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Preparation and Spectroscopic Characterization of Two Manganese(II)semiquinone Complexes

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Summary. The complexes [*CTA*][Mn(II)(*SQ*)$_3$] were isolated in the solid state and purified. *SQ* is the *o*-semiquinone of *L-dopa* or dopamine and *CTA* is the cetyltrimethylammonium cation. These complexes were characterized by *Raman*, infrared, EPR and thermogravimetry (TG) techniques. The EPR spectra of the solids presented an intense signal characteristic of the *o*-semiquinone radical anion with $g = 2.0062$ and $g = 2.0063$ for *L-dopa* and dopamine, respectively. Six characteristic lines around the organic radical signal confirm the presence of the Mn^{2+} ion. The most intense *Raman* bands were observed at $\bar{\nu} = 1360$ for dopamine and at $1356\,cm^{-1}$ for *L-dopa* and assigned to a C–O stretching with major C_1–C_2 character. The absence of an intense *Raman* band at ca. $\bar{\nu} = 1480\,cm^{-1}$, characterizes the ligands as an *o*-semiquinone radical anion. Broad bands in the $\bar{\nu} = 400$–$750\,cm^{-1}$ region can be assigned to deformations associated with the five-member ring chelate including the manganese ion, the oxygens, and the C_1–C_2 bonds. The more intense IR bands for the dopamine and the *L-dopa*-derived ligands at $\bar{\nu} = 1233$ and $1229\,cm^{-1}$ are assigned to $\bar{\nu}$CO. Mass loss mechanisms for the two complexes, based on the TG results, were proposed and confirm the formula proposed.

Keywords. *Raman* spectroscopy; EPR spectroscopy; Coordination chemistry; Manganese; Catecholamines.

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Introduction

The kinetic and mechanistic study of the oxidation reaction of substances with highly specialized biological functions such as dopamine and its precursor *L-dopa* (L-3,4-dihydroxyphenylalanine) are very important in studies on the origin and evolution of *Parkinson*'s disease [1–10]. Dopamine belongs to the catecholamine group. Free radicals and reaction intermediates are generated in this oxidation process that are indicated as the causes of death of the dopaminergic neural cells, that is, cells that produce the neurotransmitter dopamine. The oxidation process can occur through dopamine auto-oxidation or can be caused by some agent with oxidant property, such as transition metals in the form of Mn^{3+}, Mn^{2+}, MnO_2, and Fe^{3+} *etc*. Thus, the study of dopamine and *L-dopa* oxidation is very important to ascertain whether the mechanism and the products formed are of the same nature for both compounds. The fact that the products generated in the oxidative process are of the same nature may corroborate the observation that both dopamine and *L-dopa* may produce radical species that act in the dopaminergic cell membrane destruction process.

In a previous study we assigned the electronic transitions involved in the substances called chromes (dopachrome, aminochrome, and adenocrome). These are the intermediates in the catecholamine oxidation process and we assigned vibrational bands observed in the resonance *Raman* spectra [11]. We also studied the dopamine, *L-dopa*, adrenaline, and noradrenaline oxidation process using the MnO_2 oxidizing agent in the presence and absence of the $S_2O_3{}^{2-}$ [12]. We ascertained that dopamine and *L-dopa* oxidation in the presence of $S_2O_3{}^{2-}$ generates complexes that are soluble in water at $pH = 7$ with molar absorption of the order of $\varepsilon \cong 6.0 \cdot 10^3\,M^{-1}\,cm^{-1}$. These complexes were studied in solution using UV-Vis, resonance *Raman*, and EPR spectroscopies and the results suggested that they have a structure of the $[Mn(II)(SQ)_3]^-$ type where *SQ* is a anionic *o*-semiquinone.

This study presents the results of the isolation, purification and characterization by *Raman*, infrared, EPR spectroscopy, and thermogravimetry (TG) techniques of $[CTA][Mn(II)(SQ)_3]$ in the solid state, where *SQ* is the *o*-semiquinone of *L-dopa* or dopamine and *CTA* is the cetyltrimethylammonium cation.

