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Redox pathways in the carnosine–manganese system mediated by semiquinone radicals

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Abstract: The interaction of carnosine histidine containing dipeptide with the semiquinone radical of 3,4Dihydroxybenzoic dianion in dimethyl sulfoxide solution under aerobic conditions was investigated in the present study. The interaction of dipeptide-manganese system with the same semiquinone was also studied under the same conditions. The metal-binding and redox chemistry of these systems were investigated using electronic, ESR ^{1}H-NMR spectroscopies and cyclic voltammetry. The in-situ formal semiquinone radicals (extensively studied in previous works) were significantly modified upon addition of carnosine, as evidenced by the redistribution of the visible absorption bands and the change of the redox couples of the catecholic product. Subsequent influence of manganese ions induced further spectral and electrochemical changes, consistent with metal centered oxidation and formation of ligand-stabilized manganese species. Paramagnetic broadening in the ^{1}H-NMR spectra supported the presence of higher-valent manganese intermediates in solution. The combined data support a cooperative redox pathway in which semiquinone species mediate both peptide oxidation and manganese centered electron transfer. These results provide chemical insight into the understanding of multicomponent systems usually present in nature.

Keywords: carnosine; manganese; semiquinone radicals; catechol oxidation; ESR spectroscopy; cyclic voltammetry.

INTRODUCTION

L-Carnosine (β-alanyl-L-histidine) is a naturally occurring histidine-containing dipeptide widely distributed in excitable tissues such as skeletal muscle and brain. It has attracted considerable attention because of its buffering capacity,

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antioxidant activity, carbonyl scavenging properties, and ability to coordinate transition-metal ions through the imidazole and carboxylate donor groups.[1,2] These physicochemical characteristics make carnosine an important model compound for studying peptide-mediated redox and coordination processes in solution.

Catechol derivatives such as dihydroxybenzoic acids are well known to undergo oxidation in the presence of dioxygen, generating semiquinone radicals and quinonoid products through sequential one-electron transfer processes.[3–5] Such intermediates are of particular interest because they often display characteristic visible absorption bands, persistent ESR signals, and rich electrochemical behavior. In addition, semiquinone species can participate in coupled reactions with nucleophiles, peptides, and transition-metal ions, thereby modifying both the redox profile and coordination chemistry of multicomponent systems.[6]

Manganese is especially relevant in this context because it can access multiple oxidation states under mild conditions, most commonly Mn(II) and Mn(III), and frequently forms kinetically labile yet spectroscopically informative complexes with O- and N-donor ligands.[7–10] Redox-active manganese species are central to many chemical transformations, while ligand environment strongly influences their stability, electron-transfer behavior, and reactivity toward oxygen-derived intermediates.[11,12] Accordingly, mixed systems containing manganese ions, catechol-derived radicals, and chemically relevant ligands provide useful models for investigating cooperative electron-transfer pathways.

Despite the well-established metal-binding and antioxidant properties of carnosine, its behavior in radical-mediated manganese redox systems remains insufficiently understood, particularly under non-enzymatic conditions. Previous studies from our group have characterized the spectroscopic and electrochemical properties of catechol-derived semiquinone systems and their redox transformations in solution.[13,14] However, the interplay between such radical intermediates, peptide ligands, and manganese ions has not been systematically investigated.

In systems where catechol derivatives generate semiquinone species, complex reaction pathways may arise involving simultaneous radical transformations, peptide modification, and metal-centered electron transfer. The present study addresses this gap by examining the interactions among L-carnosine, Mn(II) ions, and semiquinone radicals derived from 3,4-dihydroxybenzoic acid in a controlled chemical environment. By combining spectroscopic (UV–Vis, ESR, ^{1}H-NMR) and electrochemical techniques, we aim to elucidate the redox pathways governing this multicomponent system and to define the role of semiquinone intermediates in mediating manganese oxidation and peptide transformation.

It should be emphasized that the present study focuses on a simplified chemical model system and does not attempt to directly reproduce enzymatic or biological conditions.

EXPERIMENTAL

Materials and instrumentation

All chemicals were used as received: L-carnosine (99% crystalline, Sigma-Aldrich), $MnCl_2 \cdot 4H_2O$ (Merck), manganese(II) acetate tetrahydrate (Merck), tetrabutylammonium hexafluorophosphate (98%, Fluka Chemical), tetrabutylammonium hydroxide 30-hydrate (Sigma-Aldrich), 2,3-dihydroxybenzoic acid (2,3-DHBA, Sigma-Aldrich), 3,4-dihydroxybenzoic acid (3,4-DHBA, Sigma-Aldrich), EtOH (min 99.8%, Carlo Erba), hydrogen peroxide (30%, Merck), D_2O (99.90% D, Eurisotop), and high-purity Argon (99.99%).

