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Voltammetric and spectroscopic study of the manganese-quinizarine-quinaldic acid mixed-ligand complex in dimethylsulfoxide

Mario E. Bodini,* M. Angélica del Valle and Sandra Cáceres

Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile,
Casilla 306, Santiago de Chile, Chile

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Abstract—The combination of manganese(II) with quinizarine and the monoanion of quinaldic acid in dimethylsulfoxide yields a soluble deep-blue complex whose $Mn^{II}:Qz^{2-}:AcQ^{-}$ stoichiometry is 1 : 1 : 2. This complex is oxidized in two steps each involving one equivalent of charge per metal ion as indicated by controlled-potential electrolyses at +0.30 V *vs* S.C.E. and +0.45 V *vs* S.C.E. The association between the metal ion and the ligands prevails and the oxidations produce finally a dark-red complex of the same stoichiometry as the original deep-blue species. In the latter the metal is in the oxidation state +3 and the quinizarine dianion has been oxidized to the semiquinone form. The monoanion of quinaldic acid is unchanged.

The combination of the semiquinone of quinizarine with Mn^{II} and quinaldic acid yields a species in which the metal ion presents magnetic characteristic of manganese$^{(III)}$ and the semiquinone has been reduced to the dianion of quinizarine, indicating that intramolecular charge-transfer has occurred.

The voltammetric behaviour of the Mn^{III}-semiquinone-quinaldic acid complex and its electrochemical reduction indicate that it is binuclear which upon reduction at −0.20 V *vs* S.C.E. generates a Mn^{II}–Mn^{III} mixed-valence species. The latter is in turn reduced at −0.95 V *vs* S.C.E. producing probably a mononuclear species of Mn^{II}. © 1997 Elsevier Science Ltd

Keywords: manganese; mixed-ligand complex; semiquinone; Photosystem II; quinizarine; quinaldic acid.

There is a great interest in the study of inorganic systems related to the behaviour of biological processes, in order to gain a better understanding of the role of the metal ions that are present in the mechanism of the reaction affected by this biological arrangement [1].

Among the most studied systems we can mention Photosystem II of green-plant photosynthesis [2–12], in which it is known that manganese is present as an essential element to catalyse the water oxidation to molecular oxygen, although the exact nature of the biological matrix is not known, neither is the exact role of this metal ion in the water oxidation mechanism [13,14]. From the mechanistic point of view this process is difficult because two water molecules must interact, four protons must be released and four electrons have to be transferred to produce one molecule of dioxygen. Thermodynamically, this process would require the energy corresponding to UV radiation. However, this process takes place in green plants after the absorption of four photons of visible light due to a complex molecular system in which four equivalents of charge accumulate in the reaction centre [15].

Five states have been recognized in the process of oxidation of water in Photosystem II (S_0, S_1, S_2, S_3 and S_4) according to Joliot [16]. Therefore, the S_4 state is the result of the accumulation of four equivalents of oxidation which provides the energy requirement to sustain the oxidation reaction. Mechanistically, this reaction is difficult so that it must be catalyzed by the action of a manganese centre in which this metal ion is associated in a 2 or 3 atoms cluster with a bridge between them from a ligand in their coordination sphere. The substrate would bind to this complex as part of the oxidation mechanism [9,11,17]. This mechanism has been studied very thoroughly but so far it is not known at the molecular level because no crystallographic data are available.

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* Author to whom correspondence should be addressed. Fax: 52-2-5525692.

An important piece of information is the report indicating that the step from S_2 to S_3 states in the Joliot scheme does not involve a change in the oxidation state of the metal ion, indicating that a radical species is involved as a ligand bound to one of the manganese atoms [18, 19].

In our group we have studied the redox chemistry of complexes of manganese with 1,4-dihydroxy-9,10-naphthoquinone (quinizarine) and its oxidation product (semiquinone) [20] as well as the manganese complexes with quinaldic acid [21].

We know that Mn^{III} is stabilized through its complexation with quinaldic acid and that quinizarine can be oxidized to the radical semiquinone form and as such it still behaves as a ligand with manganese ions.

