

ELECTROCHEMICAL AND SPECTROSCOPIC STUDY OF THE MALTITOL COMPLEXES OF MANGANESE IN DIFFERENT OXIDATION STATES

László NAGY¹, Tamás GAJDA¹, Tibor PÁLI² and Kálmán BURGER^{1*}

(¹A. József University, Department of Inorganic and Analytical Chemistry, H-6701 Szeged, P.O. Box 440, ²Institute of Biophysics, Biological Research Center of the Hungarian Academy of Sciences, H-6701 Szeged, P.O. Box 521)

Received February 20, 1987

Accepted for publication March 18, 1987

Manganese complexes of maltitol (4-*O*- α -Glycopyranosyl-D-sorbitol) have been studied in aqueous alkaline solution by polarographic, potentiometric, pH-metric, spectrophotometric and ESR methods. The results show that stable complexes of manganese(II), manganese(III), and manganese(IV) are formed with compositions $[\text{Mn}^{\text{II}}\text{L}_3(\text{OH})_4]^{6-}$, $[\text{Mn}^{\text{III}}\text{L}_3(\text{OH})_6]^{6-}$ and $\text{Mn}^{\text{IV}}\text{L}(\text{OH})_4]^{2-}$ where L represented the dianion of maltitol. Some (electrochemical and magnetic) evidence has been obtained that the manganese(II) complex dimerizes at higher pH; possible structures for the complexes are suggested on the basis of the data. Oxidation of the manganese(II) maltitol complex with stoichiometric amounts of hydrogen peroxide produces stable solutions of manganese(III) (brown) and of the manganese(IV) complex (cherry red); oxidation of the manganese(II) maltitol complex with dioxygen also yields the above mentioned two complexes. The conditional stability constants of manganese(II), and (III) maltitol complexes have been determined by polarography on the basis of the competition between maltitol and EDTA for manganese in strongly alkaline media.

Introduction

It is well known that manganese plays a significant role in some biological redox systems of vital importance, e.g. photosystem II in green plant photosynthesis [1, 2] and mitochondrial superoxide dismutase [3]. The +2, +3 and +4 oxidation states of manganese are believed to be involved in these processes, although their role has not been cleared completely until now.

Doležal investigated the interaction of some polyhydroxy ligands with manganese of different oxidation states by polarography. The results have shown that these ligands effectively stabilize the +3 and +4 oxidation states of manganese in aqueous, alkaline solution [4–9]. Later Sawyer studied the redox behaviour of the manganese-sorbitol system, considered the most stable among these types of complexes [10]. They investigated a large number of manganese complexes formed with aliphatic and aromatic polyhydroxy

* To whom correspondence should be addressed.

ligands too [11–13]. Searching for a model of the photosynthetic water oxidation several complexes containing manganese central atoms in different oxidation states were prepared and characterized [14, 15]. The behaviour of manganese in different biological systems was reviewed by Sawyer [16].

Recently we started a systematic study of transition metal complexes formed with sugar-type ligands [17–20]. This paper summarized the results of our studies on maltitol complexes of manganese(IV), (III), and (II) obtained by electrochemical and spectroscopic methods.

Experimental

The polarograms were recorded on a Radelkis Universal Polarograph OH-105. A saturated calomel electrode served as reference, the mercury height was usually 55 cm, the capillary constants $m = 2.10 \text{ mg s}^{-1}$, $t = 3.2 \text{ s}$.

For controlled-potential electrolysis a Radelkis Model OH-404 Universal coulometric analyzer was used. A mercury pool electrode served as working, and a platinum coil as counter electrode. The reference electrode was a saturated one. The inert atmosphere was ensured by bubbling oxygen-free nitrogen through the solution.

The spectrophotometric measurements were performed with a UNICAM SP 800 recording spectrophotometer equipped with quartz cells of proper thickness. The solutions in the reference cell contained concentration of sodium hydroxide and maltitol equimolar to those in the sample cell.