Results and Discussion

The TG curves, Fig. 1A and 1B, showed the mass loss of the samples of manganese compounds derived from *L-dopa* and dopamine, respectively, as a function of temperatures between 40 and 600°C.

A mass loss mechanism for the *L-dopa* derived complex based on the TGA results is presented in Eqs. (1)–(4) below.

$$[C_{19}H_{42}N][(Mn)(C_9H_9NO_4)_3]\cdot H_2O \xrightarrow[50-160^\circ C]{} [C_{19}H_{42}N][(Mn)(C_9H_9NO_4)_3] + H_2O \qquad (1)$$

$$[C_{19}H_{42}N][(Mn)(C_9H_9NO_4)_3] \xrightarrow[160-250^\circ C]{} [C_{19}H_{42}N][(Mn)(C_9H_9NO_4)_2] + C_9H_9NO_4 \qquad (2)$$

$$[C_{19}H_{42}N][(Mn)(C_9H_9NO_4)_2] \xrightarrow[250-360^\circ C]{} [(Mn)(C_9H_9NO_4)_2] + C_9H_9NO_4 + C_{19}H_{42}N \qquad (3)$$

$$[(Mn)(C_9H_9NO_4)] \xrightarrow[360-600^\circ C]{} (Mn_xO_y) \qquad (4)$$

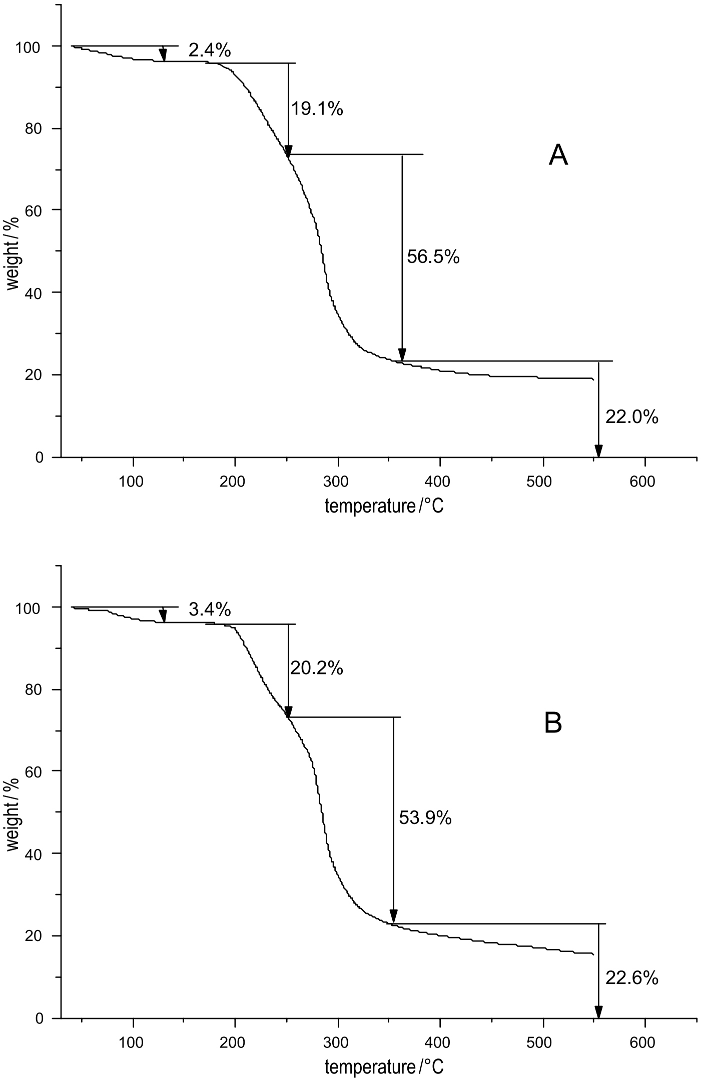

Fig. 1. TG curves of the complexes (A) [*CTA*][Mn(II)(*L-dopa-SQ*)$_3$] and (B) [*CTA*][Mn(II)(dopamine-*SQ*)$_3$]

The theoretical and experimental values detected for each stage of the mechanisms proposed above were: (1) 3.3 and 2.4%, (2) 20.3 and 19.1%, (3) 49.9 and 56.5%, (4) 26.0 and 22.0%.