Our present goal is to study the behaviour of a mixed-ligand complex of manganese with these two ligands in an aprotic medium like dimethylsulfoxide in order to mimic the hydrophobic environment that prevails in the polypeptide matrix and to stabilize the radical species that might form as an intermediate after the electron-transfer processes.

The results obtained by cyclic voltammetry, UV-vis spectroscopy and magnetic susceptibility measurements facilitate the understanding of the very complex redox chemistry of biological systems containing manganese.

EXPERIMENTAL

Equipment

A three-electrode potentiostat (Tacussel Model PRT-20-2X potentiostat-galvanostat with a Model GSTP wave generator) was used for the cyclic voltammetric and controlled-potential electrolysis experiments. A current integrator based on operational amplifiers was used as a coulometer in the controlled-potential electrolyses. Cyclic voltammograms were recorded on a Hewlett-Packard Model 7004-A X-Y recorder. The electrochemical cell was equipped with a Beckman platinum-inlay working electrode (area 0.23 cm^2), a platinum coil auxiliary electrode and an Ag/AgCl reference electrode filled with an aqueous tetramethylammonium chloride solution and adjusted to 0.00 V *vs* S.C.E. The latter was contained in a Pyrex tube with a soft-glass cracked tip; this electrode was placed inside a Luggin capillary. For controlled-potential electrolysis a platinum mesh working electrode was employed. A Milton Roy Model Spectronic 3000 diode array Spectrophotometer was used for UV-vis spectrophotometric measurements. The magnetic susceptibility measurements were made with a Bruker AC-200 P spectrometer by the method of Evans [22].

Reagents

The reagents for the investigation and synthesis included $Mn(ClO_4)_2 \cdot 6H_2O$ (G. Frederick Smith), tetrabutylammonium hydroxide (TBAOH, 1.0 M in methanol, Aldrich), tetramethyl-ammonium chloride (Aldrich) and tetraethylammonium perchlorate (TEAP) (G. Frederick Smith). The ligands quinaldic acid (QAc) and quinizarine (Qz) were obtained from Aldrich and the latter was purified by recrystallization in acetic acid.

Aldrich "Gold Label" dimethylsulfoxide (DMSO) was used without further purification for all the experiments. High purity argon was used to deaerate solutions.

Since the solvation water of $Mn(ClO_4)_2 \cdot 6H_2O$ interfered with the stoichiometric formation of the complexes under study, $[Mn^{II}(DMU)_6][ClO_4]_2$ {DMU = dimethylurea} [23] was used in all the experiments in which the manganese complexes were formed *in situ*. As a source of manganese(III) $[Mn^{III}(urea)_6][ClO_4]_3$ [24] was used in all the experiments.

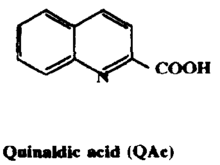
RESULTS AND DISCUSSION

The ligands quinizarine [1,4-dihydroxi-9,10 anthraquinone = Qz] and quinaldic acid [2-quinoline-carboxylic acid = QAc] and their complexes with manganese have been previously studied in our group [20,21]. The spectroscopic and voltammetric behaviour of the different species involved in these systems are known and now we will try to form and to study the mixed-ligand complexes formed by Mn^{II} and Mn^{III} with these two ligands in order to understand the charge-transfer processes undertaken by the metal centre in an environment with these type of donor groups.

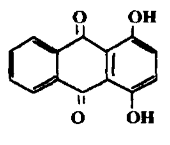
The combination of manganese(II) with the dianion of quinizarine in a 1 : 1 mole ratio yields an insoluble blue product which dissolves upon addition of the monoanion of quinaldic acid producing a deep-blue solution.

Figure 1 shows the spectra of solutions containing the dianion of quinizarine and the monoanion of quinaldic acid and of this solution in the presence of manganese(II) in dimethylsulfoxide (DMSO). The absorption maxima in the visible region are different from those either of the simple complexes with the ligands under study or the combination of these ligands in the absence of the metal ion. Therefore, we conclude that a new species is being formed under these conditions.

