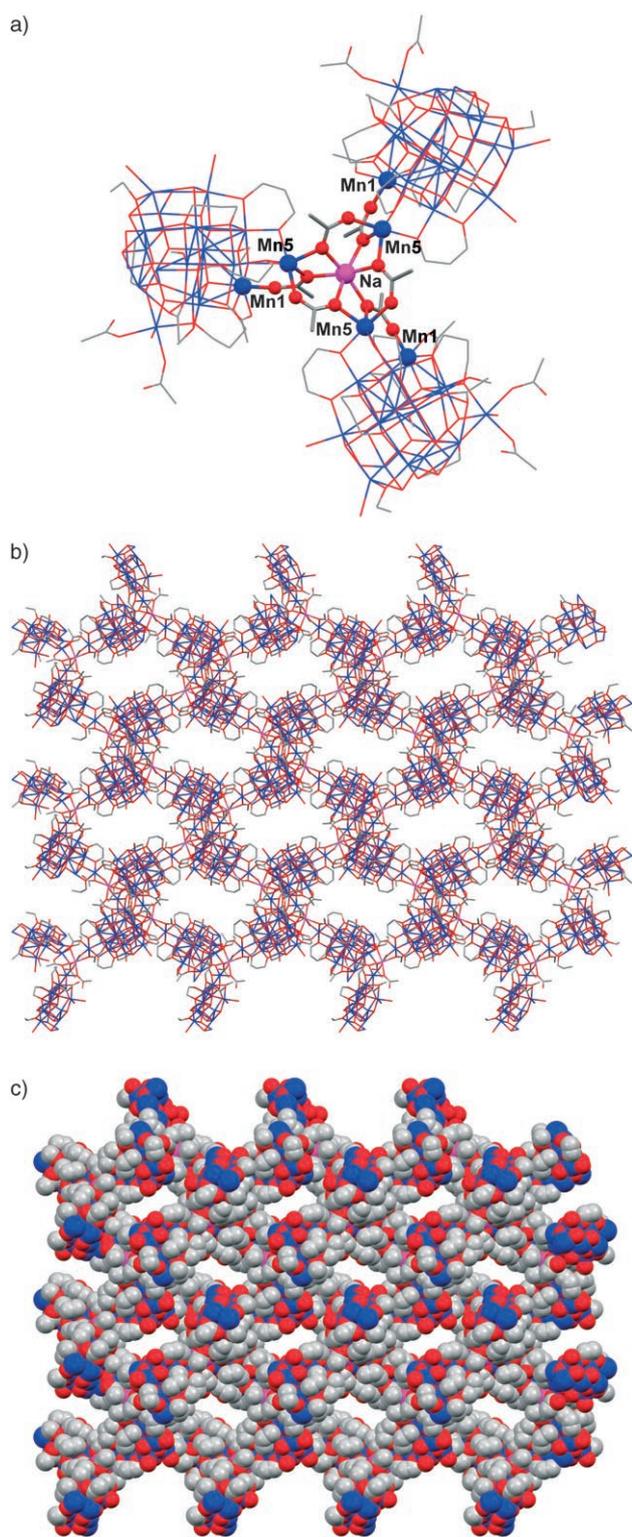
Each Mn $_{19}$  aggregate is connected through three  $\mu_3$ -O $_2$ CMe $^-$  ligands to a Na $^+$  ion. One of the  $\mu_3$ -O $_2$ CMe $^-$  groups links Mn1 and Mn5 with the Na $^+$  ion, whereas the other two  $\mu_3$ -O $_2$ CMe $^-$  groups link Mn5 with the Na $^+$  ion and the symmetry-related Mn5 ions of two other Mn $_{19}$  units, resulting in a 3D coordination polymer (Figure 2a). To our knowledge, Mn $_{19}$  is the highest-nuclearity repeating unit reported for a manganese coordination polymer. Note that although the Mn $_{19}$  units are bridged not only through the Na $^+$  ions, but also directly through  $\mu_3$ -O $_2$ CMe $^-$  ligands, the shortest Mn⋯Mn separation between the Mn $_{19}$  units is relatively large (5.52(1) Å). A close examination of the packing of **1** revealed a highly ordered 3D structure that contains large channels with dimensions of approximately 12 × 16 Å $^2$  (Figure 2b,c). These channels are nearly empty, containing only a very small proportion of H $_2$ O molecules and OH $^-$  counterions. In fact, approximately 44% of the crystal structure of {**1**·3 H $_2$ O} $_{\infty}$  is void space.

