Salicylate-Mediated Assembly of the Discrete **Mixed-Valence Nonanuclear Manganese Complex**  $|Mn_9O_4(O_2CPh)_8(sal)_4(salH)_2(py)_4|$ (salH<sub>2</sub> = salicylic acid, py = pyridine)\*\*

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Recent developments in Fe<sup>111</sup> chemistry have established that high nuclearity (>4) complexes can be prepared with carboxylate or mixed carboxylate/amine ligation even in the expected absence of metal-metal bonds to assist aggregation. Iron complexes of this kind have been prepared by hydrolytic reactions from smaller nuclearity complexes and, to date, octanuclear<sup>[1]</sup> and undecanuclear<sup>[2]</sup> species have been structurally characterized. These units are held together by oxide and hydroxide bridges. The efforts of our own research program have been concentrated on the neighboring 3d metal Mn, and we have reported the nonhydrolytic bipyridine(bpy)-mediated conversion of trinuclear  $[Mn_3O(O_2CR)_6L_3]^{0,\Theta}$  (R = Me, Ph; L = pyridine(py), H<sub>2</sub>O) into tetranuclear species containing the non-planar [Mn<sub>4</sub>O<sub>2</sub>] core.<sup>[3,4]</sup> We have now found that use of salicylic acid (salH2) instead of bpy in these reactions leads to still higher aggregation and herein report the preparation of the remarkable nonanuclear complex 1.

## $[Mn_3O_4(O_2CPh)_8(sal)_4(salH)_2(py)_4]$ 1

To a stirred brown solution of [Mn<sub>3</sub>O(O<sub>2</sub>CPh)<sub>6</sub>(py)<sub>2</sub>-(H<sub>2</sub>O)]<sup>[5]</sup> in MeCN was added solid salicylic acid (3 equiv.) under aerobic conditions. The acid soon dissolved, and the homogeneous dark brown solution was left undisturbed overnight at room temperature. The resulting black crystals of 1 were collected by filtration, washed with hexane, and dried in vacuo;<sup>[6]</sup> yield ca. 40%.

The X-ray structure<sup>[7]</sup> of 1 is shown in Figure 1. Charge considerations necessitate a mixed-valence description (8 Mn<sup>III</sup>, Mn<sup>II</sup>) and the unique central atom Mn(1) is assigned as the Mn<sup>11</sup> atom through which there is a crystallographic two-fold axis relating the two halves of the molecule. The average Mn(1)-O distances (2.312 Å) are similar to those in the eight-coordinate Mn<sup>II</sup> complex [Mn(NO<sub>3</sub>)<sub>4</sub>]<sup>21</sup> (2.306 Å).<sup>[8]</sup> The eight Mn<sup>111</sup> atoms are six-

coordinate and are disposed in two tetranuclear Mn<sub>4</sub>(µ<sub>3</sub>-O)2 units, each with a butterfly structure. Figure 2a shows a stereoview of 1; Figure 2b shows a top view of one of the [Mn<sub>4</sub>O<sub>2</sub>]-units, and it can be seen to be similar to that in discrete [Mn<sub>4</sub>O<sub>2</sub>]-containing complexes.<sup>[4]</sup> The two Mn<sub>4</sub>O<sub>2</sub> units and central Mn(1) in 1 are held together via four  $\mu_3$ - $\eta^3$ -sal<sup>2</sup> groups (o-oxidobenzoate). Peripheral ligation is by four terminal py, eight bridging PhCO<sub>2</sub><sup>o</sup> (benzoate), and two bridging salH<sup>o</sup> groups (salicylate). The latter, one at each end of the molecule, are bound only through their



Fig. 1. Crystal structure of complex 1. To avoid congestion, only one of each symmetry-related pair of Mn and O atoms are labeled. Primed and unprimed atoms are related by the twofold rotation axis through Mn(1). Selected atomic separations: Mn(1)-Mn(2,3,4,5), 3.814(6)-3.983(6) Å; Mn(1)-O(6,7,16,17), 2.240(14)-2.385(14) Å.

carboxylate functions; the OH-groups with the oxygen atoms O(60) and O(60)' are not involved in metal ligation. This conclusion is supported by the near coplanarity between the Ph ring and its carboxylate group, and the resulting close approach of O(60) to O(51) (2.59(2) Å), suggesting a hydrogen-bonded O(60)-H···O(51) unit. A similar situation has been seen in Mo" and Rh" complexes containing µ-salH bridges.<sup>[9, 10]</sup> Overall, the Mn<sub>9</sub> unit can be considered a purely inorganic example of a 'sandwich' compound not supported by metal-metal bonding and with the central Mn and two outer [Mn<sub>4</sub>O<sub>2</sub>] units representing the three layers.

Variable temperature, solid-state magnetic susceptibility studies have been performed on powdered samples of 1 in the temperature range 300.9 K to 5.0 K. The effective magnetic moment per molecule,  $\mu_{eff}$ , gradually decreases from a value of 11.82  $\mu_B$  at 300.9 K to a value of 5.83  $\mu_B$  at 5.0 K. Extensive coupling is thus indicated and attempts are in progress to elucidate the precise nature and magnitude of the magnetic interactions between the various Mn atoms of

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Fig. 2. a) Stereoview of the crystal structure of 1. b) Top view of one end of complex 1 clarifying the structure of the  $[Mn_4(\mu_1-O)_2]$  unit. Selected atomic separations: Mn(3)-Mn(4), 2.817(6); Mn(3)-Mn(2), 3.406(6); Mn(3)-Mn(5), 3.408(6); Mn(4)-Mn(2), 3.443(6); Mn(4)-Mn(5), 3.425(6); Mn(2)-Mn(5), 5.914(6) Å.

this complicated and relatively low symmetry molecule.<sup>[11]</sup>

In summary, trinuclear  $[Mn_3O(O_2CR)_6L_3]$  complexes continue to prove useful as precursors to higher nuclearity species, and reaction with the bifunctional ligand salicylic acid leads to a convenient non-hydrolytic conversion to a discrete nonanuclear species with an unusual structure. In contrast to the octa- and undecanuclear Fe<sup>III</sup> complexes, 1 is a mixed-valence compound containing Mn<sup>II</sup> and Mn<sup>III</sup>, as found for the recently reported hexanuclear species  $[Mn_6O_2(piv)_{10}(pivH)_4]$  (pivH = pivalic acid).<sup>[12]</sup> It is interesting how these neighboring 3d metals exhibit similar, yet distinctly different, chemistry with such ligands, although it should be added that we have yet to investigate the reaction of salicylic acid with an [Fe<sub>3</sub>O]-containing complex. Further studies in high nuclearity Mn/carboxylate chemistry are in progress.<sup>[13]</sup>

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