UV-Vis spectra were recorded on Hitachi U-2000 and Varian Cary 3E spectrophotometers. IR spectra were recorded on a Perkin-Elmer 883 infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 300 MHz instrument (± 0.1 °C). X-Band EPR (ESR) spectra were recorded at NCSR "Demokritos" on a Bruker ER-200D-SCR instrument equipped with an Oxford ESR 900 cryostat. Cyclic voltammetry (CV) was performed on a Pine Research Instrumentation Bipotentiostat (Model AFCBP1). Elemental analysis (C, H, N) was carried out on a Perkin-Elmer 2400 analyzer. Raman spectra were obtained using a Renishaw inVia reflex Raman microscope (532 nm and 785 nm excitation).

Experimental procedures

For UV-Vis spectroscopy, a solution was prepared by dissolving 10 mg (0.065 mmol) of 3,4-DHBA in 25 mL of DMSO, followed by the addition of 0.100 g (0.125 mmol) of tetrabutylammonium hydroxide (TBAH). The UV-Vis spectra were recorded before and after the addition of 0.0147 g (0.065 mmol) of carnosine. Subsequently, 5 mL of a $MnCl_2 \cdot 4H_2O$ solution (0.0129 g, 0.065 mmol) in DMSO was added. For comparison, the spectrum of a solution containing equimolar isolated carnosine-manganese complex was also recorded.

For EPR (ESR) spectroscopy, the spectrum of the 3,4-DHBA dianion (C/ 0.0065 M) in DMSO was recorded at T/ 4.2 K. Measurements were also performed at T/ 4.2 K and 13 K following the addition of an equimolar amount of carnosine (0.0147 g) to 10 mL of the initial solution.

Cyclic voltammetry (CV) measurements involved adding 3 mg (0.020 mmol) of 3,4-DHBA to 20 mL of 0.1 M tetrabutylammonium chloride (TBAC) in DMSO, followed by 32 mg (0.040 mmol) of TBAH. Voltammograms were obtained for the initial solution, after the addition of 4.5 mg (0.020 mmol) of carnosine, and after adding 4 mg (0.02 mmol) of $MnCl_2 \cdot 4H_2O$. The electrochemical behavior of the isolated carnosine-manganese complex was also studied using a three-electrode setup: graphite (working), platinum/gold (auxiliary), and Ag/AgCl (reference).

^1H NMR spectra were obtained by adding carnosine (C/ 0.0065 mmol L^{-1}) and $MnCl_2 \cdot 4H_2O$ (C/ 0.0065 mmol L^{-1}) gradually to a solution of 3,4-DHBA/TBAH in DMSO-d_6. Spectra were collected at each titration step. Finally, a spectrum was recorded for a solution containing the isolated carnosine-manganese complex (Mn/carnosine 1:1) in a 1:2 mixture of 3,4-DHBA/TBAH in DMSO-d_6.

Spectra were processed uniformly for baseline correction and visualization purposes without altering the analytical content.

RESULTS AND DISCUSSION

UV-Vis and ESR spectroscopy

The dianionic form of 3,4-DHBA prepared in DMSO under aerobic conditions exhibits broad visible absorption bands centered at 672, 676, and 706 nm (Fig. S1).

These features are consistent with the formation of oxygen-stabilized semiquinone radicals arising from catechol oxidation, where overlapping mono- and di-ionized forms contribute to the observed spectral envelope.[3–5] Additional shoulders in the 320–400 nm region and a strong transition near 300 nm can be attributed to π→π* excitations associated with partial oxidation of the aromatic framework.[4,15]

Addition of equimolar carnosine produces an immediate color change to deep purple and generates new absorption bands at approximately 500 and 590 nm (Fig. S2). The redistribution of visible absorption bands, accompanied by increased molar absorptivity, indicates the formation of a new redox-active species involving chemical interaction between semiquinone intermediates and carnosine. The persistence of semiquinone- and quinonoid-type features suggests that the process involves redox coupling rather than simple radical quenching.[6]

Introduction of Mn^{2+} results in further spectral evolution, producing a brown-yellow solution with weak extended visible absorption (Fig. 1). These features are consistent with the formation of Mn(III) species, likely stabilized through coordination with oxygen- and nitrogen-donor ligands present in the system. Comparable spectral behavior observed after addition of the isolated carnosine–manganese complex (solid 24)[25] (Fig. S3) further supports the formation of electronically coupled Mn-containing intermediates.