Measurements of the molar dc magnetic susceptibility ( $\chi_M$ ) of a microcrystalline sample of {**1**·6 H $_2$ O·0.5 MeCN} $_{\infty}$  were made over the temperature range 5.0–300 K in an applied field of 0.1 T. The  $\chi_M T$  value at 300 K is 54.15 cm $^3$  mol $^{-1}$  K, and it increases with decreasing temperature to a maximum of 73.68 cm $^3$  mol $^{-1}$  K at 15.0 K, before decreasing to 69.30 cm $^3$  mol $^{-1}$  K at 5.00 K (see Supporting Information). The data indicate that **1** has a large ground spin state. Given the size of the molecule, it is not possible to apply the Kambe method to determine the individual pairwise exchange-interaction parameters between the manganese ions, and direct matrix-diagonalization methods are also computationally unfeasible. To determine the ground state, magnetization data were collected in the temperature range 1.8–10.0 K and the magnetic-field range 0.1–1 T (see Supporting Information). The data were fit by assuming that only the ground state is populated and by including axial zero-field splitting ( $D\hat{S}_z^2$ ) and Zeeman interactions. A very good fit was obtained with  $S = 23/2$ ,  $D = -0.086(3)$ , and  $g = 1.99(1)$ .

As described elsewhere,<sup>[3b,4d]</sup> reliable conclusions about the  $S$  value can be provided by ac magnetic-susceptibility measurements, which can also detect the slow magnetization relaxation suggestive of SMMs. Frequency-dependent out-of-phase ac susceptibility signals ( $\chi_M''$ ) were indeed detected for **1** below approximately 2.8 K (but no peaks were observed), along with a concomitant decrease in the in-phase signal (Figure 3). Extrapolation of the  $\chi_M'' T$  versus  $T$  plots to 0 K (from temperature ranges not affected by the decrease in  $\chi_M'$  arising from slow relaxation) gives a value of approximately 70 cm $^3$  mol $^{-1}$  K, which is consistent with that expected for an

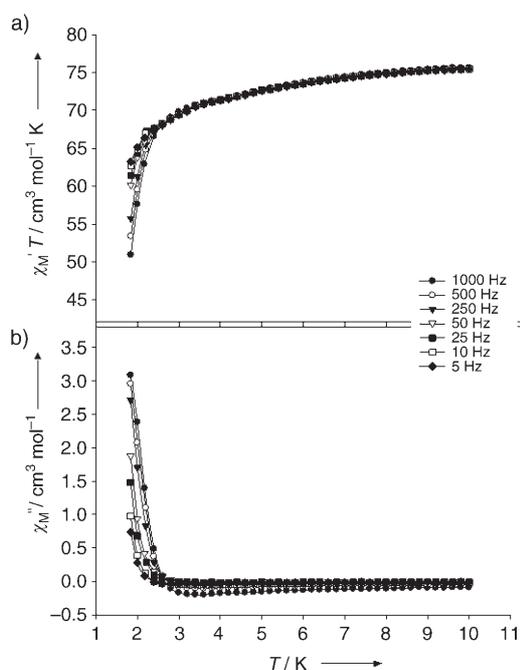


**Figure 1.** a) The molecular structure of **1**. b) The manganese–oxygen core of **1**; the green lines connecting the manganese ions emphasize the triangular-pyramidal-frustum topology. Na pink, Mn blue, O red, C gray. Hydrogen atoms and the free OH $^-$  ion are omitted for clarity.



**Figure 2.** The polymeric structure of  $\{1.3 \text{H}_2\text{O}\}_\infty$ . a) View emphasizing the connectivity of the Mn<sub>19</sub> units. b) Wire-frame and c) space-filling representations viewed along the *c* axis, emphasizing the large channels. Na pink, Mn blue, O red, C gray. Hydrogen atoms, free OH<sup>-</sup> ions, and cocrystallized H<sub>2</sub>O molecules are omitted for clarity.

