

## The Crystal Structure of $[\text{Mn}(\text{salpn})(\text{acetate})]_2(\text{H}_2\text{O})_3$ ; the First Example of a Manganese(III) Schiff Base Polymeric Complex Containing a Dimeric Repeat Unit [salpn = *N,N'*-bis(salicylidene)-1,3-diaminopropane]

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The crystal structure of  $[\text{Mn}(\text{salpn})(\text{OAc})]_2(\text{H}_2\text{O})_3$  shows it to be a polymeric array, with the  $\text{Mn}(\text{salpn})$  units bridged by acetate groups in an *anti-anti* configuration, with three hydrogen-bonded water molecules per monomer; the two ligands per monomer are rotated 180° with respect to each other.

The chemistry of manganese in various oxidation states is currently receiving much attention owing to its importance in many biological systems. It is firmly established that manganese is essential to superoxide dismutase<sup>1</sup> and azide insensitive catalase.<sup>2</sup> Of perhaps most importance is the realization that manganese plays an essential and specific role in the water oxidising complex (WOC) of photosystem II (PSII).<sup>3,4</sup> This is supported by manganese depletion studies carried out on spinach leaf chloroplasts,<sup>5</sup> in which manganese depletion and subsequent restoration, reduced and regained the O<sub>2</sub>-evolving capacity of the chloroplast, respectively. It is also known that four manganese atoms are necessary for high rates of oxygen evolution, but there is some doubt as to their exact nature and role.

We have concentrated on producing dinuclear species, with a view to producing an effective model of the active site in PSII. The dinuclear model has received much attention and

some recent XANES studies<sup>6-9</sup> have confirmed that there are, (i) four manganese ions in the chloroplasts (extracted from spinach leaves), and (ii) that they are in two inequivalent binuclear environments. It has also been shown that these binuclear species contain  $\mu_2$ -oxo bridges and possibly a di- $\mu_2$ -carboxylato bridge in their two respective environments. A number of workers have prepared dinuclear manganese complexes containing  $\mu_2$ -oxo<sup>10</sup> and di- $\mu_2$ -carboxylate bridges,<sup>11</sup> but only our group have produced molecular oxygen from water *via* light activation of such complexes.<sup>12</sup> Very few of these complexes have been polymeric, however.<sup>13-15</sup> Here, we report the first example of a polymer containing a dimeric repeat unit, with the structure  $[\text{Mn}(\text{salpn})\text{-OAc-Mn}(\text{salpn})\text{-OAc}]_n$ , with three hydrogen-bonded water molecules per dimer [salpn = *N,N'*-bis(salicylidene)-1,3-diaminopropane].

The complex was prepared from the reaction of the sodium

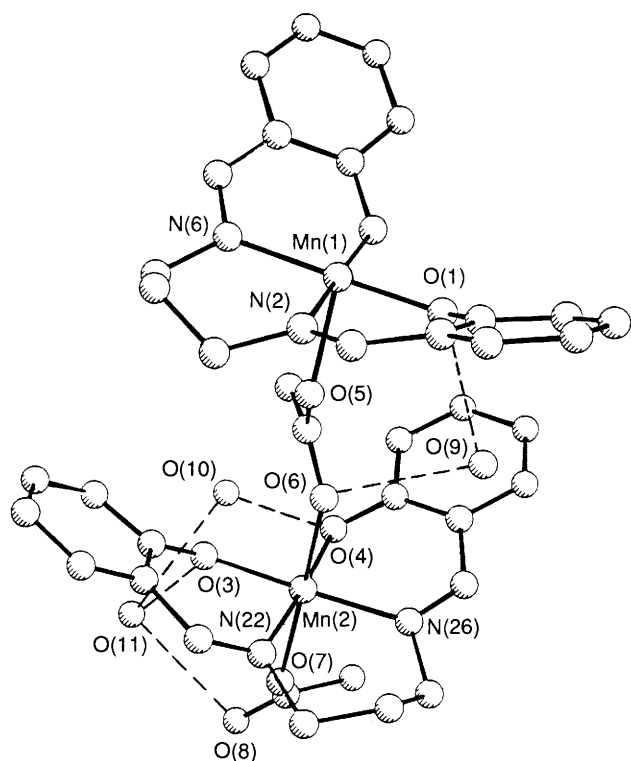


Fig. 1  $[\text{Mn}(\text{salpn})(\text{OAc})]_2 \cdot 3\text{H}_2\text{O}$ , where broken lines indicate intramolecular hydrogen bonds. (All other atoms shown are carbon; hydrogen atoms are omitted for clarity).

salt of the ligand,  $\text{Na}_2\text{salpn}$  with  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  in methanol. Bringing the solution to reflux, followed by volume reduction and slow evaporation from hexane, produced smoky, green-brown crystals suitable for X-ray diffraction studies.<sup>†</sup>