For pH measurement a Radelkis Model OP 208/1 precision digital pH-meter was used.

The potentiometric measurements were performed with the same type of digital pH-meter. A platinum indicator electrode and a saturated calomel reference electrode were used.

The ESR spectra were recorded with a JEOL-JES-PE I. spectrometer in a standard quartz cuvette. When working with solutions sensitive to oxygen, the cuvette was sealed.

The electrochemical and spectroscopic measurements were carried out in solutions thermostated to $20 \pm 0.5 \text{ }^\circ\text{C}$.

Solutions of manganese(II) ($\text{MnSO}_4 \cdot n \text{ H}_2\text{O}$) were standardized complexometrically. Fresh stock solutions of maltitol (Fluka) were prepared daily. Manganese(III) acetate was prepared according to [21]. Its manganese(III) content was determined iodometrically. The 10 mol dm^{-3} sodium hydroxide solution was purified according to D'Ans and Mattner [22]. All other solutions used were prepared from p.a. chemicals.

Results and Discussion

Polarographic studies

The polarographic characteristics of the manganese-maltitol system together with the results of controlled-potential electrolysis data performed to help the assignment of the polarographic waves to the corresponding electron transfer processes, are presented in Table I.

The analysis of the polarograms was performed by plotting $\lg i / (i_d - i)$ against E (where E and i are the corresponding potential and current values and i_d the diffusion current) to determine the value of the half-wave potential ($E_{1/2}$) and — in the knowledge (from the controlled potential measurements) of the number of electrons (n) participating in the electrode reaction — the

Table I

Polarographic characteristics of manganese maltitol complexes and the results of the corresponding controlled potential electrolysis studies. Conditions: 2.16×10^{-3} mol dm $^{-3}$ manganese; 0.17 mol dm $^{-3}$ maltitol; 0.95 mol dm $^{-3}$ sodium hydroxide

Electrode process	$E_{1/2}$ (V) vs. SCE	i_d (μ A)	α	Controlled pot electrolysis (V) vs. SCE	n
Mn(II) \longrightarrow Mn(III)	-0.625	1.04	0.73	—	—
Mn(III) \longrightarrow Mn(IV)	-0.347 ^a	1.16 ^a	1.00 ^a	—	—
	-0.356 ^b	1.80 ^b	0.92 ^b	—	—
Mn(II) \longrightarrow Mn(0)	-1.715	2.32	0.75	-1.75	1.90
Mn(IV) \longrightarrow Mn(III)	-0.382	2.64	0.80	—	—
Mn(III) \longrightarrow Mn(II)	-0.69 ^b	1.48 ^b	0.60 ^b	—	—
	-0.85 ^c	2.08 ^c	0.30 ^c	—	—
Mn(II) \longrightarrow Mn(IV)	—	—	—	-0.22	2.1
Mn(IV) \longrightarrow Mn(0)	—	—	—	1.75	3.7

α Is the transfer coefficient, expressing the degree of irreversibility of the electrode process.

n Change in the number of electrons determined by controlled potential electrolysis

^{a, b, c} the data determined from polarograms of manganese(II), (III), (IV) maltitol complexes, respectively.

degree of reversibility of the process characterized by α in the equation (1);

$$\log \frac{i}{i_d - i} = \frac{\alpha n}{0.059} (E_{1/2} - E) \quad (1)$$

Similarly to manganese(II) in alkaline sorbitol solutions [9], it was found also in the present systems that manganese(II) yields one cathodic and two anodic waves in the presence or excess maltitol in strongly alkaline media (pH > 12) under an inert atmosphere (Fig. 1a, curve 2). It should be noticed that the ligand cannot be reduced or oxidized at the dropping mercury electrode. The height of the first wave with a more negative half-wave potential ($E_{1/2} = -0.625$ V vs. SCE) is a little smaller than that of the wave with a more positive half-wave potential ($E_{1/2} = -0.340$ V vs. SCE). The reduction wave is twice as high as the second oxidation wave. The manganese(II)-maltitol complex could easily be oxidized by the oxygen content of air in alkaline media. This resulted in a colour change of the solution (it turned brown) and the first anodic wave shifted to the cathodic region, and took on a redox character. Similar results were obtained when manganese(III)-acetate prepared according to [21] was added to the solution containing the manganese(II)-maltitol complex.

