





**Figure 2.** Cross sections perpendicular to the  $\omega_3$  axis of the 3D NOE-HOHAHA  $^1\text{H}$  spectrum of a 20 mM solution of **1** in  $\text{D}_2\text{O}$  at 304 K and  $\text{pH} = 7$ . Cross sections are shown at the  $\omega_3$  resonance positions of GlcNAc-1 H-1 (A), Man-4 H-2 (B), and Man-4' H-2 (C). The NOE, HOHAHA, and back-transfer lines are indicated. The phase-sensitive spectrum was recorded at 500 MHz on a Bruker AM500 spectrometer by using a phase cycle of four steps on the pulse after the NOE mixing period. Combined with a phase cycle of two steps for axial peak suppression this yielded 8 scans for each FID. Acquisition was preceded by two dummy scans. Positive and negative frequencies in  $\omega_1$  and  $\omega_2$  were separated by independent TPPI on the preparation pulse and the pulse prior to the  $t_2$  evolution period. FIDs were recorded at a size of 1 K. This was repeated independently for 144 incremental  $t_1$  and  $t_2$  values, resulting in a total measuring time of approximately 63 h. During the relaxation delay of 0.45 s the HDO resonance was suppressed by radiation. Spectral width in all three time domains was 2272.7 Hz. The NOE mixing time was 0.35 s. Isotropic mixing was induced by an MLEV-17 sequence of 94 ms with trim pulses at the beginning and the end. Data were zero-filled twice in the  $t_1$  and  $t_2$  domain before Fourier transformation. Cosine bell windows were used in all three time domains. The resulting data set of  $256 \times 256 \times 512$  points was base line corrected in all frequency domains by a third-order polynomial fit.

back to spin  $a$  during the isotropic mixing period.

For the analysis of 3D NMR spectra, cross-sectional planes perpendicular to the  $\omega_3$  axis (called  $\omega_3$  cross sections) can be used (see Figure 1C). The three special planes of Figure 1B intersect this cross section at the three lines indicated as NOE, HOHAHA, and back-transfer lines. These lines intersect all at one point which lies on the body diagonal of the cube. Cross-diagonal peaks lying on the NOE or HOHAHA lines in the cross section taken at  $\omega_3 = \omega_a$  represent single magnetization transfer (by NOE or isotropic mixing, respectively) to a proton  $a$ . These lines are therefore similar to columns in 2D NOE or 2D HOHAHA spectra. All other cross peaks are due to double magnetization transfer.

Figure 2 shows three  $\omega_3$  cross sections of the 3D spectrum of **1**. In Figure 2A a cross section of H-1 of GlcNAc-1 at 5.05 ppm shows an example of the unambiguous assignment of NOE's in 3D NMR. The HOHAHA line (diagonal) shows the  $J$ -coupled connectivities to other protons of the same residue. The two cross peaks on the NOE line (horizontal) are also found on the back-transfer line (vertical), indicating two intrasidue NOE's between H-1 and the H-3 and H-5 protons located on the same side of the sugar ring. This is confirmed by the 3D cross peak between H-3 and H-5. The remaining cross peaks on the HOHAHA line are assigned to the H-2 and H-4 protons on the basis of earlier 2D HOHAHA experiments with different isotropic mixing times (unpublished results). These resonances also have an intrasidue 3D NOE cross peak. On the horizontal line at the  $\omega_2$  position of the H-4 of GlcNAc-1 the indicated cross peak can be easily assigned as an NOE to the GlcNAc-2 anomeric proton, confirming the 1-4 linkage between these residues. In 2D NOE spectra the NOE between the anomeric GlcNAc-2 H-1 and the GlcNAc-1 H-4 hidden in the bulk region could not have been unambiguously assigned due to overlap of the latter resonance with other signals. However, in 3D NMR by the double magnetization transfer (NOE and HOHAHA) this NOE can be correlated to the uniquely assigned anomeric proton of GlcNAc-1.

Another example is given in Figure 2B showing a  $\omega_3$  cross section of Man-4 H-2 at 4.19 ppm. The cross peaks on the HOHAHA line of this residue were assigned by comparing the cross sections at the Man-4 H-2 frequency with that of Man-4 H-1 (data not shown). Interresidue NOE cross peaks between the anomeric proton of GlcNAc-5 and the H-1 and H-2 protons of Man-4 are present. The presence of an NOE between Man-4 H-5 and Man-3 H-2 has been the subject of extensive discussion. The existence of this NOE was disputed by Homans et al.,<sup>5</sup> but it was finally proved by Cumming et al. in an elaborated study with a synthesized specifically deuterated trimannoside.<sup>6</sup> In the 3D spectrum of the complete biantennary structure this NOE effect is found in a direct way in Figure 2B.

