Binuclear Homoleptic Manganese(III,III) and Manganese(IV,III) Complexes with Deprotonated d-Mannose from Aqueous Solution**

Andreas Geisselmann, Peter Klüfers,* and Bernd Pilawa

A significant principle of bioinorganic chemistry is that the potentials of (mostly oligonuclear) redox systems increase only gradually with increasing oxidation state when the respective higher oxidation number of the central metal is stabilized by deprotonation of the Brønsted acid ligands.[1] Carbohydrates, which are polybasic acids and ubiquitous in organisms, should be of some significance for such reactions. However, the polyanionic ligands derived from carbohydrates appear to be strongly prone to oxidation. Here we report that even anions of a “reducing” sugar are able to form surprisingly stable coordination compounds with higher oxidation states of the important “biometal” manganese, thus giving rise to unexpected chemistry in aqueous solution at circumneutral pH.

“Manganese(III) acetate”[2] is a common oxidizing agent in organic chemistry.[3] At pH 13 and under cooling with ice a stable, red solution that absorbs oxygen is formed on reaction with the reducing[4] aldohexose with a molar ratio NaOH:Mn:D-Man = 20:1:3; cMn = 0.04 mol L⁻¹. On exclusion of air, diffusion of barium chloride into the reaction solution yields red, rhombic crystals of Ba₂[Mn[β-(d-Man/H₂O)]₃·13H₂O (1, Man = mannofuranose). This is simply a homoleptic coordination compound of manno pentanions and man戍(III) formed without any redox reactions taking place. Complex 1 is isotypic with analogous metalates of the nonoxidizing trivalent states of vanadium, chromium, iron, aluminum, and gallium with entirely deprotonated d-mannose ligands.[5]

In the binuclear anions (Figure 1 a), the manganese(III) atoms are the central atoms of two edge-sharing, distorted octahedra. The assignment of the oxidation state is particularly supported by the Jahn–Teller (JT) distortion of the high-spin d⁹ central atoms, which may be separated from distortion due to steric strain by comparison with the isotypic compounds (Figure 2). The coordination of the second metal-atom site may be analyzed analogously. The resulting tetragonal elongation is the same when iron(III) and manganese(III) are compared as two ions with the same crystal radius.[7]

When calcium hydroxide is used instead of caustic soda, stable solutions may be prepared even for biochemically more relevant circumneutral pH values. When a molar ratio of Ca:Mn₃d-Mn-3:2:6 (cM₃ = 0.04 mol L⁻¹) is used, a red-brown solution of pH 7 is obtained; use of 3.5 equivalents of Ca(OH)₂ yields solutions of pH 9. Addition of barium chloride results in formation of a precipitate, which may be isolated as red-brown rhombic crystals when barium chloride is allowed to slowly diffuse into the reaction solution. X-ray analysis[5] reveals a mixed-valence compound of analogous structure with the formula Ba₂[Mn₃Mn[β-(d-Man/H₂O)]₃Cl-14H₂O (2). The crystals of 2 were of good quality, and the unexpected oxidation state +Ⅳ for one of the central atoms of the likewise binuclear complex anions could be unambiguously assigned (Figure 1 b): 1) All hydrogen atoms could be located with satisfactory certainty; hence, the charge of the ligands can be determined directly. (2) The Mn–O bond lengths in 2 (as in 1) lie within the range observed for other manganese compounds with MnO₃ coordination (Table 1). 3) For 2 the

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Figure 1. 1) The tetraanion in 1 (ORTEP plot, ellipsoids for the 60% probability level). Bond distances [pm] and angles [°]: from Mn1 to: O5 186.9(9), O52 191.1(8), O62 196.1(8), O31 197.0(8), O61 214.7(9), O32 218.9(9); from Mn2 to: O11 188.9(9), O12 189.6(9), O21 194.8(9), O32 205.3(7), O22 206.5(9), O31 224.4(9); Mn1···Mn2 332.3(3); Mn1·O31·Mn2 103.9(4), Mn1·O32·Mn2 103.0(4). b) The C₂ symmetric tetraanion in 2 (ORTEP plot, ellipsoids for the 70% probability level: the C₂ axis runs through the two manganese atoms). Bond distances [pm] and angles [°]: from Mn1 (MnIV) to: O5 185.1(5), O6 189.0(5), O3 191.9(5); from Mn2 (MnIII) to: O1 188.3(5), O2 196.6(4), O3 218.2(5); Mn1···Mn2 324.5(2); Mn1·O3-Mn2 104.4(2).