A similar decomposition mechanism was obtained for the complex derived from dopamine shown in Eqs. (5)–(8).

$$[C_{19}H_{42}N][(Mn)(C_8H_9NO_2)_3]\cdot H_2O \xrightarrow[50-150^\circ C]{} [C_{19}H_{42}N][(Mn)(C_8H_9NO_2)_3] + H_2O \tag{5}$$

$$[C_{19}H_{42}N][(Mn)(C_8H_9NO_2)_3] \xrightarrow[150-250^\circ C]{} [C_{19}H_{42}N][(Mn)(C_8H_9NO_2)_2] + C_8H_9NO_2 \tag{6}$$

$$[C_{19}H_{42}N][(Mn)(C_8H_9NO_2)_2] \xrightarrow[250-370^\circ C]{} [(Mn)(C_8H_9NO_2)] + C_8H_9NO_2 + C_{19}H_{42}N \tag{7}$$

$$[(Mn)(C_8H_9NO_2)] \xrightarrow[370-600^\circ C]{} (Mn_xO_y) \tag{8}$$

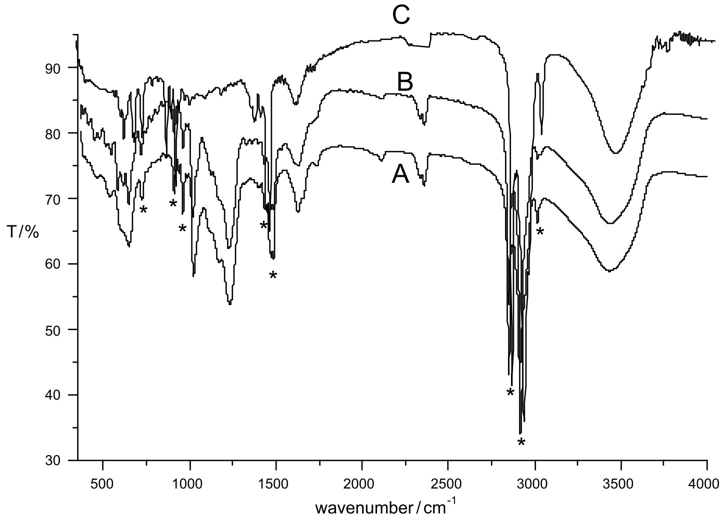

Fig. 2. IR spectra in KBr pastille of the complexes (A) [*CTA*][Mn(II)(dopamine-*SQ*)$_3$], (B) [*CTA*][Mn(II)(*L-dopa-SQ*)$_3$], and (C) *CTAB* salt; the bands marked with asterisk were attributed to the cetyltrimethylammonium cation

The theoretical and experimental values detected for each stage of the mechanism proposed above were: (5) 3.3 and 3.1%, (6) 18.5 and 20.7%, (7) 53.1 and 52.5%, (8) 25.1 and 23.5%. There is some uncertainty about the values obtained because of experimental errors in the choice of the temperature intervals for each mass loss step.

The infrared spectra of the complexes in the solid state obtained at the interval between $\bar{\nu} = 400$ and $4000\,\text{cm}^{-1}$, Fig. 2, showed that most of the spectrum could be attributed to the cetyltrimethylammonium cation.

However, there was a region between $\bar{\nu} = 980$ and $1380\,\text{cm}^{-1}$ where the cation did not absorb. More intense bands were detected in this region for the ligand derived from dopamine at $\bar{\nu} = 1233\,\text{cm}^{-1}$ and at $\bar{\nu} = 1229\,\text{cm}^{-1}$ for the *L-dopa* derived ligand and assigned to a $\bar{\nu}$CO mode. Table 1 gives an assignment of the frequencies aided by a semi-empirical calculation using the PM3 method.