An example of 3D NOE cross peaks within the bulk region is given in Figure 2C, which shows a cross section at the Man-4' H-2 frequency at 4.11 ppm. In this figure 3D cross peaks between the H-3 and H-5 protons of Man-4' and another resonance at 3.77 ppm within the bulk region are observed. The absence of a cross peak on the HOHAHA line at this frequency indicates that this

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resonance does not belong to a proton of Man-4'. Inspection of the structure of **1** shows that a likely candidate is the H-4 of the neighboring Man-3. The proximity of the Man-3 H-4 to the Man-4' H-3 and H-5 atoms would confirm the existence of a 1-6 linkage in which the conformation with  $(\phi, \psi, \omega) = (-60^\circ, 180^\circ, 180^\circ)$  must be present.

The present work illustrates the usefulness of 3D NMR techniques in structure elucidations of complicated oligosaccharides. The examples of Figure 2, parts A and B, show that unique assignments of NOE's can be made, which would have required certain assumptions in 2D NMR. Furthermore the observation of NOE's between protons within the bulk region would be very difficult in 2D NMR.

**Acknowledgment.** This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Foundation of Scientific Research (NWO). Thanks to Profs. G. Spik and J. Montreuil, Université des Sciences et Techniques de Lille Flandres Artois, France, for the gift of the diantennary compound.

### [Mn<sub>10</sub>O<sub>14</sub>{N(CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>]<sub>6</sub><sup>8+</sup>: A Mixed-Valence Polyoxomanganese Polycation Possessing Structural Similarities to Naturally Occurring Layered Manganese Oxides

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Early transition element polyoxoanions have received a great deal of attention for many years,<sup>1,2</sup> in part because of the analogy between these compounds and extended metal oxide materials. As a consequence, many discrete polyoxo anionic aggregates of V(V), Nb(V), Ta(V), Mo(VI), and W(VI) have been characterized. In contrast, there are relatively few well-defined polyoxo/hydroxo complexes of manganese and iron. This situation is presumably a consequence of the difficulty in controlling the hydrolytic or oxidative aggregation chemistry of these latter elements. High-nuclearity<sup>3</sup> carboxylate-bridged polyoxo Mn and Fe complexes, including those with 9,<sup>4,5</sup> 11,<sup>6</sup> and 12<sup>7</sup> metal atoms, have been reported recently. In addition, hydrolysis of Fe(tacn)Cl<sub>3</sub> yields an octanuclear complex.<sup>8</sup> Our interest in manganese oxo chemistry originates not only from the desire to understand and control the formation of soluble polyoxo aggregates as analogues of metal oxide surfaces but also because the oxygen-evolving complex of photosystem II most likely consists of a polynuclear manganese-oxo complex.<sup>9</sup> Herein we report the synthesis, isolation, and structure of a discrete polyoxomanganese cation,

[Mn<sub>10</sub>O<sub>14</sub>(tren)<sub>6</sub>]<sup>8+</sup> (**1**), which resembles in some respects the layered structures<sup>10</sup> of naturally occurring manganese oxide minerals chalcophanite (ZnMn<sub>3</sub>O<sub>7</sub>·3H<sub>2</sub>O),<sup>11a,12</sup> and lithiophorite ((Al,Li)MnO<sub>2</sub>(OH))<sub>2</sub>.<sup>11b,12</sup>

In a previous report,<sup>13</sup> we described the synthesis of a binuclear manganese complex obtained by controlled air oxidation of a solution containing Mn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and tren. In that case, air exposure was terminated after 2 h to yield a green complex, [Mn<sub>2</sub>O<sub>2</sub>(tren)<sub>2</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub> (**2**). It was noted that further air oxidation resulted in a brown solution. Characterization of a brown species from this latter solution constitutes the basis of this communication. The synthesis of **1** is initiated by dissolving 1.6 g of Mn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2MeCN and 0.64 g of tren in 10 mL of MeCN under N<sub>2</sub>. After overnight exposure to the air, 5 mL of Et<sub>2</sub>O was carefully layered on top of the MeCN solution. The crystals of **1**(CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·6MeCN that deposit over 3 days lose solvent rapidly when removed from the mother liquor. However, they were suitable for X-ray diffraction experiments,<sup>14</sup> provided crystal mounting and data collection were carried out at low temperature in order to prevent loss of MeCN from the crystal lattice. The remaining crystals were collected and washed with Et<sub>2</sub>O and dried in vacuo to yield 0.49 g of product<sup>15</sup> (47% yield) which analyzes as the desolvated cluster.