According to the results discussed above and the controlled potential electrolysis data, the cathodic wave can be assigned to the reduction of manganese(II) to manganese(0), and the two anodic waves to the oxidation of manganese(II) to manganese(III) and of manganese(III) to manganese(IV), respectively.

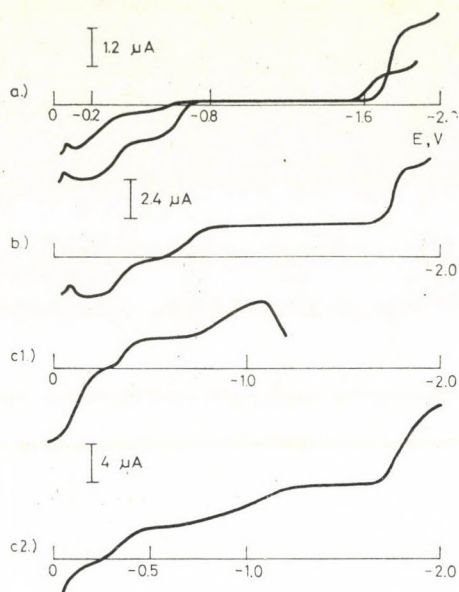


Fig. 1. Polarograms of the manganese-maltitol system; [maltitol] = $0.167 \text{ mol dm}^{-3}$; $[\text{OH}^-] = 0.95 \text{ mol dm}^{-3}$; [manganese] = $2.16 \times 10^{-3} \text{ mol dm}^{-3}$. a) manganese(II) complex, a1: pH = 12.0; a2: pH = 13.38. b) manganese(III) complex, for manganese(IV) complex pH = 12.0. c1. curve recorded immediately after oxidation, c2. curve recorded 12 hours after oxidation

The logarithmic analysis of the polarographic waves showed that the second oxidation wave is reversible, while the first anodic and the cathodic waves are quasireversible. The dependence of the limiting current on the height of the mercury column proved that all waves are diffusion-controlled.

At lower pH values ($\text{pH} < 12$) the first anodic wave almost disappeared while the height of the second anodic wave became equal to that of the cathodic one. Both waves correspond to two-electron processes, the transformation of manganese(II) to manganese(III) does not appear in an independent wave. Similar results were obtained in the case of the manganese(II)-lactobionate complex [17].

In alkaline media the colourless manganese(II)-maltitol complex is water-soluble and can be oxidized by dioxygen to a manganese(IV)-maltitol complex. The oxidation rate is decreased gradually with increasing sodium hydroxide and maltitol concentration in the solution. The oxidation state of manganese was checked iodometrically.

The polarogram of the manganese(IV)-maltitol complex recorded immediately after its preparation by oxidation with dioxygen exhibits one anodic ($E_{1/2} = -0.18 \text{ V}$) and two cathodic waves ($E_{1/2}^1 = -0.382 \text{ V}$ and $E_{1/2}^2 = -0.850 \text{ V}$ vs. SCE). The second cathodic wave is strongly irreversible. The two cathodic waves can be assigned to the reduction of manganese(IV)

to manganese(III) and manganese(III) to manganese(II), respectively. The anodic wave corresponds to two-electron processes according to the controlled-potential electrolysis measurements. The height of the above mentioned wave decreased slowly in solution to zero during its storage for days. The rate of this decrease increases with decreasing hydroxide ion concentration. When hydrogen peroxide was added to the solution, the diffusion current of this wave increased. These results indicated that in the oxidation of the manganese(II) and (III) maltitol complexes with molecular oxygen, the latter is reduced to peroxide anion in alkaline solution. A reversible wave due to the HO_2^-/O_2 couple is observed at -0.18 V vs. SCE. Similar observation was made for the manganese(II)-sorbitol system in [10]. The oxidation wave at -0.18 V assigned to the HO_2^-/O_2 complex is not influenced by the presence of manganese. This shows that the peroxide anion does not interact with the manganese(IV)-maltitol complex.