This is the first example of a manganese(III) Schiff base polymer containing acetate bridges to contain a dimeric repeat unit. Moreover, all previously reported examples of manganese(III) complexes with this stoichiometry show the ligands to be overlapping, leading to strong  $\pi$ - $\pi$  interactions between them.<sup>13-15</sup> This complex, however, has its two ligands per monomer (see Fig. 1) orientated at  $180^\circ$  with respect to each other and, as a consequence of this, there is no  $\pi$ - $\pi$  interaction. The two bridging acetate groups adopt an *anti-anti* configuration along the symmetry axis, thus producing a linear  $\text{Mn}-\text{OAc}-\text{Mn}-\text{OAc}$  chain propagated along the central axis as is illustrated by Fig. 2. IR studies show two characteristic stretches for  $\nu_{\text{C}-\text{O}}/\text{cm}^{-1}$  at 1544 and 1404, respectively, the difference in energy of which is characteristic of bridging carboxylate groups.<sup>17,18</sup>

<sup>†</sup> Crystal data:  $\text{C}_{38}\text{H}_{44}\text{Mn}_2\text{O}_{11}\text{N}_4$ ,  $M = 842.66$ , monoclinic, space group  $P2_1/n$  ( $n = 14$ ),  $a = 17.162(9)$ ,  $b = 18.595(6)$ ,  $c = 12.774(5)$  Å,  $\beta = 106.64(3)^\circ$ ,  $V = 3906(5)$  Å<sup>3</sup>,  $D_c = 1.433$  g cm<sup>-3</sup>,  $Z = 4$  (from least-squares refinement of 20 carefully centred reflections in the range  $14.20 < 2\theta < 24.30^\circ$ ). Employing graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å) on an UNKNO diffractometer producing 6316 unique reflections from 6630 reflections and employing the  $\omega/2\theta$  scanning technique ( $2\theta_{\text{max}} 48.0^\circ$ ). Structure solutions were obtained by direct methods (DIRDIF)<sup>16</sup> with hydrogen atoms constrained to chemically reasonable positions, with the exception of those of water, which were omitted. Final residual factors were  $R = 0.075$  and  $R_w = 0.050$ , respectively. All non-hydrogen atoms were treated anisotropically, giving hydrogen atoms an isotropic parameter common to each molecular ion. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

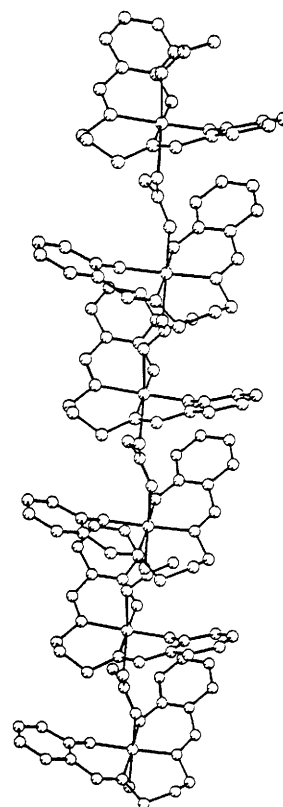


Fig. 2  $[\text{Mn}(\text{salpn})(\text{OAc})]_n$ , showing the orientation of ligands and *anti-anti* configuration of the acetate groups. (Water molecules are omitted for clarity).

The two manganese ions are in distorted octahedral environments with elongation of the Mn-O bond along the symmetry axis, *i.e.*  $\text{Mn}(1)\cdots\text{O}(1) = 1.896(6)$  and  $\text{Mn}(2)\cdots\text{O}(4) = 1.881(5)$  Å, which are consistent with distorted octahedral complexes. However,  $\text{Mn}(1)\cdots\text{O}(5) = 2.175(5)$  and  $\text{Mn}(2)\cdots\text{O}(7) = 2.157(5)$  Å are considerably longer than the Mn $\cdots$ O bond lengths quoted above. This distortion is expected for a high-spin,  $d^4$ , Mn<sup>III</sup> ion undergoing Jahn-Teller distortion. The room-temperature magnetic moment of the complex is  $4.43 \mu_B$  suggesting that the two manganese atoms may have a degree of antiferromagnetic coupling. However, the  $\text{Mn}(1)\cdots\text{Mn}(2)$  distance is  $6.411(3)$  Å, which suggests that the interaction should be very slight. The three oxygen atoms labelled in Fig. 1 as O(9), O(10) and O(11), respectively, are those of three lattice water molecules. The close proximity of these around the chain leads to an extensive network of hydrogen bonding around the structure, which shows similarities to a previously reported dimer.<sup>19</sup> It is believed that this hydrogen bonding helps to support the structure, which may be partially substantiated by the results of thermogravimetric analyses, where the complex showed a 5.4% weight loss over a temperature range of 70–120 °C. The weight change corresponds to the loss of 2.5 H<sub>2</sub>O, after which the sample rapidly decomposes. This temperature range and the gradual nature of the decomposition indicate that the water molecules do have a structural function.<sup>‡</sup>

This structure, together with those reported previously for complexes of manganese(III) Schiff bases, shows that a diverse range of structural possibilities are possible,<sup>10,12,19,20</sup> making this an interesting and unpredictable area of manganese chemistry.

<sup>‡</sup> FAB mass spectrometric data also agree with the dimeric formulation, showing a parent ion peak at 843, as well as fragments at 783, 729 and 335, respectively, which correspond to the parent ion losing one acetate group, one acetate group plus three water molecules and the monomeric Mn(salpn)<sup>+</sup> unit, respectively.

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