Although the complex structure was satisfactorily defined, the nature of the dioxolene ligand was not so easy to define. The ligand may be of the *o*-quinone (*Q*), dianion catecholate (*Cat*), or *o*-semiquinone radical anion (*SQ*) nature, Fig. 3, due to the easy interconversion among these forms [13, 14].

EPR and *Raman* spectroscopy were used to define the nature of the ligand. The EPR spectra of the solids were obtained, Fig. 4, where an intense signal of the typically organic radical can be observed with $g = 2.0062$ and 2.0063 of the *L-dopa* and dopamine derived complexes, respectively, that could be attributed to an *o*-semiquinone radical anion (*SQ*).

The six characteristic lines around the radical signal confirm the presence of the Mn^{2+}. This pattern is typical for an octahedral-type structure, where the ligands are the three *SQ* radicals. Therefore, the formula [*CTA*][Mn(II)(*L-dopa-SQ*)$_3$] and [*CTA*][Mn(II)(dopamine-*SQ*)$_3$] can be assigned to the complexes.

Table 1. Observed *Raman* and IR wavenumbers (cm^{-1}) and a tentative assignment based on a PM3 semi-empirical calculation for the dopamine and *L-dopa* derived manganese complexes

Assignment	*CTA*	[*CTA*][Mn(II)(*dop-SQ*)$_3$]		[*CTA*][Mn(II)(*L-dop-SQ*)$_3$]		Calculated
	IR	IR[a]	*Raman*	IR	*Raman*	
CTA	3017 m	3017 m		3017 w		
CTA	2943 sh	2946 sh		2945 sh		
CTA	2917 vs	2919 vs		2919 vs		
CTA	2848 vs	2850 vs		2850 vs		
		1737 w	1711 vw	1730 w	1704 vw	
		1657 m		1631 m		
		1629 m		1606 m		
$\bar{\nu}$CC			1584 s		1584 s	1594
$\bar{\nu}$CC, $\bar{\nu}$CO			1494 m		1489 m	1514
CTA	1486 vs	1486 s		1486 s		
CTA	1472 vs	1473 s		1470 s		
CTA(?)	1431 m	1436 s		1433 s		
$\bar{\nu}$CC, $\bar{\nu}$CO			1360 vs		1356 vs	1400
$\bar{\nu}$CO		1233 vs	1253 m	1229 vs	1250 m	1270
		1170 sh	1173 vw	1168 sh	1167 w	
		1116 sh	1100 vw	1122	1112 vw	
		1023 vs		1021 vs		
					1090 vw	
					1017 vw	
			997 sh		995 sh	
$\bar{\nu}$CC			982 m		983 m	1007
CTA	962 s	962 m		962 m		
$\bar{\nu}$CC			942 s		943 s	1004
CTA	936 m	937 w		940 vw		
CTA	911 s	911 m		911 m		
$\bar{\nu}$CC			891 m		881 m	923
			873 m		790 vw	
CTA	729 s	729 m		729 m		
CTA	719 s	721 m				
			728 vw		730 vw	
$\bar{\nu}$Mn–O, $\bar{\nu}$CC		649 s	652 w	647 s	653 m	719
$\bar{\nu}$Mn–O		619 sh	612 m	615 s	612 m	636
		600 sh		584 s		
		539 w		545 vw		
			510 vw		508 w	
					486 w	
CTA	450 w		453 w		450 w	
			363 w		405 vw	
			350 w		352 w	

[a] s = strong, vs = very strong, w = weak, vw = very weak, sh = shoulder, m = medium

