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 D-mannose (D-Man) and sodium hydroxide solution (molar ratio NaOH:Mn:D-Man $= 20:1:3$, $c_{Mn} = 0.04$ mol L^{-1}). On exclusion of air, diffusion of barium chloride into the reaction solution yields red, rhombic crystals of $Ba_2[Mn_2^{III}(\beta\text{-D-Man}f H_{-5})_2] \cdot 13 H_2O$ (**1**, Man$f$ = mannofuranose).[5] This is simply a homoleptic coordination compound of mannose pentaanions and manganese(III) formed without any redox reactions taking place. Complex **1** is isotypic with analogous metalates of the nonoxidizing trivalent states of vanadium, chromium, iron, aluminium, and gallium with entirely deprotonated D-mannose ligands.[6] In the binuclear anions (Figure 1a), 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 d^4 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

[*] Prof. Dr. P. Klüfers, Dipl.-Chem. A. Geisselmann
Institut für Anorganische Chemie der Universität
Engesserstrasse, Gebäude 30.45, D-76128 Karlsruhe (Germany)
Fax: (+49) 721-608–4290
E-mail: kluefers@achibm2.chemie.uni-karlsruhe.de
Dr. B. Pilawa
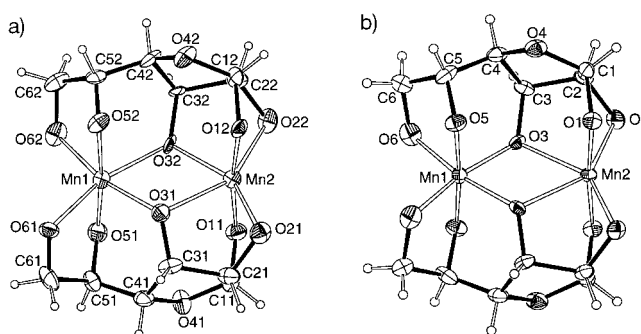Physikalisches Institut der Universität Karlsruhe

Figure 1. a) The tetraanion in **1** (ORTEP plot, ellipsoids for the 60% probability level). Bond distances [pm] and angles [°]: from Mn1 to: O51 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 205.5(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 C_2 symmetrical tetraanion in **2** (ORTEP plot, ellipsoids for the 70% probability level; the C_2 axis runs through the two manganese atoms). Bond distances [pm] and angles [°]: from Mn1 (Mn^{IV}) to: O5 185.1(5), O6 189.0(5), O3 191.9(5); from Mn2 (Mn^{III}) to: O1 188.3(5), O2 196.6(4), O3 218.2(5); Mn1···Mn2 324.5(2); Mn1-O3-Mn2 104.4(2).
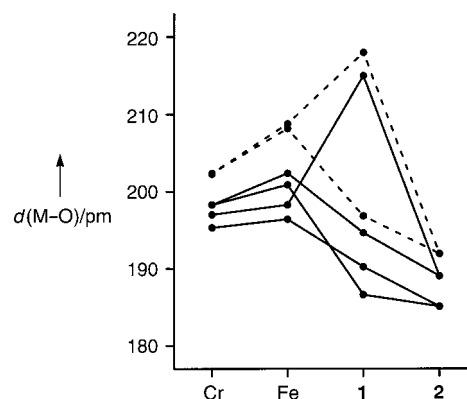

Figure 2. Bond lengths between the central metal and O atoms of the open-chain part of the deprotonated mannose ligands (O3,5,6) in $Ba_2[M_2^{III}(\beta\text{-D-Man}f H_{-5})_2] \cdot 13 H_2O$ (M = Cr, Fe)[6] as well as in **1** and **2**. The data points for bonds to bridging O atoms (O3) are connected by dashed lines. The variance of the distance for crystal field stabilized chromium(III) is smaller than for the high-spin d^5 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 MnO$_6$ octahedra in **1** takes place along the O61-Mn1-O32 and O31-Mn2-O22 axes.

relevant circumneutral pH values. When a molar ratio of Ca:Mn^{III}:D-Man $= 3:2:6$ ($c_{Mn} = 0.04$ 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.[8] 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 $Ba_2[Mn^{IV}Mn^{III}(\beta\text{-D-Man}f H_{-5})_2]Cl \cdot 14 H_2O$ (**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 1b): 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 MnO$_6$ coordination (Table 1). 3) For **2** the