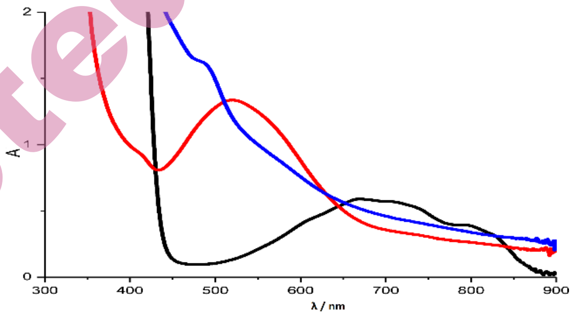


Fig. 1. Electronic spectra of 3,4-DHBA dianion in DMSO (black line), upon addition of carnosine (1:1 ratio, red line) and subsequent addition of equimolar $MnCl_2 \cdot 4H_2O$ (blue line).

A solution of 3,4-DHBA dianion in DMSO under aerobic conditions exhibits a strong ESR signal characteristic of a radical species (Fig. 2). The signal remains largely unchanged upon increasing the temperature to 15 or 30 K, indicating appreciable persistence of the paramagnetic intermediate under the experimental conditions.

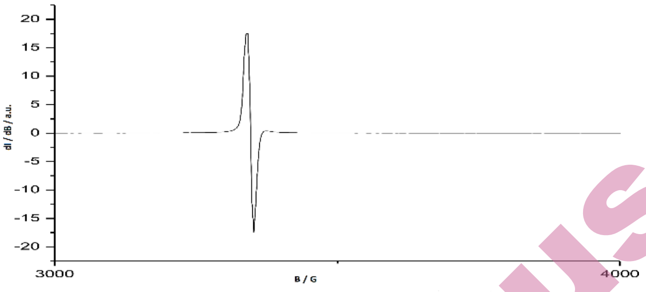


Fig. 2. ESR spectrum of a cyan solution of the 3,4-DHBA dianion (C/ 0.0065 M) in DMSO under aerobic conditions, recorded at T/ 4.2 K. Microwave power 0.3 mW, modulation amplitude 1.0 G, receiver gain 26 dB.

The addition of carnosine to the radical-containing solution in a 1:1 molar ratio leads to measurable changes in the ESR spectrum (Fig. 3), indicating interaction between the semiquinone species and the dipeptide. These observations indicate chemical transformation of the radical species upon interaction with carnosine, supporting the involvement of semiquinone intermediates in subsequent redox processes.

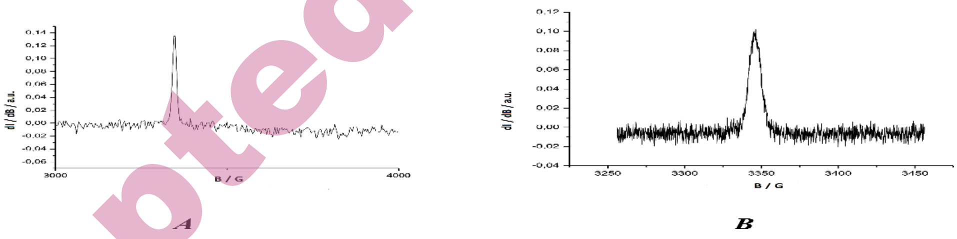
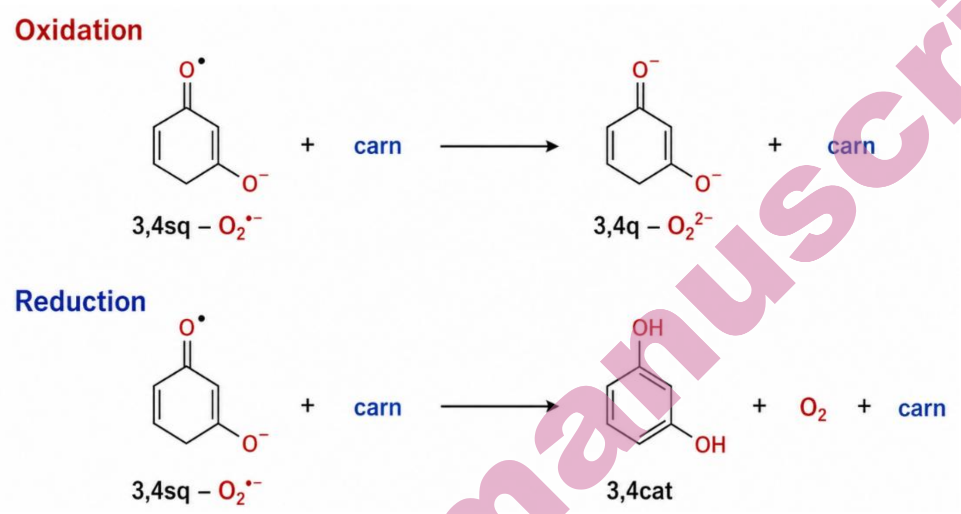