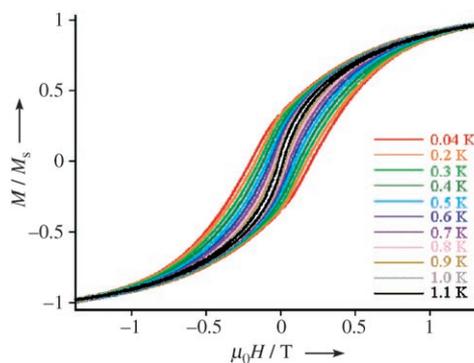
$S = 23/2$  system (assuming  $g \approx 1.98$ ). The ac susceptibility data, thus, support the  $S = 23/2$  ground state determined from fits of the magnetization data.



**Figure 3.** Temperature-dependence of a) the in-phase ( $\chi_M'$ ) and b) the out-of-phase ( $\chi_M''$ ) ac magnetic susceptibility of  $\{1.0.5 \text{MeCN} \cdot 6 \text{H}_2\text{O}\}_\infty$  at the indicated ac frequencies.

Scans of magnetization versus dc field made on single crystals using a micro-SQUID (superconducting quantum interference device) setup confirmed that **1** is a SMM.<sup>[9]</sup> Below 1.1 K, hysteresis loops, the diagnostic behavior of magnets, were detected (Figure 4), their coercivity increases with decreasing temperature, as expected for SMMs. However, the hysteresis loops do not show steps characteristic of the quantum tunneling of magnetization (QTM); this behavior is typical for large SMMs, which are more susceptible to step-broadening effects associated with low-lying excited states, intermolecular interactions, and distributions of local environments due to ligand and solvent disorder.<sup>[3a,4e,f,5b]</sup>

In summary, the use of H<sub>2</sub>pd and H<sub>2</sub>mpd in manganese-carboxylate chemistry resulted in the isolation of two novel 3D coordination polymers based on an unprecedented Mn<sub>19</sub>



**Figure 4.** Field-dependence of the magnetization (hysteresis loops) of single crystals of  $\{1.3 \text{H}_2\text{O}\}_\infty$  at the indicated temperatures; the magnetization (*M*) is normalized to its saturation value (*M<sub>s</sub>*).

repeating unit. These 3D networks were prepared under mild conditions (room temperature and atmospheric pressure) with self-assembly processes directed by metal–ligand coordination, and have open-framework structures with nanometer-sized channels. The  $\text{Mn}_{19}$  repeating unit has an aesthetically pleasing structure, in which the manganese ions have a triangular-pyramidal-frustum topology. The repeating unit also has a large ground spin state of  $S = 23/2$  and displays SMM behavior (in-phase and out-of-phase ac magnetic susceptibility signals, and hysteresis loops in scans of magnetization versus dc field). Attempts to remove the cocrystallized solvent molecules from  $\{1\cdot 3\text{H}_2\text{O}\}_\infty$  and  $\{2\cdot 3\text{H}_2\text{O}\}_\infty$  are underway, as are studies of the thermal stability, permanent porosity, and  $\text{N}_2$  sorption of the compounds; these investigations will be reported elsewhere in the near future. Finally, the supramolecular architecture of  $\{1\cdot 3\text{H}_2\text{O}\}_\infty$  and  $\{2\cdot 3\text{H}_2\text{O}\}_\infty$  offers a variety of possibilities for accessing interesting new materials, including the insertion (in the channels) of guest molecules (either organic or inorganic, paramagnetic or diamagnetic) that can affect the structural and magnetic properties.

### Experimental Section

$\{1\cdot 0.5\text{MeCN}\cdot 6\text{H}_2\text{O}\}_\infty$ :  $\text{H}_2\text{pd}$  (0.085 mL, 1.176 mmol) and  $\text{NaClO}_4$  (0.058 g, 0.470 mmol) were added to a solution of  $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3]$  (0.200 g, 0.235 mmol) in MeCN (10 mL). The reaction mixture was then stirred magnetically for 1 h, resulting in a dark brown slurry. After filtration, the dark brown filtrate was left undisturbed at room temperature. After several weeks, dark brown crystals appeared, and these were allowed to grow for a few more weeks to give X-ray quality crystals. The crystals were then separated by filtration, washed with MeCN and dried in vacuum (yield: 0.023 g, 23% based on total Mn content). Elemental analysis (%) calcd for  $\text{C}_{46}\text{H}_{104.5}\text{N}_{0.5}\text{O}_{59}\text{Mn}_{19}\text{Na}$  ( $1\cdot 0.5\text{MeCN}\cdot 6\text{H}_2\text{O}$ ): C 20.65, H 3.94, N 0.26; found: C 20.90, H 3.76, N 0.18.