In the case of reversible and quasireversible electrode processes, polarographic data can be used to determine the composition (metal : ligand : OH^- ratio) of the complexes in solution.

The dependence of the half-wave potential of the reduction of manganese(II)-maltitol complex as a function of the hydroxide ion and maltitol concentrations, respectively, has been determined (Fig. 2). Assuming that in

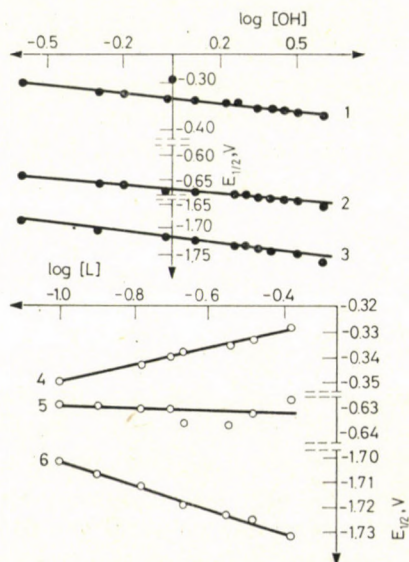


Fig. 2. Polarographic half-wave potential as a function of hydroxide ion and maltitol concentrations, respectively. $[\text{manganese}] = 2.16 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{OH}^-] = 0.95 \text{ mol dm}^{-3}$, $[\text{maltitol}] = 0.167 \text{ mol dm}^{-3}$. Curves 1 and 4 $\text{Mn}^{3+}/\text{Mn}^{4+}$, curves 2 and 5 $\text{Mn}^{2+}/\text{Mn}^{3+}$, curves 3 and 6 $\text{Mn}^{2+}/\text{Mn}^0$

the concentration range studied only the complex of maximum coordination number is formed on the basis of the relationship [23]:

$$\Delta E_{1/2} = -p \frac{0.0591}{n} \Delta \log C_x$$

the maximum coordination number (p) could be calculated where C_x is the ligand or hydroxide ion concentration, and n the change in the number of electrons during the electrode process. The results are presented in Table II.

Table II

Changes due to the electrode process in the number of ligands bonded by one manganese central atom

Electrode process	Changes in the number of ligands per metal ion in the electrode processe	
	OH ⁻	maltitol
Mn(II) \longrightarrow Mn(0)	-2.05	-1.44
Mn(II) \longrightarrow Mn(III)	-0.85	-0.08
Mn(III) \longrightarrow Mn(IV)	-0.95	+0.52
Mn(III) \longrightarrow Mn(IV)*	-1.04	+0.60

* Determined from the shift of half wave potential of manganese(III) maltitol complex.

As we can see, upon the reduction of manganese(II) to manganese(0) two hydroxide ions and 1.5 ligand molecules are liberated per one manganese central atom. According to the results obtained by the ESR method and discussed later, the manganese(II)-maltitol complex dimerizes even in weakly alkaline solution. Comparing this observation with the data presented in Table II, we can get the composition of manganese(II)-maltitol complex as $[\text{Mn}_2^{\text{II}}\text{mal}_3(\text{OH})_4]^{6-}$.