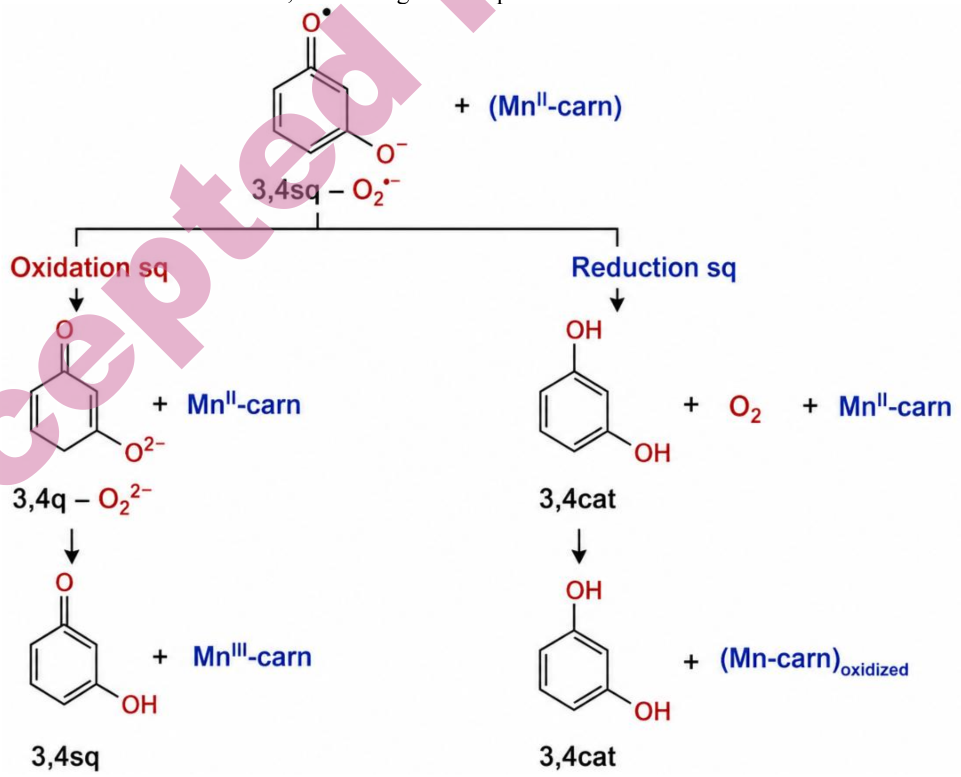
Fig. 3. ESR spectra of a green DMSO solution containing the 3,4-DHBA dianion (C/ 0.0065 M) and carnosine (C/ 0.0065 M): (A) recorded at T/ 4.2 K and (B) recorded at 13 K. Microwave power 0.3 mW, modulation amplitude 1.0 G, receiver gain 26 dB.

If the reaction between the radical and the dipeptide involved reduction of the semiquinone species (e.g., in a superoxide-associated form, 3,4-SQ•–O_2^-), regeneration of the catechol form of DHBA would be expected. In such a case, partial decolorization of the solution might occur, as catechol derivatives typically exhibit weak absorption in the visible region, while the released molecular oxygen would not be expected to react rapidly with carnosine under the present conditions.

Conversely, if the process involves oxidation of the semiquinone, formation of the corresponding quinone species and hydrogen peroxide is plausible. Both species are known to participate in oxidative reactions with nucleophilic sites of peptides, including the imidazole moiety of carnosine. Under these conditions, the development of brown-green coloration is expected, consistent with the experimental observations.



Scheme 1. Proposed reaction pathways for the interaction between 3,4-DHBA semiquinone radical and carnosine, illustrating the competitive oxidative and reductive routes.



Scheme 2. Proposed mechanism for the metal-assisted electron transfer between 3,4-DHBA semiquinone and the Mn(II)–carnosine complex.

The oxidative pathway likely involves the formation of a semiquinone–carnosine intermediate, which may facilitate interaction with dioxygen-derived species and contribute to charge-transfer stabilization within the system.

Electrochemical behavior

Cyclic voltammetry (CV) of the 3,4-DHBA dianion reveals two well-defined quasi-reversible redox couples (Fig. S4), consistent with sequential one-electron catechol/semiquinone/quinone transformations.[1] The peak separation suggests moderately fast electron transfer with partial chemical follow-up reactions, likely involving oxygen coordination.

