

# Trimanganese complexes with a linear Mn<sup>II</sup>Mn<sup>III</sup>Mn<sup>II</sup> assemblage bridged by carbohydrates

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Reaction of manganese(II) salts (MnX<sub>2</sub>·nH<sub>2</sub>O, X = Cl, Br, NO<sub>3</sub>) with tris[(N-aldosyl)aminoethyl]amines L<sup>n</sup>, prepared by the reaction between tris(aminoethyl)amine (tren) with aldose [D-mannose (D-man) (L<sup>1</sup>)] or L-rhamnose [L-rha = 6-deoxy-L-man) (L<sup>2</sup>)] *in situ*, affords red-orange crystals formulated as [(MnL<sup>n</sup>)<sub>2</sub>Mn(H<sub>2</sub>O)]X<sub>3</sub> (n = 2, X = Cl **1**; n = 2, X = Br **2**; n = 2, X = NO<sub>3</sub> **3**; n = 1, X = Cl **4**), complexes **3** and **4** are characterized by X-ray crystallography.

Carbohydrates are indispensable building blocks and energy sources to living organisms and play important roles in many biological functions.<sup>1</sup> Interactions of carbohydrates with metal ions have become a significant subject in the bioinorganic field, since many sugar-metabolizing enzymes have been revealed to function with metal ions such as Mg<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, and Zn<sup>2+</sup> in the active sites.<sup>2–6</sup> Xylose isomerases, which promote the aldose–ketose isomerization, involves carboxylate-bridged dinuclear Mg<sup>2+</sup>, Mn<sup>2+</sup> and Co<sup>2+</sup> ions in the active site with a *ca.* 4.9 Å metal–metal separation.<sup>4</sup> The similar dinuclear centre of Mg<sup>2+</sup> or Mn<sup>2+</sup> with a *ca.* 3.7 Å separation also promotes the cleavage of phosphate esters in fructose 1,6-bisphosphatase.<sup>5</sup> We have studied the chemistry of transition-metal complexes with carbohydrates utilizing N-glycosidic bond formation,<sup>7</sup> and wish to report herein the synthesis and characterization of novel trimanganese complexes with a linear Mn<sup>II</sup>Mn<sup>III</sup>Mn<sup>II</sup> core bridged by carbohydrates.

The potentially heptadentate N-glycoside ligands, tris[(N-aldosyl)aminoethyl]amine L<sup>n</sup>, prepared by the reaction between tris(aminoethyl)amine (tren) with aldose [D-mannose (D-man) (L<sup>1</sup>) or L-rhamnose (L-rha = 6-deoxy-L-man) (L<sup>2</sup>)] *in situ*, were treated with manganese(II) salts (MnX<sub>2</sub>·nH<sub>2</sub>O; X = Cl, Br, NO<sub>3</sub>) in methanol. The work-up of the resultant solutions afforded red-orange crystals formulated as [(MnL<sup>n</sup>)<sub>2</sub>Mn(H<sub>2</sub>O)]X<sub>3</sub>·nH<sub>2</sub>O in 10–42% yield (1·11H<sub>2</sub>O: n = 2, X = Cl; 2·10H<sub>2</sub>O: n = 2, X = Br; 3·8H<sub>2</sub>O: n = 2, X = NO<sub>3</sub>; 4·2H<sub>2</sub>O: n = 1, X = Cl).<sup>†</sup> These trimanganese–sugar complexes were assumed to have an almost identical structure to each other on the basis of electronic absorption and circular dichroism spectra<sup>8</sup> and magnetic susceptibilities, μ<sub>eff</sub> = 15.1–16.0 μ<sub>B</sub> per Mn<sub>3</sub> unit (23 °C, solid state).<sup>‡</sup>