Figure 2. Bond lengths between the central metal and O atoms of the open-chain part of the deprotonated manno ligands (O₃·S·6) in Ba₂[Mn[β-(d-Man/H₂O)]₃·13H₂O (M = Cr, Fe)[6] as well as in 1 and 2. The data points for bonds to bridging O atoms (O₃) are connected by dashed lines. The variance of the distance for crystal field stabilized chromium(III) is smaller than for the high-spin d⁵ Fe(III) ion, which shows no crystal-field effects; furthermore, the distances are larger when bridging O atoms are involved. The tetragonal distortion of the MnO₆ octahedra in 1 takes place along the O61-Mn1-O32 and O31-Mn2-O22 axes.

diagnostic JT distortion of the trivalent stage is cancelled, and, hence, the variance of the bond lengths is as small as for the isoelectronic chromium(II) ion.

In 1 the spins of the high-spin manganese centers ($S = 2$) are coupled antiferromagnetically ($J = -3$ cm$^{-1}$). In 2 ($S = 3/2$ and $S = 2$) ferromagnetic coupling is observed; the coupling constant is $+19$ cm$^{-1}$.[9] For 2 $\chi T$ increases from 4.8 emu K mol$^{-1}$ at 300 K with decreasing temperature until a maximum of 7.6 emu K mol$^{-1}$ is reached at 20 K.

Neutral solutions from which 2 may be isolated are surprisingly stable. They remain visually unchanged for some days, and even heating for 1 h to 80 °C does not alter the appearance of the solutions. The UV/Vis spectrum of a solution that has been stored at room temperature for one week indicates a slight decrease in the MnIV content. The solutions do not absorb oxygen from air. Hence, 2 may be prepared even under a nitrogen atmosphere by partial disproportionation of manganese(III).

The dependence of equilibrium (1) ($\beta$-d-Man/H$_2$O) on pH can be quantified by UV/Vis spectroscopy on exclusion of oxygen (Figure 3). The formation of the MnIVMnIII species, which can be monitored by means of the red shift of the charge-transfer absorption, is complete below pH 10 when sodium counterions are present, whereas the MnIII species is stable against disproportionation above pH 11. The isobestic point at the right of Figure 3 is defined precisely by five of the seven spectra; there are further species only in the narrow range between pH 10 and 10.5 (deviation of the extinction values at the isobestic point at 13 400 cm$^{-1}$: 2 L mol$^{-1}$ cm$^{-1}$, too low for pH 10; 1 L mol$^{-1}$ cm$^{-1}$, too high at pH 10.5). Disproportionation takes place at a somewhat lower pH when calcium is the counterion. In this case the spectrum of a solution at pH 9.5 indicates a mixture of approximately equal parts of the MnIII and the MnIVMnIII species. The equilibrium is reversible in solutions containing either sodium or calcium as counterions.

The unexpected inertness of the higher oxidation states of manganese towards a reducing sugar is best highlighted by experiments on oxygen absorption. When the pH value of neutral solutions containing calcium ions is shifted to the weakly alkaline region, oxygen is absorbed (with a decrease in pH).[10] The result of the reaction with excess oxygen in a noncoordinating buffer at pH 9.5 is depicted in Figure 4: At room temperature, the deprotonated mannose ligands are not oxidized, even by pure oxygen in the presence of the proven reduct catalyst manganese. Instead, the MnIVMnIII compound is formed quantitatively, and O$_2$ absorption is then brought to a standstill! Further absorption of oxygen, which then results in decomposition of the solution, needs strongly alkaline conditions. A binuclear MnV species, which was recently found for binuclear complexes with bridging boronato ligands,[12] has not been observed yet with mannose ligands.