For the analysis of the oxidation waves of the manganese(II) and of the reduction waves of the manganese(IV) complex the relation [24]

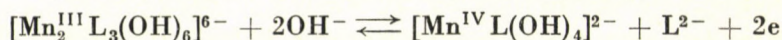
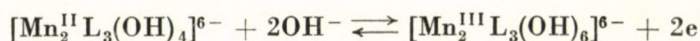
$$\Delta E_{1/2} = -(p - q) \frac{0.0591}{n} \Delta \log C_x$$

was used, where C_x is the concentration of the ligand, p is the number of ligands per metal ion in the oxidized complex, and q is the number of ligands per metal ion in the reduced complex. According to these data, the oxidation of manganese(II) to manganese(III) requires one additional hydroxide ion. The results also indicate that the number of maltitol molecules per manganese atom does not change in this oxidation process. However, oxidation of the manganese(III) to manganese(IV) complex appears to require the coordination of an additional hydroxide ion but the number of maltitol molecules bound

to the manganese central ion decreased by 0.5 per metal atom, indicating the formation of two monomeric manganese(IV) complexes from the dimeric manganese(III) species.

Taking into consideration the results shown in Table II, the manganese-maltitol complexes participated in the electrode reactions according to the following equations:

a) oxidation of manganese(II) to manganese(III) and manganese(III) to manganese(IV), respectively,



b) reduction of manganese(II) complex to metal



The equilibrium constants of the formation of the manganese maltitol complexes in alkaline media could not be determined by the conventional De Ford—Hume method [25], because of the precipitation of metal hydroxide in alkaline media. Therefore the corresponding conditional stability constants were determined on the basis of the competition between maltitol and EDTA (as auxiliary) ligands for the manganese central ion.

This method is based on the fact that all manganese EDTA complexes are polarographically inactive and the limiting current of the polarographic wave of the manganese maltitol complexes increases linearly according to the Ilkovič equation with manganese concentration.

Due to the addition of EDTA to the solution containing the manganese(II) and manganese(III)-maltitol complexes, respectively, the height of the original Mn(II) → Mn(0) or Mn(III) → Mn(II) wave (i_{d1}) decreased considerably (to i_{d2}). Knowing the total concentrations of manganese, maltitol, hydroxide ions and of EDTA used as auxiliary ligand, as well as the composition of the complexes determined above, and the stability constants of the manganese-EDTA complexes [26], the corresponding conditional stability

Table III

Overall formation equilibrium constants (β complex products)
of the manganese maltitol complexes

Total concentrations (mol dm ⁻³)			Composition of the complexes	log β values
Mn	maltitol	OH ⁻		
3.25 × 10 ⁻³	0.17	0.95	[Mn ₂ ^{II} L ₃ (OH) ₄] ⁶⁻	27.2
3.25 × 10 ⁻³	0.17	0.95	[Mn ₂ ^{III} L ₃ (OH) ₆] ⁶⁻	52.5 (51.5)*

* Determined spectrophotometrically.

constants could be calculated from the decrease of the diffusion current due to the presence of EDTA in the solution. The detailed calculation mode is presented in our previous paper [17]. The results are presented in Table III.

Potentiometric studies

The polarographic data confirmed that the redox wave with $E_{1/2} = -0.347$ V (SCE) corresponds to the oxidation (or reduction) of the maltitol complexes of manganese(III) (or manganese(IV)). This assumption was verified by the potentiometric titration of manganese(II) complex with hexacyanoferrate(III) and hydrogen peroxide standard solutions, respectively.

The oxidation with hexacyanoferrate(III) involves two steps. The polarogram of the solution after oxidation show only cathodic waves. Similar results have been obtained by Doležal et al. for the manganese(II)-sorbitol system [9].

The potentiometric titration of manganese(II)-maltitol complex with hydrogen peroxid standard solution showed two steps and the titrant consumption in both steps was equal with the theoretical value.