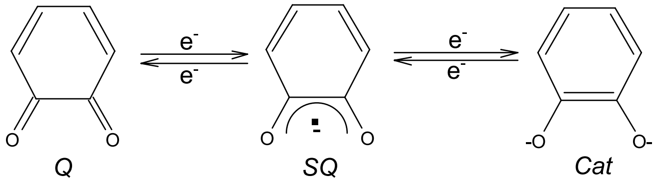

Fig. 3. Interconversion among the *o*-quinone, dianion-catecholate, and *o*-semiquinone forms

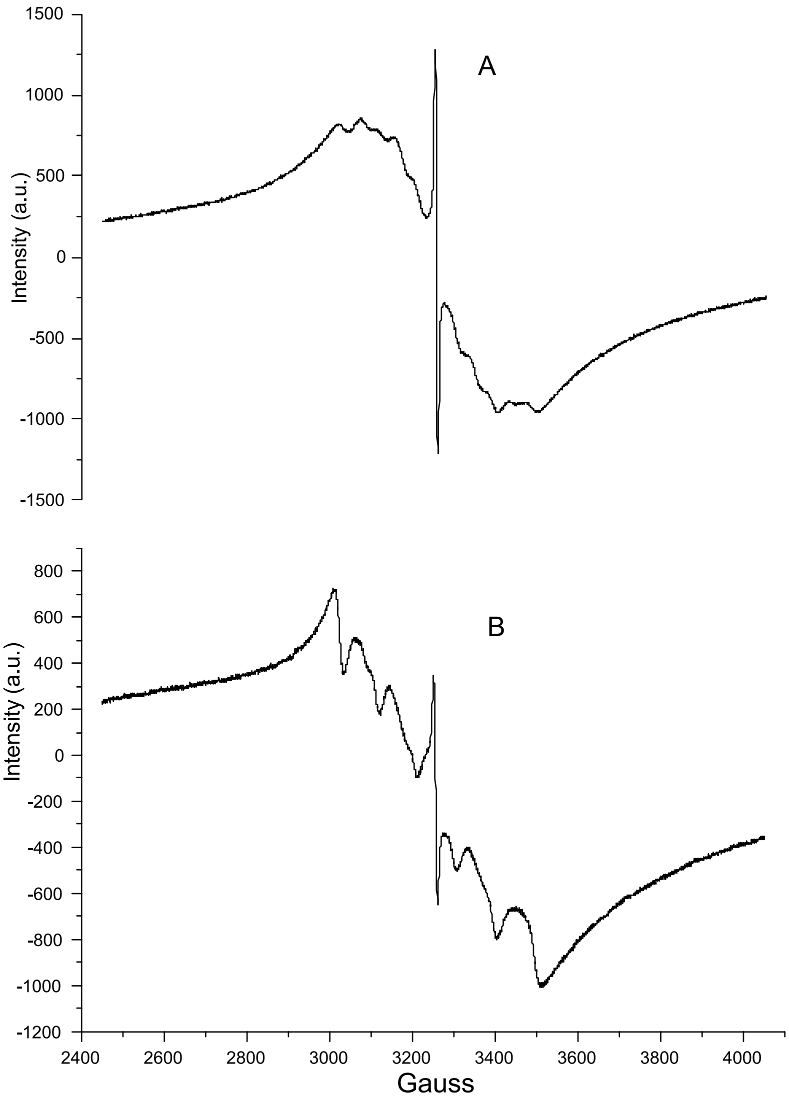

Fig. 4. EPR spectra of the complexes (A) [*CTA*][Mn(II)(*L-dopa-SQ*)$_3$], $g = 2.0062$ and (B) [*CTA*][Mn(II)(dopamine-*SQ*)$_3$], $g = 2.0063$

Figure 5 shows the *Raman* spectra of the complexes in the solid state derived from dopamine and *L-dopa*, respectively.