Table 1. Mean Mn−O bond lengths [pm] in manganese compounds with octahedral O_6 coordination.[a]

	Mn^{III}	Mn^{IV}
1: Mn1	200.2 ± 12.0	–
1: Mn2	201.7 ± 12.2	–
2	201.0 ± 12.6	188.7 ± 2.8
$[Mn^{IV}(cat)_3]^{2-}$[b][14]	–	189.5 ± 1.7
groutite (α-MnO(OH))[15]	204.1 ± 16.4	–
pyrolusite(β-MnO$_2$)[16]	–	188.7

[a] Crystal radius of six-coordinate high-spin Mn^{3+}: 78.5, of Mn^{4+}: 67.0 pm.[7] [b] (cat = catecholate).

diagnostic JT distortion of the trivalent stage is cancelled, and, hence, the variance of the bond lengths is as small as for the isosteric chromium(III) 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** χT 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 Mn^{IV} 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).[10] The dependence of equilibrium (1) (L = β-D-Man$f$H$_{-5}$) on pH can be quantified

$$1.5 [Mn_2^{III}L_2]^{4-} + 5 H_2O \rightleftharpoons [Mn^{III}Mn^{IV}L_2]^{3-} + Mn^{2+} + LH_5 + 5 OH^- \quad (1)$$
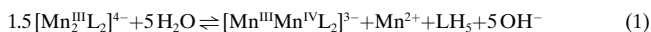
by UV/Vis spectroscopy on exclusion of oxygen (Figure 3). The formation of the $Mn^{IV}Mn^{III}$ species, which can be monitored by means of the red shift of the charge-transfer absorption, is complete below pH 10 when sodium counterions are present, whereas the Mn_2^{III} species is stable against disproportionation above pH 11. The isosbestic point at the right of Figure 3 is defined precisely by five of the seven
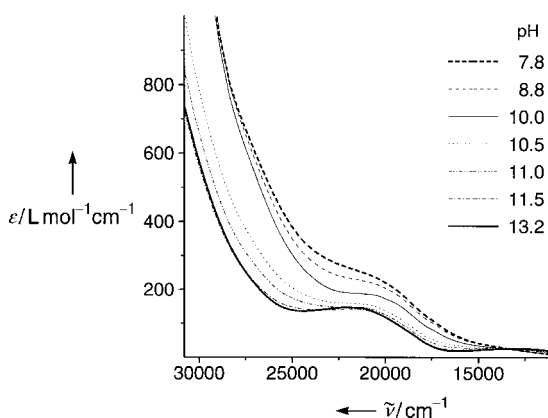

Figure 3. UV/Vis spectra of alkaline solutions (NaOH) of manganese(III) acetate and D-mannose (Mn^{III}:D-Man = 2:5, c_{Mn} = 0.064 mol L^{-1}) at various pH values (recorded under nitrogen and cooling with ice).

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 Mn_2^{III} and the $Mn^{IV}Mn^{III}$ 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).[11] The result of the reaction with excess oxygen in a noncoordinating buffer at pH 9.5 is depicted in Figure 4: At
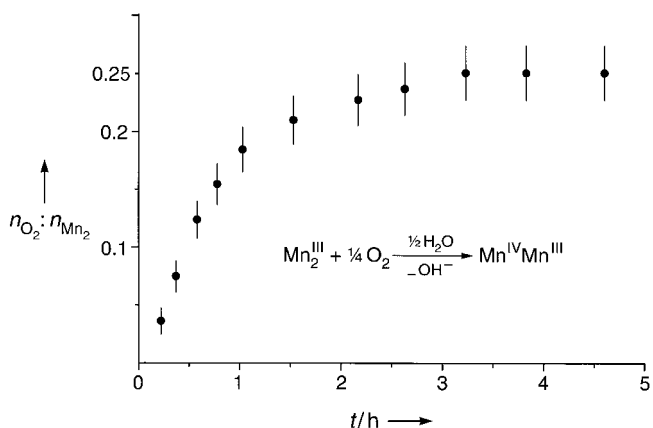