Complexes 1 and 2 are related to the manganese (hydr)oxides not only in terms of atomic distances (Table 1), but also electrochemical potentials. The known mixed-valence state as in 2 is the (rather poorly defined) “groutellite” (MnO$_2$(OH)), which is formed in the course of electrochemical reduction of ramsdellite (MnO$_2$) to groutite (MnO(OH)) domains on half-reduction. In 1 M KOH groutellite is reduced to groutite (MnO(OH)) at room temperature, vigorous stirring); the volumetrically determined molar ratio $n_{\text{O}_2} : n_{\text{Mn}}$ is 1:2 L mol$^{-1}$ with oxygen (ca. pH 9.5, room temperature, vigorous stirring); the volumetrically determined molar ratio $n_{\text{O}_2} : n_{\text{Mn}}$ is 1:2 L mol$^{-1}$ with oxygen (ca. pH 9.5, room temperature, vigorous stirring).

Table 1. Mean Mn–O bond lengths [pm] in manganese compounds with octahedral O$_6$ coordination.[8] 

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<tr>
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<th>Mn$^{\text{II}}$</th>
<th>Mn$^{\text{IV}}$</th>
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<tbody>
<tr>
<td>1: Mn1</td>
<td>200.2 ± 12.0</td>
<td>–</td>
</tr>
<tr>
<td>1: Mn2</td>
<td>201.7 ± 12.2</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>201.0 ± 12.6</td>
<td>188.7 ± 2.8</td>
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</tbody>
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**Figure 3.** UV/Vis spectra of alkaline solutions (NaOH) of manganese(III) acetate and d-mannose (Mn$^{\text{III}}$:d-Man = 2.5, $c_{\text{Mn}}$ = 0.064 mol L$^{-1}$) at various pH values (recorded under nitrogen and cooling with ice).

**Figure 4.** Oxidation of a solution of Ca(OH)$_2$/NaOH/manganese(III) acetate-d-mannose (0.12, 0.144, 0.064, 0.15 m) buffered with 2-cyclohexylaminothanesulfonic acid (CHES, 0.24 m) with oxygen (ca. pH 9.5, room temperature, vigorous stirring); the volumetrically determined molar ratio $n_{\text{O}_2} : n_{\text{Mn}}$ is 1:2 L mol$^{-1}$ with oxygen (ca. pH 9.5, room temperature, vigorous stirring). The reaction equation given is valid for the Mn$^{\text{II}}$ part (see text); the electron balance of the disproportionated part is naturally the same, however, Mn$^{\text{IV}}$ oxidation and complexation needs more OH$^-$ ions than are released in the parallel reaction. The OH$^-$ consumption determined by titration shows about equal concentration of the species of equilibrium (1).

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gram of the manganese system shows a quasi-reversible Mn$^{III}$ → Mn$^{II}$Mn$^{III}$ transition in strongly alkaline solution at a potential of −0.31 V versus AgCl/AgCl$^{-}$ (−0.09 V versus SHE; Figure 5). In the pH range of the disproportionation of the Mn$^{III}$ species, increasingly higher scan speeds are required to achieve reoxidation. When the potential range is extended to more negative values, reduction to manganese(II) is observed about 0.3 V below the quasi-reversible stage, as with the oxides. The manganese(II) species now formed in higher concentration decompose quickly with respect to various scan speeds applied; therefore, no reoxidation is observed in these experiments, and the individual cycles are no longer identical. We will report on a deeper insight into the interplay between stereo and redox chemistry, which may be obtained from experiments with rac-manganese as ligand.

Keywords: bioinorganic chemistry • carbohydrates • cyclic voltammetry • manganese • redox chemistry


[2] Commercially available manganese(III) acetate dihydrate is 95% pure; in addition to Mn$^{III}$ it contains Mn$^{II}$ and manganese dioxide. The latter remains undissolved when manganese solutions are prepared and has to be removed by filtration.


[4] Attempts to crystallize cupric complexes of reducing sugars resulted in the Fehling reaction within a few minutes, even when cooling with ice.