The cyclic voltammograms of the solution with a $Mn^{II} : Qz : QAc : base = 1 : 1 : 2 : 4$ mole ratio (Fig. 2) show that no reduction peak is observed for free



Quinaldic acid (QAc)



Quinizarine (Qz)

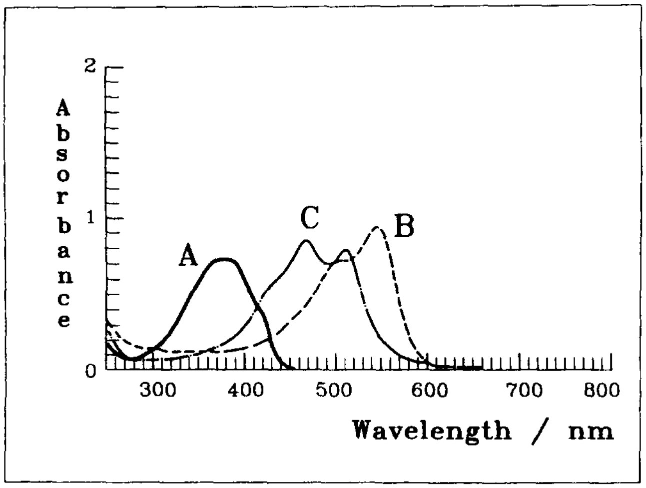


Fig. 1. UV-vis spectra of a solution that is: (A) (—) 1 mM quinizarine and 2 mM quinaldic acid; (B) (---) solution A plus 4 mM TBAOH; and (C) (·—·) solution B plus 1 mM Mn^{II}. The solvent is DMSO.

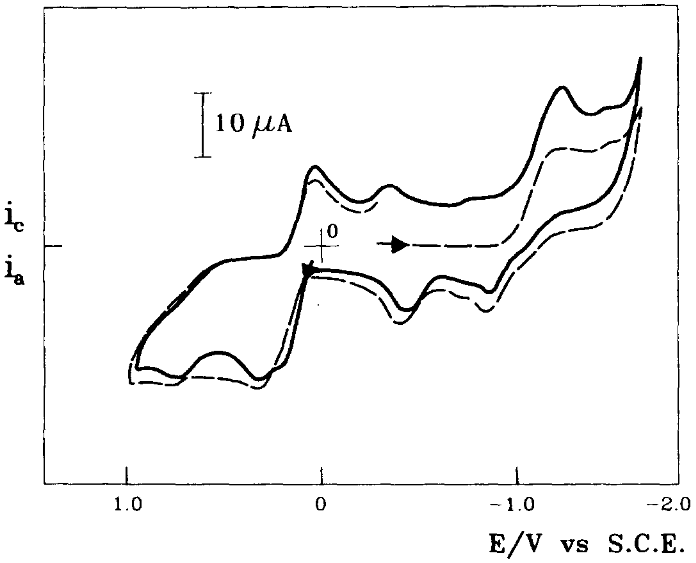


Fig. 2. Cyclic voltammogram of a solution that is 1 mM in manganese(II), 1 mM in quinizarine, 2 mM in quinaldic acid and 4 mM in TBAOH. The supporting electrolyte is 0.1 M TEAP and the scan rate is 0.1 V s^{-1}. The solvent is DMSO.

manganese(II), indicating that this ion is present only as a complex. On the other hand, the voltammetric peaks that have been assigned to the ligands are not observed in this case, which indicates that under these conditions the mole ratio in the solution corresponds exactly to the stoichiometric relation and, therefore, we do not observe an excess of either the metal ion or any of the ligands. The reduction peaks observed are different from those shown by the simple complexes with quinizarine or quinaldic acid [20,21]. Therefore, we conclude that a new mixed-ligand species has been formed.

The mixed-ligand complex was formed in solution using manganese(III) and its stoichiometry was determined using an analogous procedure as the one described for the Mn^{II} complex. The Mn^{III} mixed-ligand complex shows a cyclic voltammogram that presents an anodic peak at +0.56 V *vs* S.C.E. which corresponds to the oxidation of bound quinizarine to the corresponding semiquinone. The other voltammetric peaks, both cathodic and anodic, correspond to redox processes of bound quinizarine as described in a previous work on the manganese–quinizarine system [20]. The UV-vis spectrum of this solution shows absorption maxima at 548 and 586 nm having extinction coefficients of 7610 and 7250 M^{-1} cm^{-1}, respectively. The magnetic susceptibility of this solution was 5.01 B.M. which confirms that in solution a species of Mn^{III} prevails (theoretical value = 4.9 B.M.).