Spectroscopic studies

ESR measurements

The ESR spectrum of the aqueous solution of 2.85×10^{-3} mol dm⁻³ manganese(II) in presence of 0.1 mol dm⁻³ maltitol (pH < 6.0) showed 6 lines of almost the same intensity, which corresponds to the 5/2 nuclear spin of manganese [27]. This spectrum is practically identical to that of any manganese(II) salt solution of similar concentration. The spectrum was 650 G broad with a g value of 2.017 ± 0.017 .

Increasing the pH of this solution step by step by adding sodium hydroxide in an inert atmosphere did not cause any change in the pattern of the spectrum till pH 9.80; only intensity decreased (Fig. 3, curve A, B, C). The further increase of pH resulted, however, in very significant changes. At pH = 10.35 the intensity of the six-line pattern became almost zero. A further pH increase did not cause essential changes in the ESR spectrum.

On the basis of the ESR data, strong dimerization reaction of the manganese(II)-maltitol complex appears to occur in alkaline solution resulting in a dramatic decrease of the number of unpaired electrons. This reaction goes to completion in solutions of lower pH compared with the manganese(II) gluconate and saccharose complexes studied earlier [11, 18]. The maltitol molecule has one sorbitol moiety which can strongly bind manganese(II). In spite of this, no evidence in the literature was published for the dimerization of manganese(II)-sorbitol complex [9, 10].

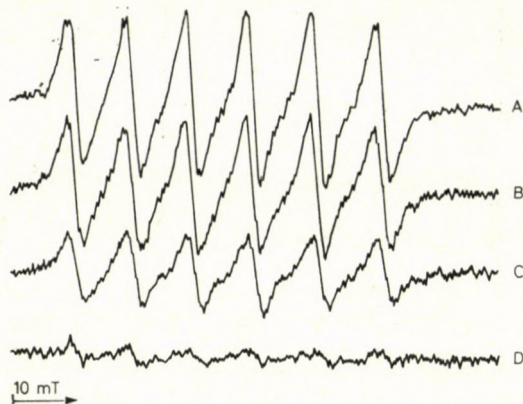


Fig. 3. Change of the ESR spectra of manganese(II)-maltitol complex with the pH of the solution [manganese(II)] = 3.15×10^{-3} mol dm $^{-3}$; [maltitol] = 0.25 mol dm $^{-3}$ pH of A, B, C, curves were 6.5; 9.45; 9.78 and 10.75, respectively. Microwave power and modulation amplitude were 30 mW and 0.5 mT, respectively. Magnetic field position was determined by using diphenylpicrylhydrazyl (DDPH)

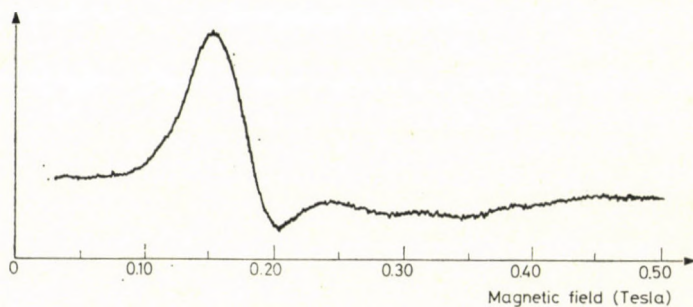


Fig. 4. ESR spectra of manganese(IV)-maltitol complex prepared in the solid state. Instrumental conditions like in Fig. 3

When oxygen was bubbled through the alkaline solution of the manganese(II)-maltitol complex the ESR signal disappeared, indicating the dimeric structure of manganese(III)-maltitol complex. This observation was confirmed by the fact that the same compound prepared in solid state according to the method published earlier [17] is ESR inactive too. At the same time the manganese(IV)-maltitol complex has a well-developed ESR signal shown in Fig. 4. This spectrum can be interpreted as that of high-spin d^3 ions bonded to oxygen donor atoms with distorted octahedral symmetry.