[5] Crystal structure analyses: General: Stoe IPDS area detector, MoK$_{α}$ (graphite monochromator, $λ$ = 71.069 pm), direct methods (SHELXS), full-matrix refinement on $F^{2}$ (SHELXL), H atoms at C in calculated positions, maximum shift: 0.001 a, geometrical analysis and graphics by PLATON, ORTEP, and SCHAKAL. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@ifz-karlsruhe.de), on quoting the depository numbers CSD-407817 (1) and -407818 (2). 1: $C_{x}H_{y}Ba_{2}Mn_{3}O_{12}$. 13.5H$_{2}$O, $M_{r} = 977.97$, $ρ_{calc} = 2.3042$ g cm$^{-3}$, crystal size 0.18 × 0.08 × 0.05 mm, rhombohedral, $P_{2}_{1}/2_{1}/2_{1}$, $a = 10.7547(8)$, $b = 14.8992(12)$, $c = 17.5938(15)$ Å, $V = 2819.2(4)$ Å$^3$, $Z = 4$, $T = 200$ K, $μ = 3.732$ mm$^{-1}$, 19209 hkl measured, $2θ_{max} = 56$: 6483 hkl unique, Lp correction, $R_{wp} = 0.0112$, numerical absorption correction (6 faces), mean $o(I)/I = 0.1255$, 4199 hkl with $I > 2σ(I)$, $w^{-1} = σ(F)^2 + 0.0036σ(F)^2$, $P = \max(F)^2/2σ(F)^2$, abs. structure parameter (according to H. D. Flack, Acta Crystallogr. Sect. A 1991, 39, 386–388; 0.03(4), 3.5 water molecules disordered, H atoms of some water molecules localized and not refined for 2, 426 parameters, 25 restraints, $R_{wp} = 0.0529$, $R_{1}(F^2) = 0.1142$, $S = 1.009$, min./max. difference density: −2.974/1.583 e Å$^{-3}$ near Ba; 2: $C_{x}H_{y}Ba_{2}MnCl_{3}O_{12}$. 14H$_{2}$O, $M_{r} = 1022.43$, $ρ_{calc} = 2.1192(1)$ g cm$^{-3}$, crystal size 0.20 × 0.04 × 0.03 mm, rhombohedral, $C22_{2}$, $a = 1643.4(2)$, $b = 1294.0(1)$, $c = 1507.0(2)$ pm, $V = 3204.7(6)$ × 10$^6$ pm$^3$, $Z = 4$, $T = 200$ K, $μ = 3.375$ mm$^{-1}$, 12681 hkl measured, $2θ_{max} = 56$: 3809 hkl unique, Lp correction, $R_{wp} = 0.0961$, numerical absorption correction (6 faces), mean $o(I)/I = 0.0954$, 2881 hkl with $I > 2σ(I)$, $w^{-1} = σ(F)^2 + 0.0314σ(F)^2$, $P = \max(F)^2/2σ(F)^2$, abs. structure parameter: −0.02(3), one common O–H bond length for all water molecules and $d(H\cdotsO) = 1.57 \times d(O\cdotsO)$, one common $U_{eq}$ for all H atoms, 242 parameters, 22 restraints, $R_{wp} = 0.0386$, $R_{1}(F^2) = 0.0797$, $S = 0.910$, max. difference density: 1.041 e Å$^{-3}$ near Ba.


[8] Almost neutral solutions may also be obtained with sodium hydroxide (see Figure 3). However, a dark precipitate is formed within a few hours, whose formation may be slowed down by cooling with ice.

[9] The magnetization of polycrystalline samples were measured with a SQUID magnetometer (Quantum Design Magnetic Property Measurement System) between 2 and 300 K at magnetic fields between 0.1 and 1 T.

[10] Disproportionation is quick; the UV/Vis spectrum of a solution at pH 7, recorded immediately after preparation, is the same as that of the mother liquors of the crystals and of the crystal powder of the latter was measured as the diffuse reflexion versus barium sulfate; analysis with the Kubelka–Munk function.