$\{2\cdot 6\text{H}_2\text{O}\}_\infty$  was prepared by a similar procedure to that described for  $\{1\cdot 0.5\text{MeCN}\cdot 6\text{H}_2\text{O}\}_\infty$ , except twice the amount of solvent was used (20 mL MeCN), and a 1:1, rather than 1:2, ratio of  $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3]$ · $\text{NaClO}_4$  was used. The yield was 25%. Elemental analysis (%) calcd for  $\text{C}_{54}\text{H}_{121}\text{O}_{59}\text{Mn}_{19}\text{Na}$  ( $2\cdot 6\text{H}_2\text{O}$ ): C 23.32, H 4.38; found: C 23.55, H 4.45.

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- [1] a) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804; b) R. Sessoli, D. Gatteschi, A. Ganeschi, M. A. Novak, *Nature* **1993**, *365*, 141; c) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66.
- [2] a) D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278; *Angew. Chem. Int. Ed.* **2003**, *42*, 268; b) E. K. Brechin, *Chem. Commun.* **2005**, 5141; c) G. Christou, *Polyhedron* **2005**, *24*, 2065.
- [3] a) A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem.* **2004**, *116*, 2169; *Angew. Chem. Int. Ed.* **2004**, *43*, 2117; b) A. J. Tasiopoulos, W. Wernsdorfer, K. A. Abboud, G. Christou, *Inorg. Chem.* **2005**, *44*, 6324; c) C. J. Milios, C. P. Raptopoulou, A. Terzis, F. Lloret, R. Vicente, S. P. Perlepes, A. Escuer, *Angew. Chem.* **2004**, *116*, 212; *Angew. Chem. Int. Ed.* **2004**, *43*, 210; d) C. M. Zaleski, E. C. Depperman, C. Dendrinou-Samara, M. Alexiou, J. W. Kampf, D. P. Kessissoglou, M. L. Kirk, V. L. Pecoraro, *J. Am. Chem. Soc.* **2005**, *127*, 12862; e) C. M. Zaleski, E. C. Depperman, J. W. Kampf, M. L. Kirk, V. L. Pecoraro, *Angew. Chem.* **2004**, *116*, 4002; *Angew. Chem. Int. Ed.* **2004**, *43*, 3912; f) S. Maheswaran, G. Chastanet, S. J. Teat, T. Mallah, R. Sessoli, W. Wernsdorfer, R. E. P. Winpenny, *Angew. Chem.* **2005**, *117*, 5172; *Angew. Chem. Int. Ed.* **2005**, *44*, 5044.
- [4] a) R. T. W. Scott, S. Parsons, M. Murugesu, W. Wernsdorfer, G. Christou, E. K. Brechin, *Angew. Chem.* **2005**, *117*, 6698; *Angew. Chem. Int. Ed.* **2005**, *44*, 6540; b) S. Piligkos, G. Rajaraman, M. Soler, N. Kirchner, J. van Slageren, R. Bircher, S. Parsons, H.-U. Gudel, J. Kortus, W. Wernsdorfer, G. Christou, E. K. Brechin, *J. Am. Chem. Soc.* **2005**, *127*, 5572; c) R. T. W. Scott, S. Parsons, M. Murugesu, W. Wernsdorfer, G. Christou, E. K. Brechin, *Chem. Commun.* **2005**, 2083; d) M. Murugesu, W. Wernsdorfer, K. A. Abboud, G. Christou, *Angew. Chem.* **2005**, *117*, 914; *Angew. Chem. Int. Ed.* **2005**, *44*, 892; e) D. Fogueat-Albiol, T. A. O'Brien, W. Wernsdorfer, B. Moulton, M. J. Zaworotko, K. A. Abboud, G. Christou, *Angew. Chem.* **2005**, *117*, 919; *Angew. Chem. Int. Ed.* **2005**, *44*, 897; f) A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clerac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem.* **2006**, *118*, 5048; *Angew. Chem. Int. Ed.* **2006**, *45*, 4926.