Upon addition of equimolar carnosine, a positive shift in the first redox couple is observed, accompanied by an irreversible oxidation wave at 0.68 V (Fig. 4). This behavior indicates that carnosine perturbs the redox equilibrium through chemical coupling rather than simple hydrogen bonding. The irreversible feature can be attributed to oxidative modification of the imidazole-containing dipeptide or formation of electrochemically unstable quinonoid adducts.

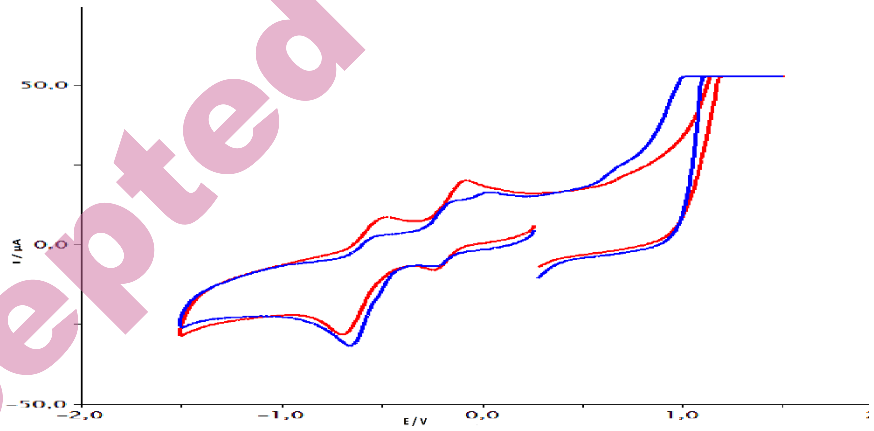
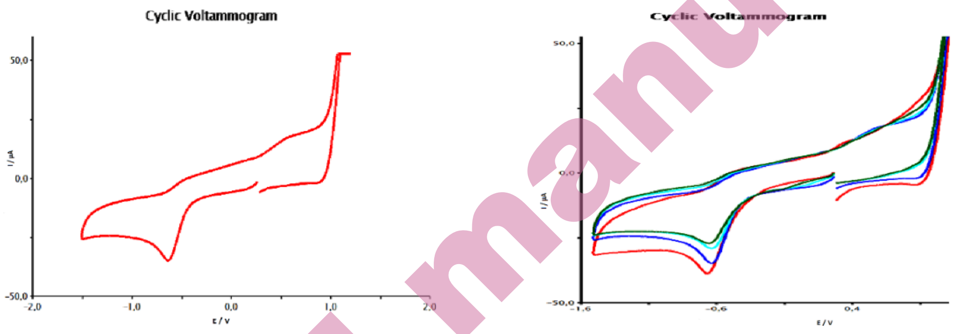


Fig. 4. Cyclic voltammograms of 3,4-DHBA dianion in DMSO before (red line) and after addition of carnosine (blue line). Scan rate: 100 mV s^{-1}.

Introduction of Mn^{2+} dramatically alters the voltammetric profile (Fig. 5). The attenuation of the semiquinone oxidation signal and the emergence of broad irreversible processes between 0.30–0.80 V are consistent with manganese-centered oxidation.

These signatures are consistent with Mn^{2+} → Mn^{3+} conversion followed by rapid ligand coordination. The disappearance of the semiquinone oxidation signal and persistence of a multi-electron reduction wave indicate kinetically slow Mn(II) oxidation to Mn(III), likely occurring within a DHBA-associated coordination environment.

Comparable irreversible behavior observed for the isolated carnosine-manganese complex (solid 27)[25] (Fig. S5) reinforces the assignment of ligand-stabilized Mn(III) intermediates. Overall, the electrochemical data support a mechanism in which semiquinone radicals act as transient electron shuttles, likely promoting manganese oxidation while undergoing peptide-mediated trapping.



A B

Fig. 5. Cyclic voltammograms of the 3,4-DHBA dianion in DMSO with carnosine: A) immediately after Mn^{2+} addition; B) time-dependent evolution: 0 min (red), 2 min (blue), 4 min (green), 6 min (pink), and 8 min (black). Scan rate: 100 mV s^{-1}.

A comparative summary of the electrochemical parameters for all investigated systems is provided in Table 1.

Table 1. Summary of redox potentials for the investigated systems in DMSO.