In order to obtain a species in which we can effectively accumulate oxidation equivalents to be transferred to some substrate and act as a catalyst, either in a biological or an industrial process, we attempted to prepare a mixed-ligand complex in which the metal ion would be present as $Mn^{(III)}$ and quinizarine would be oxidized to the radical semiquinonic form. A solution of the latter species was prepared by exhaustive controlled-potential electrolysis at −0.1 V *vs* S.C.E. of a solution of quinizarine in the presence of two equivalents of base. Then manganese(III) was added to give the same concentration as the semiquinone, and finally quinaldic acid was added along with the equivalents of base to neutralize its proton so that the concentration of the monoanion results twice as large as the one of manganese or the semiquinone. Figure 3(A) shows that no oxidation processes are observed in the cyclic voltammogram of this solution if the potential is scanned initially in the positive direction. Scanning initially in the negative direction we observe that after the reduction processes have taken place a reversal of the scan direction shows anodic peaks at +0.2 V *vs* S.C.E. and at +0.7 V *vs* S.C.E. which correspond to the oxidation of Mn^{II} to Mn^{III} and the oxidation of quinizarine to the corresponding semiquinone, respectively. The UV-vis spectrum of this solution is shown in Fig. 3(B). The spectroscopic characterization of the manganese(III)–semiquinone–quinaldic anion complex shows that two absorption maxima are observed at 549 and 587 nm having extinction coefficients of 3310 and 2910 M^{-1} cm^{-1}, respectively. On the other hand, a wide band observed at 486 nm is probably due to the presence of the semiquinonic species. The magnetic susceptibility of this solution turns out to be 4.96 B.M., indicating that in this case we are in the presence of Mn^{III} (theoretical value = 4.9 B.M.).

A very interesting result was obtained in the combination of Mn^{II} with the semiquinone of quinizarine, in the presence of quinaldic acid. The resulting solution presents a UV-vis spectrum identical to the one obtained for a solution of Mn^{III} and the dianion of quinizarine. The magnetic susceptibility of this solution was 4.81 B.M. which corresponds to the presence of Mn^{III}. This indicates that in this case an intramolecular charge-transfer takes place oxidizing the

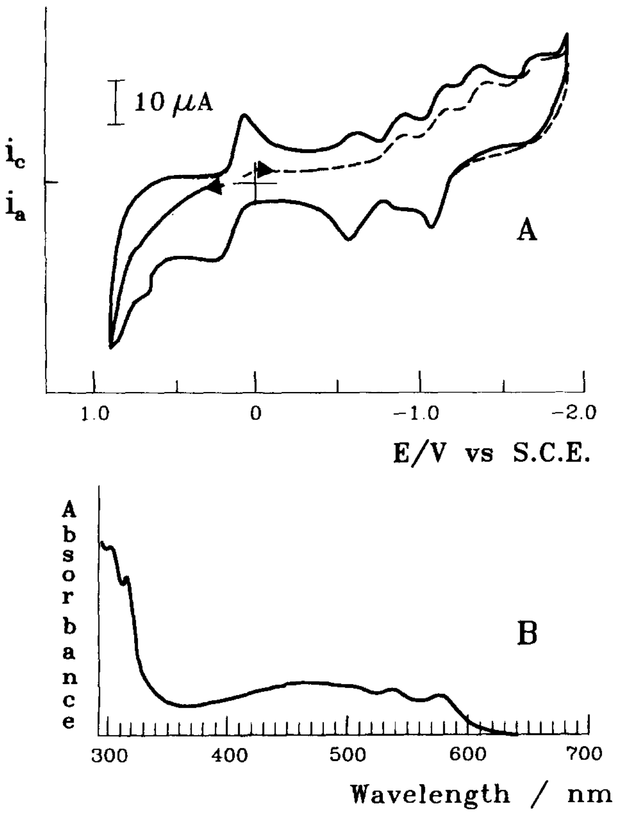


Fig. 3. Cyclic voltammogram (A) and UV-vis spectrum (B) of a solution of 1.0 mM in Mn^{III}, 1.0 mM in the semiquinone of quinizarine, 2.0 mM in quinaldic acid and 4.0 mM in TBAOH. For the electrochemical experiment the supporting electrolyte is 0.1 M TEAP and the scan rate is 0.1 V s^{-1}. The spectrum was taken using a 1 mm path-length cell. In all cases the solvent was DMSO.