Figure 4. Oxidation of a solution of Ca(OH)$_2$/NaOH/manganese(III) acetate/D-mannose (0.12, 0.144, 0.064, 0.15 M) buffered with 2-cyclohexyl-aminoethanesulfonic acid (CHES, 0.24 M) with oxygen (ca. pH 9.5, room temperature, vigorous stirring); the volumetrically determined molar ratio of absorbed oxygen and binuclear complex is drawn as a sum curve. The reaction equation given is valid for the Mn_2^{III} part (see text); the electron balance of the disproportionated part is naturally the same, however, Mn^{II} 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).

room temperature, the deprotonated mannose ligands are not oxidized, even by pure oxygen in the presence of the proven redox catalyst manganese. Instead, the $Mn^{IV}Mn^{III}$ 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 Mn_2^{IV} 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 stage as in **2** is the (rather poorly defined) "groutellite" (Mn$_2$O$_3$(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 between $+0.05$ and -0.05 V (versus the standard hydrogen electrode, SHE).[13] Correspondingly, the cyclic voltammo-

gram of the mannose system shows a quasi-reversible $Mn_2^{III} \leftrightarrow Mn^{IV}Mn^{III}$ transition in strongly alkaline solution at a potential of -0.31 V versus AgCl/Ag,Cl$^-$ (-0.09 V versus SHE; Figure 5). In the pH range of the disproportionation of the Mn_2^{III} species, increasingly higher scan speeds are required to achieve reoxidation. When the potential range is extended
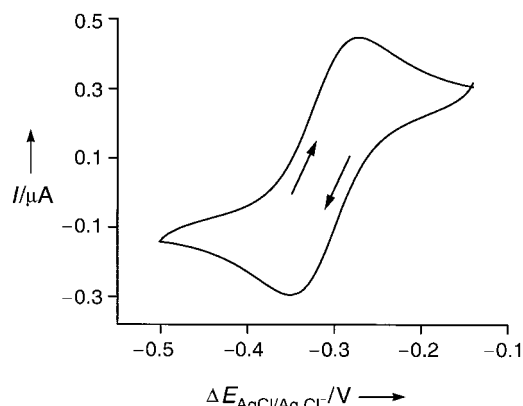

Figure 5. Cyclic voltammogram for the $Mn_2^{III}/Mn^{III}Mn^{IV}$ redox pair (0.005 M manganese(III) acetate, 0.0138 M mannose, pH 13.5, 40 mV sec^{-1} scan speed, Hg working electrode, the second cycle is depicted). The transition is quasi-reversible ($\Delta E = 79$ mV; cf. 56.5 mV for a reversible single-electron transition[17]). Reversibility decreases with decreasing pH value. The potential is almost independent of pH in the range pH 12 to 14; in the range of pH 9 to 12 the pH dependence corresponds to an addition of about one proton to the reduced form (dilution is much larger in the voltammetric investigation than for other experiments; thus, protolysis reactions are more important).

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*-mannose as ligand.

[1] For multinuclear manganese complexes, see L.-E. Andréasson, Tore Vänngård, *Encyclopedia of Inorganic Chemistry, Vol. 4* (Ed.: R. B. King), Wiley, New York, **1994**, pp. 2101–2111.

[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 mannose solutions are prepared and has to be removed by filtration.

[3] R. D. Cannon, R. P. White, *Prog. Inorg. Chem.* **1988**, *36*, 195–298, and references therein.