The centrosymmetric structure of **1** is shown from two perspectives in Figure 1.<sup>16</sup> On the basis of charge considerations, there are four Mn(III) and six Mn(IV) atoms in the cation. As is the case for other trapped valence manganese complexes **2**,<sup>13</sup> [Mn<sub>4</sub>O<sub>3</sub>Cl<sub>6</sub>(HIm)(CH<sub>3</sub>COO)<sub>3</sub>]<sup>2+</sup> (**3**),<sup>17</sup> and the dodecanuclear carboxylate species [Mn<sub>12</sub>O<sub>12</sub>(CH<sub>3</sub>COO)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>] (**4**),<sup>7</sup> for example, Mn(III) atoms can be identified by the presence of axial bond distances which are elongated due to Jahn-Teller distortions. Thus, Mn(3) and Mn(5),<sup>18</sup> which have long Mn-N distances of 2.291 (2), 2.287 (2), and 2.283 (2) Å are assigned as Mn(III) ions. In contrast, the longest Mn-N distance for Mn(4) is 2.065 (3) Å and is assigned as Mn(IV) along with the remaining Mn atoms, Mn(1) and Mn(2). Three types of bridging oxo groups are present in the structure, including six doubly bridging atoms (O(5), O(6), O(7)) and two types of triply bridging oxo atoms. Of the eight μ<sub>3</sub>-oxo bridges, four (O(3), O(4)) have a "t-shaped" geometry similar to that found in [Fe<sub>3</sub>O(TiEO)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub>Cl]<sub>3</sub>.<sup>5,19</sup> The remaining four oxo groups (O(1), O(2)) are in sites of near trigonal microsymmetry and well out of the plane of the three manganese atoms to which they are attached. Compounds **3** and **4** have similar nonplanar μ<sub>3</sub>-oxo bridges.

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(14) X-ray analysis: The compound [Mn<sub>10</sub>O<sub>14</sub>(tren)<sub>6</sub>](CF<sub>3</sub>SO<sub>3</sub>)<sub>8</sub>·6MeCN crystallizes in the triclinic system space group P $\bar{1}$ , with  $a = 15.658$  (7) Å,  $b = 15.681$  (3) Å,  $c = 15.557$  (3) Å,  $\alpha = 115.80$  (1)°,  $\beta = 92.26$  (2)°,  $\gamma = 119.21$  (2)°,  $V = 2842$  Å<sup>3</sup>,  $\rho(\text{calcd}) = 1.756$  g cm<sup>-3</sup>, and  $Z = 1$ . With the use of 8003 reflections collected at 163 K with Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation out to  $2\theta = 45^\circ$  on a single-crystal X-ray diffractometer, the structure was solved by a combination of Patterson and direct methods (SHELXS 86) and difference Fourier methods and refined to  $R$  ( $R_w$ ) values of 3.6% (4.7%).

(15) Anal. Calcd for C<sub>44</sub>H<sub>108</sub>F<sub>24</sub>Mn<sub>10</sub>N<sub>24</sub>O<sub>38</sub>S<sub>8</sub>: C, 18.58; H, 3.83; N, 11.82. Found: C, 18.17; H, 3.70; N, 11.58.

(16) Selected bond distances and angles (a full listing is provided as Supplementary Material): Mn(1)-O(1) 1.980 (2), Mn(1)-O(2) 1.874 (2), Mn(1)-O(3) 1.914 (2), Mn(1)-O(5) 1.804 (2), Mn(1)-O(1') 1.898 (2), Mn(1)-N(21) 2.058 (2), Mn(3)-O(2) 1.918 (2), Mn(3)-O(5) 1.828 (2), Mn(3)-O(4') 2.136 (2), Mn(3)-N(11) 2.291 (2), Mn(3)-N(31) 2.070 (3), Mn(3)-N(41) 2.083 (2), Mn(1)-O(1)-Mn(1') 96.7 (1), Mn(1)-O(1)-Mn(2) 93.95 (8), Mn(2)-O(1)-Mn(1') 96.89 (6), Mn(1)-O(3)-Mn(2) 99.4 (1), Mn(1)-O(3)-Mn(5) 165.4 (2), Mn(2)-O(3)-Mn(5) 92.51 (9), Mn(1)-O(5)-Mn(3) 98.0 (1), Mn(2)-O(6)-Mn(5) 96.6 (1).

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