UV-vis spectrophotometric measurements

The UV-visible spectra for the manganese(II) manganese(III), and manganese(IV)-maltitol complexes are presented in Fig. 5. The spectrum of the manganese(II) complex does not have any characteristic maxima, the

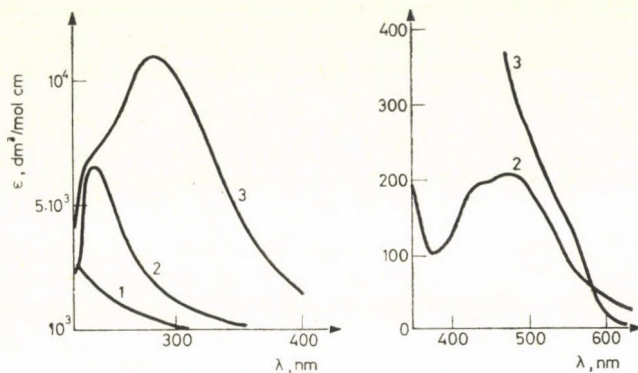


Fig. 5. Absorption spectra of the manganese-maltitol complexes in 1.0 mol dm^{-3} sodium hydroxide; (1) manganese(II); (2) manganese(III); (3) manganese(IV)

absorbance increases toward the UV range, similarly to the spectra of the corresponding gluconate [11], lactobionate [17], and saccharose [18] complexes. The manganese(III) complex in solution has two absorption maxima at 237 nm ($\epsilon = 6540 \text{ M}^{-1} \text{ cm}^{-1}$) and at 480 nm ($\epsilon = 202 \text{ M}^{-1} \text{ cm}^{-1}$) and one shoulder at about 434 nm. In the spectra of the manganese(IV) maltitol complex there is one shoulder at about 500 nm and one maximum at 284 nm ($\epsilon = 10.960 \text{ M}^{-1} \text{ cm}^{-1}$; ϵ represent the molar absorptivities).

Spectrophotometric measurements as a function of pH and of maltitol concentration, confirm that several different manganese(III) complexes are formed. For example Fig. 6 illustrates the effect of pH variation. The manganese(III) complex was prepared from manganese(II) by oxidation with one equivalent of hydrogen peroxide. The presence of an isosbestic point in the figure indicates that two species are in equilibrium. A similar study of

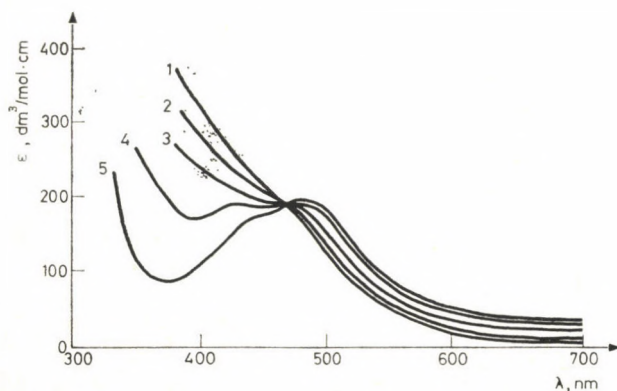


Fig. 6. Absorption spectra of the manganese(III)-maltitol complexes as a function of pH. [manganese(III)] = $4.95 \times 10^{-3} \text{ mol dm}^{-3}$; [maltitol] = 0.1 mol dm^{-3} . (1) pH = 11.8; (2) 12.3; (3) 12.7; (4) 13.1; (5) 13.5

the manganese(III) complexes of D-gluconate [11], of D-glucarate and sorbitol [10] has shown that they also exist in at least two distinct forms. The determination of the mechanism of this transformation needs further investigation.

Oxidation of the manganese(III)-maltitol complex with dioxygen results in the formation of the intensely red manganese(IV) complex. The absorption spectra confirm that the structure of this complex is distorted octahedral. We have made a similar conclusion from the ESR measurements for the manganese(IV)-maltitol complex prepared in the solid state.