[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, Mo$_{K\alpha}$ (graphite monochromator, $\lambda = 71.069$ pm), direct methods (SHELXS), full-matrix refinement on F^2 (SHELXL), H atoms at C in calculated positions, maximum shift: 0.001 σ, 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@fiz-karlsruhe.de), on quoting the depository numbers CSD-407 817 (**1**) and -407 818 (**2**). **1**: $C_{12}H_{14}Ba_2Mn_2O_{12} \cdot 13.5 H_2O$, $M_r = 977.97$, $\rho_{calcd} = 2.3042(1)$ g cm^{-1}, crystal size $0.18 \times 0.08 \times 0.05$ mm, rhombic, $P2_12_12_1$, $a = 10.7547(8)$, $b = 14.8992(12)$, $c = 17.5938(15)$ Å, $V = 2819.2(4)$ Å^3, $Z = 4$, $T = 200$ K, $\mu = 3.732$ mm^{-1}, 19 209 *hkl* measured, $2\theta_{max} = 56°$, 6483 *hkl* unique, Lp correction, $R_{int} = 0.1126$, numerical absorption correction (6 faces), mean $\sigma(I)/I = 0.1255$, 4199 *hkl* with $I > 2\sigma(I)$, $w^{-1} = \sigma^2(F_o) + (0.0636 P)^2$, $3P = \max(F_o^2; 0 + 2F_c^2)$, abs. structure parameter (according to H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876–881): 0.03(4), 3.5 water molecules disordered, H atoms of some water molecules localized and refined as for **2**, 426 parameters, 25 restraints, $R_{2\sigma} = 0.0529$, $R_w(F^2) = 0.1142$, $S = 1.009$, min./max. difference density: $-2.974/1.583$ e Å^{-3} near Ba1. **2**: $C_{12}H_{14}Ba_2ClMn_2O_{12} \cdot 14 H_2O$, $M_r = 1022.433$, $\rho_{calcd} = 2.1192(1)$ g cm^{-1}, crystal size $0.20 \times 0.04 \times 0.03$ mm, rhombic, $C222_1$, $a = 1643.4(2)$, $b = 1294.0(1)$, $c = 1507.0(2)$ pm, $V = 3204.7(6) \cdot 10^6$ pm^3, $Z = 4$, $T = 200$ K, $\mu = 3.373$ mm^{-1}, 12 681 *hkl* measured, $2\theta_{max} = 56°$, 3809 *hkl* unique, Lp correction, $R_{int} = 0.0961$, numerical absorption correction (6 faces), mean $\sigma(I)/I = 0.0954$, 2881 *hkl* with $I > 2\sigma(I)$, $w^{-1} = \sigma^2(F_o) + (0.0314 P)^2$, $3P = \max(F_o^2; 0 + 2F_c^2)$, abs. structure parameter: $-0.02(3)$, one common O–H bond length for all water molecules and $d(H\cdots H) = 1.57 \times d(O-H)$, one common U_{iso} for all H atoms, 242 parameters, 22 restraints, $R_{2\sigma} = 0.0386$, $R_w(F^2) = 0.0797$, $S = 0.910$, max. difference density: 1.041 e Å^{-3} near Ba.

[6] J. Burger, C. Gack, P. Klüfers, *Angew. Chem.* **1995**, *107*, 2950–2951; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2647–2649.

[7] R. D. Shannon, *Encyclopedia of Inorganic Chemistry, Vol. 2* (Ed.: R. B. King), Wiley, New York, **1994**, pp. 929–942.

[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 **2** (the latter was measured as the diffuse reflexion versus barium sulfate; analysis with the Kubelka–Munk function).

[11] D. T. Sawyer et al. (compiled in K. Burger, L. Nagy, *Biocoordination Chemistry* (Ed.: K. Burger), Ellis Horwood, Chichester, **1990**, pp. 236–283, 269) investigated the redox chemistry of manganese complexes of sugar acids as a function of pH. As a result, higher oxidized manganese species form at higher pH. In the presence of D-gluconate the onset of oxidation of manganese(II) is at about pH 6.

[12] U. Bossek, H. Hummel, T. Weyhermüller, K. Wieghardt, S. Russell, L. van der Wolf, U. Kolb, *Angew. Chem.* **1996**, *108*, 1653–1656; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1552–1554.

[13] Y. Chabre, J. Pannetier, *Prog. Solid State Chem.* **1995**, *23*, 1–130.

[14] J. A. R. Hartmann, B. M. Foxman, S. R. Cooper, *J. Chem. Soc. Chem. Commun.* **1982**, 583–584; D.-H. Chin, D. T. Sawyer, W. P. Schaefer, C. J. Simmons, *Inorg. Chem.* **1983**, *22*, 752–758.

[15] L. S. D. Glasser, L. Ingram, *Acta Crystallogr. Sect. B* **1968**, *24*, 1233–1236.

[16] W. H. Baur, *Acta Crystallogr. Sect. B* **1976**, *32*, 2200–2204.

[17] J. Heinze, *Angew. Chem.* **1984**, *96*, 823–840; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 831–847.