- [5] a) A few examples of multidimensional coordination polymers that behave as SMMs exist, in which the repeating units are linked in a variety of different modes (through coordination bonds,<sup>[5b]</sup> a diamagnetic metal ion,<sup>[5c]</sup> or hydrogen bonds<sup>[5d]</sup>); the common feature is that the magnetic interactions between the repeating units are negligible: b) H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K. Sugiura, M. Yamashita, R. Clerac, *J. Am. Chem. Soc.* **2006**, *128*, 3770; c) M. Murugesu, W. Wernsdorfer, K. A. Abboud, E. K. Brechin, G. Christou, *Dalton Trans.* **2006**, 2285; d) L. M. Wittick, K. S. Murray, B. Moubaraki, S. R. Batten, L. Spiccia, K. J. Berry, *Dalton Trans.* **2004**, 1003.
- [6] Crystallographic data for  $\{1\cdot 3\text{H}_2\text{O}\}_\infty$ :  $\text{C}_{45}\text{H}_{97}\text{O}_{56}\text{NaMn}_{19}$ ,  $M_r = 2601.05$ , cubic, space group  $P2_13$ ,  $a = 24.0430(9)$  Å,  $V = 13898.4(9)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.275$  g cm<sup>-3</sup>, 47607 reflections collected, 8117 unique ( $R_{\text{int}} = 0.0724$ ),  $R1 = 0.0720$ ,  $wR2 = 0.1987$ , for 5293 reflections with  $I > 2\sigma(I)$ . Crystallographic data for  $\{2\cdot 3\text{H}_2\text{O}\}_\infty$ :  $\text{C}_{54}\text{H}_{115}\text{O}_{56}\text{NaMn}_{19}$ ,  $M_r = 2727.29$ , cubic, space group  $P2_13$ ,  $a = 24.4332(6)$  Å,  $V = 14586.2(6)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.227$  g cm<sup>-3</sup>, 76818 reflections collected, 8506 unique ( $R_{\text{int}} = 0.0907$ ),  $R1 = 0.0812$ ,  $wR2 = 0.2062$ , for 4214 reflections with  $I > 2\sigma(I)$ . CCDC-618951 ( $\{1\cdot 3\text{H}_2\text{O}\}_\infty$ ) and CCDC-618950 ( $\{2\cdot 3\text{H}_2\text{O}\}_\infty$ ) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
- [7] Bond-valence sum calculations gave oxidation states of 2.82–3.09 (Mn<sup>III</sup>) and 1.99–2.11 (Mn<sup>II</sup>) for the manganese ions of **1**, and oxidation states of 2.65–3.13 (Mn<sup>III</sup>) and 1.92–2.29 (Mn<sup>II</sup>) for the manganese ions of **2**; W. Liu, H. H. Thorp, *Inorg. Chem.* **1993**, *32*, 4102.
- [8] Bond-valence sum calculations for the oxygen atoms of **1** gave values of 1.52–1.92 for the O<sup>2-</sup> ions, 0.63 for the OH<sup>-</sup> ions, 0.33 for the H<sub>2</sub>O molecules, and 1.83–2.06 for the RO<sup>-</sup> groups of the pd<sup>2-</sup> ligands. Bond-valence sum calculations for the oxygen atoms of **2** gave values of 1.66–1.80 for the O<sup>2-</sup> ions, 0.60 for the OH<sup>-</sup> ions, 0.49 for the H<sub>2</sub>O molecules, and 1.81–2.24 for the RO<sup>-</sup> groups of the mpd<sup>2-</sup> ligands; a) I. D. Brown, R. D. Shannon, *Acta Crystallogr. Sect. A* **1973**, *29*, 266; b) G. Donnay, R. Allman, *Am. Mineral.* **1970**, *55*, 1003.
- [9] W. Wernsdorfer, *Adv. Chem. Phys.* **2001**, *118*, 99.