*

The authors gratefully acknowledge the financial support by the Ministry of Education and the Hungarian Academy of Sciences (A-MM 294/1984).

REFERENCES

- [1] Heat, R. L.: *Int. Rev. Cytol.*, **34**, 49 (1979)
- [2] Cheniae, G. M.: *Annu. Rev. Plant. Physiol.*, **21**, 467 (1970)
- [3] Keele, B. B., McCord, J. M., Fridovich, I.: *J. Biol. Chem.*, **24**, 6176 (1970)
- [4] Doležal, J., Langmyhr, J.: *Anal. Chim. Acta*, **61**, 73 (1972)
- [5] Chughtai, N., Doležal, J., Zyka, J.: *Microchem. J.*, **1975**, 20
- [6] Donoso, G., Doležal, J., Zyka, J.: *Electroanal. Chem. Interfacial Electrochem.*, **49**, 461 (1974)
- [7] Doležal, J., Juláková, E., Cerny, M., Kopanica, M.: *J. Electroanal. Chem. Interfacial Electrochem.*, **52**, 261 (1974)
- [8] Doležal, J., Kekulova, H.: *J. Electroanal. Chem. Interfacial Electrochem.*, **69**, 239 (1976)
- [9] Velikov, B. L., Doležal, J.: *J. Electroanal. Chem. Interfacial Electrochem.*, **71**, 91 (1976)
- [10] Richens, D. T., Smith, C. G., Sawyer, D. T.: *Inorg. Chem.*, **18**, 706 (1979)
- [11] Bodini, M. E., Willis, L. A., Riechel, T. L., Sawyer, D. T.: *Inorg. Chem.*, **15**, 1538 (1976)
- [12] Bodini, M. E., Sawyer, D. T.: *J. Am. Chem. Soc.*, **98**, 6366 (1976)
- [13] Magers, K. D., Smith, C. G., Sawyer, D. T.: *Inorg. Chem.*, **17**, 515 (1978)
- [14] Mabad, B., Inchagues, J., Hwang, Y. T., Hendrickson, D. T.: *J. Am. Chem. Soc.*, **107**, 2801 (1985)
- [15] Nair, B. U., Dismukes, G. C.: *J. Am. Chem. Soc.*, **105**, 124 (1983)
- [16] Lawrence, G. D., Sawyer, D. T.: *Coord. Chem. Rev.*, **27**, 173 (1978)
- [17] Nagy, L., Horváth, I., Burger, K.: *Inorg. Chim. Acta*, **107**, 179 (1985)
- [18] Nagy, L., Gajda, T., Burger, K., Páli, T.: *Inorg. Chim. Acta*, **123**, 35 (1986)
- [19] Nagy, L., Burger, K., Kürti, J., Mostafa, M. A., Korecz, L., Kiricsi, I.: *Inorg. Chim. Acta*, **124**, 55 (1986)
- [20] Nagy, L., Yamaguchi, T., Ohtaki, H., Nomura, M.: to be published
- [21] Brauer, G.: "Handbook of Preparative Inorganic Chemistry", Vol. 2, p. 1469. Academic Press, New York 1965
- [22] D'Ans, J., Mattner, J.: *Angew. Chem.*, **64**, 488 (1952)
- [23] Heyrovsky, J., Kuta, J.: "Principles of Polarography", p. 86. Academic Press, New York 1966
- [24] Kolthoff, I. M., Ligane, J. J.: "Polarography", Vol. I. Chap. 12. Interscience, New York 1952
- [25] DeFord, D. D., Hume, D. N.: *J. Am. Chem. Soc.*, **73**, 5321 (1951)
- [26] Martell, A. E., Smith, R. M.: "Critical Stability Constants", Vol. I. Plenum Press, New York/London 1977
- [27] Ayscough, P. B.: "Electron Spin Resonance in Chemistry", p. 54. Methuen and Co. Ltd., London 1967