The structures of **3** and **4** were determined by X-ray crystallography to comprise a linearly ordered trimanganese core bridged by two carbohydrate residues with a Mn···Mn separation of 3.845(2) Å (**3**) and 3.911(5) (av.) Å (**4**) and a Mn–Mn–Mn angle of 180.0° (**3**) and 171.0(1)° (**4**), Fig. 1. The terminal Mn atoms are seven-coordinate with a distorted monoface-capped octahedral geometry ligated by L<sup>n</sup> through three oxygen atoms of C-2 hydroxy groups, three N-glycosidic nitrogen atoms, and a tertiary amino nitrogen atom, as observed in [CoL<sup>2</sup>]SO<sub>4</sub> **6**.<sup>7i</sup> The C<sub>3</sub> helical configurations and the NO

chelate conformations are denoted as Δ-*lcl*(λ<sub>3</sub>) and Λ-*lcl*(δ<sub>3</sub>), respectively, for **3** and **4**.<sup>7i</sup> The central Mn atoms are five-coordinate ligated by four oxygen atoms of carbohydrate residues in the L<sup>n</sup> ligands and one water molecule, resulting in a square-pyramidal geometry. On the basis of the bond lengths, the oxidation states of the terminal and central manganese atoms are assumed to be Mn<sup>II</sup> and Mn<sup>III</sup>, respectively. This formulation of Mn oxidation states is also consistent with the relatively nitrogen-rich coordination sphere on the terminal Mn atoms. The C-2 and C-3 hydroxy groups of the bridging sugar moieties are also estimated to be deprotonated from the short bond lengths to the central Mn atom (1.88–1.96 Å). Alternatively, the complex cations can be viewed as two seven-coordinate manganese(II) complexes, [MnL<sup>n</sup>]<sup>2+</sup>, trapping a Mn<sup>III</sup> ion through a sugar tentacle. To our knowledge, the present trimanganese complex is the first example of Mn<sup>II</sup>–Mn<sup>III</sup>Mn<sup>II</sup> linear assemblage, whereas many Mn<sup>II</sup><sub>3</sub><sup>8</sup> and Mn<sup>III</sup>–Mn<sup>II</sup>Mn<sup>III</sup><sup>9</sup> compounds have already been reported.

The structurally characterized examples of dimetal complexes with bridging carbohydrates are extremely rare. Only two structures have been reported, namely, [Mo<sub>2</sub>O<sub>5</sub>(D-lyx)]<sup>710</sup> (lyx = lyxose) and [Mn<sub>2</sub>{N,N'-(D-man)<sub>2</sub>-N,N'-Me<sub>2</sub>en}{N-(D-man)-N,N'-Me<sub>2</sub>en}(MeOH)]Cl<sub>2</sub> **8**,<sup>7a</sup> both of which involve a

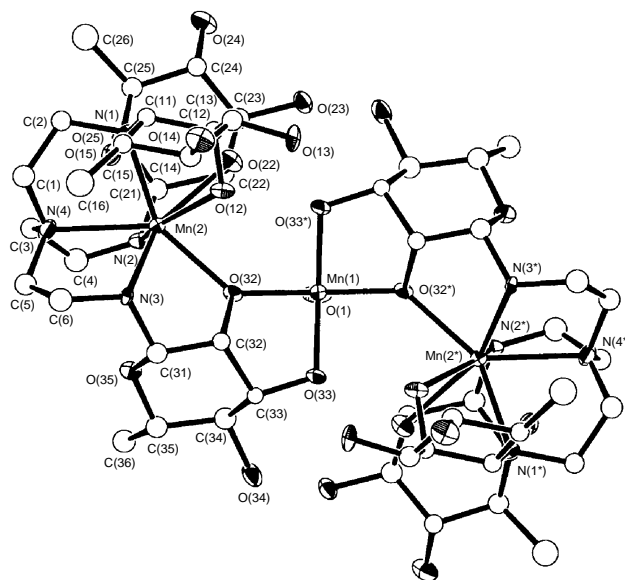


Fig. 1 ORTEP diagram of the complex cation of [(MnL<sup>2</sup>)<sub>2</sub>Mn(H<sub>2</sub>O)]<sup>3+</sup>, viewed down vertical to the central square plane. Selected bond lengths (Å) and angles (°): Mn(1)–O(1) 2.16(1), Mn(1)–O(32) 1.891(7), Mn(1)–O(33) 1.921(8), Mn(2)–O(12) 2.299(9), Mn(2)–O(22) 2.579(9), Mn(2)–O(32) 2.250(8), Mn(2)–N(1) 2.25(1), Mn(2)–N(2) 2.24(1), Mn(2)–N(3) 2.23(1), Mn(2)–N(4) 2.43(1) Å; Mn(1)–O(32)–Mn(2) 136.3(4).