System	Epa (V)	Epc (V)	ΔEp (V)	Electrochemical behavior
3,4-DHBA dianion	~0.45	~0.30	~0.15	Quasi-reversible catechol/semiquinone redox couple
3,4-DHBA + carnosine (1:1)	~0.50	~0.32	~0.18	Positive shift; appearance of irreversible oxidation at ~0.68 V
3,4-DHBA + carnosine + Mn^{2+}	-	-	-	Broad irreversible processes (0.30–0.80 V); Mn-centered oxidation
Carnosine–Mn complex	-	-	-	Predominantly irreversible behavior; ligand-stabilized Mn(III) formation

Epa: anodic peak potential; Epc: cathodic peak potential; ΔEp: peak-to-peak separation.

The stability of Mn(III) species in solution is strongly dependent on ligand environment. In the absence of stabilizing ligands, Mn(III) is typically prone to disproportionation. However, coordination to oxygen- and nitrogen-donor ligands, such as carnosine and catechol-derived species, can provide both kinetic and thermodynamic stabilization. In the present system, the persistence of electrochemical and spectroscopic signatures attributed to Mn(III) suggests that ligand coordination effectively stabilizes the higher oxidation state, at least on the experimental timescale.

NMR analysis

^{1}H NMR spectroscopy provides complementary evidence for interaction between carnosine and oxidized DHBA species (Fig. 6). Pronounced upfield shifts of the imidazole resonances indicate changes in the electronic environment, consistent with possible coordination or interaction with electron-deficient quinonoid structures. Such perturbations are consistent with partial redistribution of electron density within the heteroaromatic ring following oxidative coupling.

Following Mn^{2+} addition, the spectrum exhibits substantial line broadening and reduced resolution (Fig. 7), behavior typical of paramagnetic Mn(III) centers.[22,23]

The appearance of a broad resonance near 9.03 ppm is consistent with the formation of metal-associated species undergoing rapid exchange on the NMR timescale. Addition of isolated carnosine-manganese complex to the DHBA dianion generates an even more intricate spectral pattern (Fig. 8), suggesting the presence of multiple equilibrating coordination environments rather than a single dominant complex. This observation aligns with the electrochemical evidence for dynamic metal–ligand speciation.

Taken together, the NMR data support a model in which carnosine participates both as a redox-active partner and as a ligand scaffold capable of stabilizing higher oxidation states of manganese. The combined observations are consistent with a mechanism involving initial semiquinone formation, followed by peptide-mediated oxidative trapping and subsequent electron transfer to Mn(II), yielding ligand-stabilized Mn(III) intermediates.[24]

Fig. 6. ^{1}H NMR spectrum of the 3,4-DHBA/carnosine in DMSO-d_6: Insets 3 and 4 show the 5–10 ppm region processed with Resolution Booster and Global Spectral Deconvolution (GSD).

Fig. 7. ^{1}H NMR spectrum of the 3,4-DHBA/carnosine/Mn^{2+}(aq) mixture in DMSO-d_6: Panels 3 and 4 represent Resolution Booster and GSD analyses.