metal ion to its Mn^{III} form and reducing the semiquinone to the corresponding dianion. The similarity of the energy levels of the π^* orbitals of the semiquinone and the *d* orbitals of the metal ion allows this charge transfer.

With these results we can conclude that the mixed-ligand complex of manganese(II) with the dianion of quinizarine and the monoanion of quinaldic acid can be oxidized to a stable species in which the metal ion is in the +3 oxidation state and the dioxolene ligand (quinizarine) has been oxidized to its semiquinone form. The overall process can be represented by the following equation:

$$[Mn^{II}(Qz^{2-})(AcQ^-)_2]^{2-} \xrightarrow[+0.45\,V]{} [Mn^{III}(SQQz)^-(AcQ^-)_2] + 2e^- \quad (1)$$

where $(SQQz)^-$ represents the semiquinone of quinizarine.

The cyclic voltammogram of a solution of this fully oxidized complex shows reduction processes at 0.0 V *vs* S.C.E., −0.47 V *vs* S.C.E., −0.82 V *vs* S.C.E., −1.02 V *vs* S.C.E. and −1.20 V *vs* S.C.E. Considering that the first reductions must correspond to the oxidized complex controlled potential electrolysis was attempted at −0.2 V *vs* S.C.E. It was found that in this case only 0.5 equivalents of charge had been transferred per mole of manganese in the solution before residual current was attained, indicating that a half of the metal ion had been reduced. A reasonable explanation for this result is that the manganese(III) complex is a binuclear species so that only one metal centre is reduced in this electrolytic process yielding a mixed-valence Mn^{II}–Mn^{III} species after exhaustive controlled-potential electrolysis. The bridging element must be one of the ligands from each manganese centre. Either the carboxylate group from the quinaldic residue or a quinizarine molecule can act as the bridging element. Further reduction of the mixed-valence complex yields the mononuclear manganese(II) species as has been observed in previous studies of our group working with other systems that also present the tendency to form binuclear species [25,26].

$$[Mn^{III}(SQQz)(QAc)_2]_2 + e^- \xrightarrow{-0.2v}$$

$$\begin{tikzcd}
{[(SQQz)(QAc)_2 - Mn^{II}, Mn^{III} - (SQQz)(QAc)_2]^-} \arrow[d, "+e^-"', "-0.95\,V"] \\
{2Mn^{II}(SQQz)(QAc)_2]^-.}
\end{tikzcd}$$

From this work we conclude that the existence of a mixed-ligand complex is possible in which the metal ion is stabilized in the oxidation state +3 by the presence of a ligand like quinaldic acid and the second ligand can be oxidized to the corresponding semiquinone. This totally oxidized complex is probably binuclear and results in the accumulation of four oxidation equivalents per complex molecule. This mixed-ligand complex in which one of the ligands is a radical like a semiquinone would be a model for the species involved in the step from S_2 to S_3 in the Joliot scheme in which the oxidation state of manganese does not change. The intramolecular charge transfer observed between manganese(II) and the semiquinone ligand is a predictable behaviour in the case of a dioxolene ligand like quinizarine and in this case it facilitates the electron-transfer from the metal centre to any external substrate because the oxidation of the dioxolene ligand ends up with the oxidation of the metal centre.

The tendency to form binuclear species in higher oxidation states in an aprotic medium makes these compounds very attractive to be considered as effective catalysts in charge-transfer processes that also involve the transfer of some other entities like protons. Their redox chemistry is an important contribution to finally understanding the exact role and action mechanism of manganese in biological systems.

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