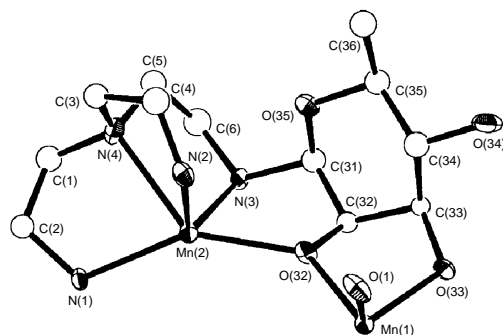


Fig. 2 A perspective drawing of the sugar bridging part in **3**

$\beta$ -furanose bridging system. In complexes **3** and **4**, a  $\beta$ -mannopyranosyl skeletal unit with a chair conformation bridges the two manganese ions with the C-2  $\mu$ -alkoxy group joining two metal ions and the C-1 *N*-glycosidic amino and the C-3 alkoxy groups coordinating to each metal centre (Fig. 2). These structural features could lead to a new general equatorial–axial–equatorial bridging system of sugars and suggested stronger affinity of the mannose-type aldoses, having 2,3-*cis* configuration, to dimetal centres than that of the glucose type aldoses which possess a 2,3-*trans* configuration.

The present study reports the unprecedented mixed-valence trimanganese(II,III,II) complexes with *N*-glycoside ligands, which could provide useful insight into the interaction of carbohydrates with dimetal ions and interesting physical properties in the multinuclear manganese chemistry.

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#### Footnotes

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† Detailed synthetic procedures and analytical, spectral, and magnetic data for **1–4** are available on request from the authors.

‡ The preliminary temperature dependent magnetic data showed a very weak antiferromagnetic interaction between the central and terminal metal centres, which could be tentatively ascribable to the relatively long metal–metal distances and the square-pyramidal geometry of the central metal ions (see X-ray structures). The detailed results will be reported in our subsequent full report. The crystals of **4** are very unstable in air and hygroscopic, and a crystal was sealed into a glass-tube capillary with a small amount of mother-liquor at low temperature. This sampling procedure may lead to the low quality of the X-ray structure.

§ *Crystal data*: for **3**·5H<sub>2</sub>O: orthorhombic, space group C222<sub>1</sub> (no. 20),  $a = 12.925(5)$ ,  $b = 21.255(7)$ ,  $c = 26.871(7)$  Å,  $U = 7382$  Å<sup>3</sup>,  $Z = 4$ ,

$D_c = 1.461$  g cm<sup>-3</sup>,  $T = -147$  °C,  $R = 0.074$ ,  $R_w = 0.074$  [ $w = 1/\sigma^2(F_o)$ ] for 2319 refs. with  $I > 3\sigma(I)$ .

**4**·6H<sub>2</sub>O: trigonal, space group  $P3_1$  (no. 144),  $a = 12.712(8)$ ,  $c = 41.053(9)$  Å,  $U = 5744$  Å<sup>3</sup>,  $Z = 3$ ,  $D_c = 1.438$  g cm<sup>-3</sup>,  $T = -147$  °C,  $R = 0.083$ ,  $R_2 = 0.091$  [ $w = 1/\sigma^2(F_o)$ ] for 3108 refs. with  $I > 3\sigma(I)$ . The structures were solved and refined with teXsan program package.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/431.

¶ An ORTEP plot of the complex cation of **4** is available on request from the authors.

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