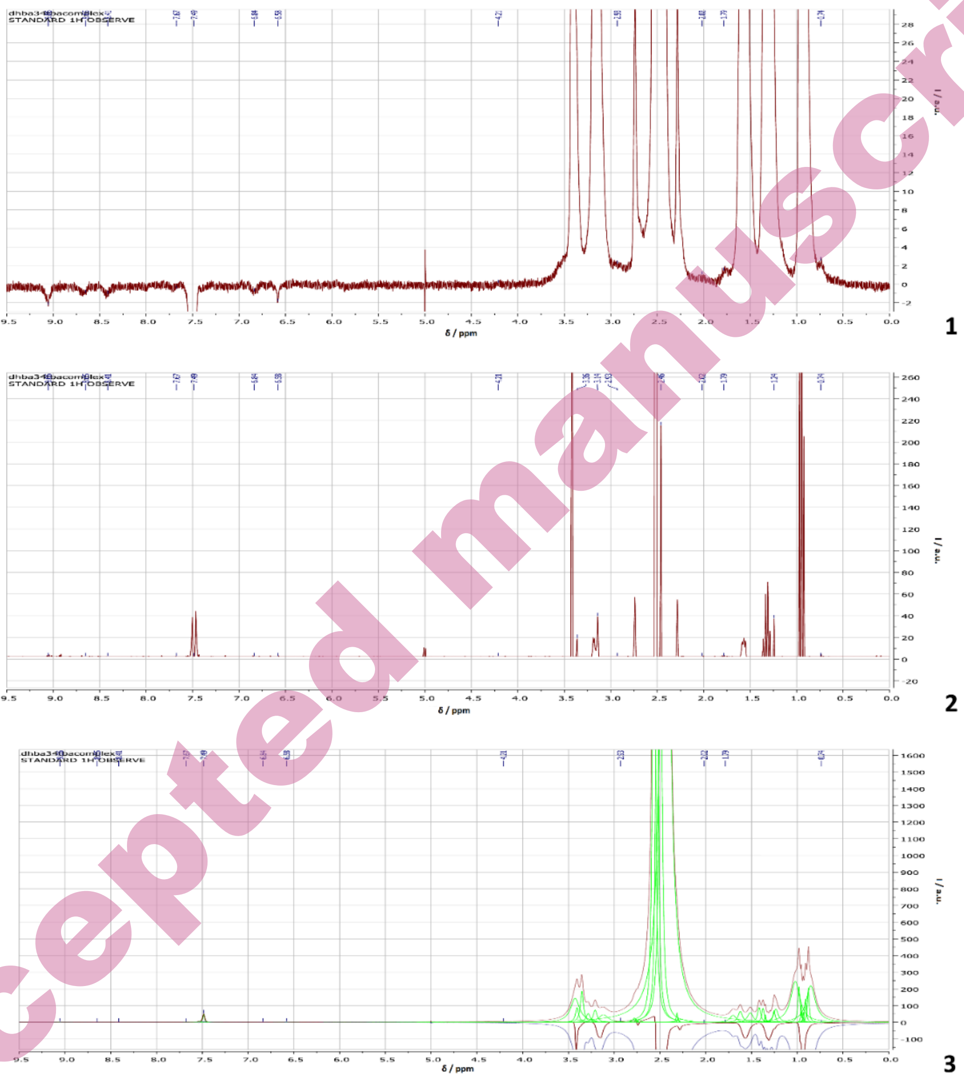


Fig. 8. ^{1}H NMR spectrum of the 3,4-DHBA/ isolated carnosine-manganese complex (solid 24)[25] in DMSO-d_6: Panels 2 and 3 show GSD and Resolution Booster analyses.

Proposed redox sequence

The spectroscopic and electrochemical results support a cooperative redox sequence in the 3,4-DHBA–carnosine–Mn^{2+} system.

1. Semiquinone formation.

Aerobic oxidation of 3,4-dihydroxybenzoic acid leads to the formation of oxygen-stabilized semiquinone radicals,[16] as evidenced by characteristic ESR signals and visible absorption bands.

2. Interaction with carnosine.

Carnosine interacts with these intermediates, likely through an imidazole-mediated pathway,[16,17] leading to attenuation of the ESR signal, redistribution of visible absorption bands, and perturbation of the catechol redox couple, consistent with the formation of quinonoid or peptide-associated species.

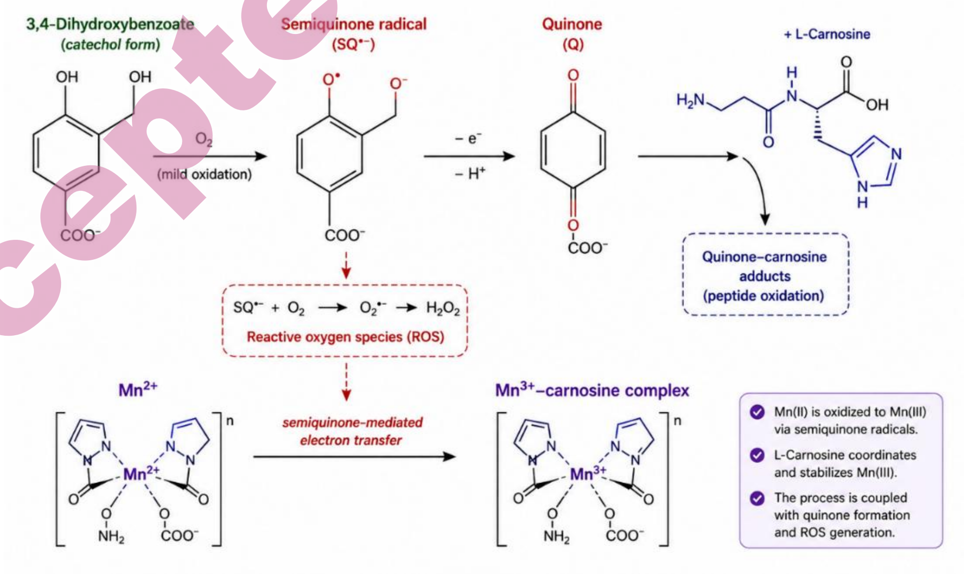
3. Semiquinone-mediated Mn oxidation.

In the presence of Mn^{2+}, semiquinone intermediates can act as electron-transfer mediators, promoting oxidation of the metal center to higher oxidation states.[18] Attenuation of semiquinone electrochemical signals and the appearance of irreversible anodic processes are consistent with coupled metal-centered redox processes.

4. Stabilization of Mn(III).

The resulting Mn(III) species are likely stabilized through coordination to oxygen-donor groups and the imidazole functionality of carnosine, forming dynamic solution structures.[18–21] Paramagnetic ^{1}H-NMR broadening and irreversible voltammetric behavior in the 0.30–0.80 V region support the presence of ligand-stabilized high-spin Mn(III) species. [9,18,21]

The proposed sequence is consistent with the observed ESR attenuation, irreversible voltammetry, and paramagnetic NMR effects, as summarized schematically in Fig. 9.



✓ Mn(II) is oxidized to Mn(III) via semiquinone radicals.

✓ L-Carnosine coordinates and stabilizes Mn(III).

✓ The process is coupled with quinone formation and ROS generation.

Fig. 9. Schematic representation of the proposed redox sequence in the 3,4-DHBA–carnosine–Mn^{2+} system illustrating semiquinone-mediated electron transfer leading to oxidation of Mn(II) to Mn(III) and stabilization of the resulting metal complex by L-carnosine.

CONCLUSION

This study establishes a coherent redox framework for the interactions between L-carnosine, Mn^{2+} ions, and semiquinone radicals derived from 3,4-dihydroxybenzoic acid under non-enzymatic conditions. Combined UV–Vis, ESR, ^{1}H-NMR, and cyclic voltammetry measurements demonstrate that semiquinone intermediates participate in both peptide oxidation and manganese-centered electron-transfer processes.

Carnosine acts as both a redox-active component and a coordinating ligand, interacting with semiquinone species and contributing to the stabilization of higher-valent manganese intermediates. The formation of ligand-stabilized Mn(III) species is supported by spectroscopic and electrochemical evidence, including paramagnetic NMR behavior and irreversible voltammetric features.

Overall, the results support a cooperative redox pathway in which semiquinone radicals function as transient electron-transfer mediators within a multicomponent system. These findings provide insight into redox interactions between manganese ions, catechol-derived species, and peptide ligands in solution, offering a chemically consistent basis for understanding such processes in complex environments.

NOMENCLATURE

- **3,4-DHBA**: 3,4-dihydroxybenzoic acid
- **DMSO**: dimethyl sulfoxide
- **ESR**: electron spin resonance
- **CV**: cyclic voltammetry
- **NMR**: nuclear magnetic resonance
- **UV-Vis**: ultraviolet-visible spectroscopy
- $\mathbf{E_{pa}}$: anodic peak potential
- $\mathbf{E_{pc}}$: cathodic peak potential
- $\mathbf{\Delta E_p}$: peak-to-peak separation
- **g**: g-factor (ESR spectroscopy)
- **δ**: chemical shift (NMR spectroscopy)

SUPPLEMENTARY MATERIAL

Additional data are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13801, or from the corresponding author on request.

ИЗВОД

РЕДОКС РЕАКЦИЈЕ У КАРНОЗИН–МАНГАН СИСТЕМУ У ПРИСУСТВУ СЕМИХИНОНСКИХ РАДИКАЛА

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У овом раду испитивана је интеракција карнозина, дипептида који садржи хистидин, са семихинонским радикалом дианјона 3,4-дихидроксибензоеве киселине у раствору диметил-сулфоксида у аеробним условима. Поред тога, испитивана је интеракција система дипептид–манган са истим семихинонским радикалом при истим условима. Координација за метал и редокс хемија ових система испитивани су применом електронске, ESR и ^{1}H NMR спектроскопије, као и цикличне волтаметрије. *In situ* формирани семихинонски радикали (детаљно проучавани у претходним радовима) били су значајно модификовани након додавања карнозина, што је потврђено прерасподелом апсорпционих трака и променом редокс парова катехолног производа. Утицај јона мангана изазвао је додатне спектралне и електрохемијске промене, у складу са оксидацијом усмереном на јон метала и формирањем комплексних врста мангана стабилизованих лигандом. Парамагнетно ширење сигнала у ^{1}H NMR спектрима указало је на присуство интермедијера мангана виших оксидационих стања у раствору. Комбиновани подаци указују на кооперативни редокс механизам у којем семихинонске врсте посредују и у оксидацији пептида и у преносу електрона усмереном на јон мангана. Ови резултати пружају увид у разумевање вишекомпонентних система који су често присутни у природи.

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