It was observed that the two spectra presented the same band profile and we did not observe the expected bands for the *CTA* cation that would indicate that we were

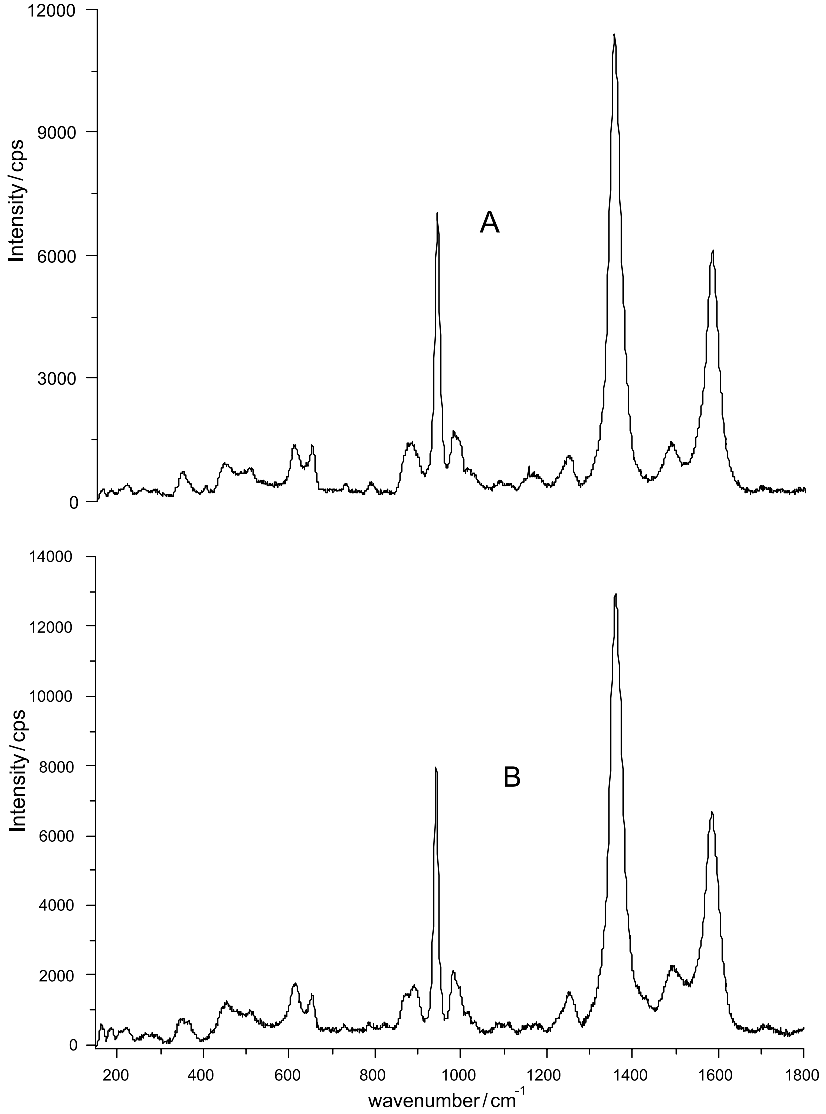

Fig. 5. Raman spectra of the complexes (A) [*CTA*][Mn(II)(*L-dopa-SQ*)$_3$] and (B) [*CTA*][Mn(II)(dopamine-*SQ*)$_3$]; excitation at $\lambda = 488$ nm, 150 mW laser power

observing a resonance *Raman* effect. The dopamine-derived complex possessed the most intense band at $\bar{\nu} = 1360\,\mathrm{cm}^{-1}$ and the *L-dopa* derived complex spectrum at $\bar{\nu} = 1356\,\mathrm{cm}^{-1}$. The frequency values of the most intense bands were very close to those obtained from the complexes in aqueous solution by resonance *Raman* spectroscopy that were found to be at $\bar{\nu} = 1373$ and $1377\,\mathrm{cm}^{-1}$ for dopamine and *L-dopa*, respectively [12]. Table 1 presents the *Raman* frequencies observed and calculated with a PM3 semi-empirical method and a tentative assignment.

It was concluded from these spectra that the anion complex obtained in solution continues to be of the same nature after precipitation but without the same intensities of the *Raman* frequencies observed in solution due to its interaction with the cation. A general criterion presented in literature was used to assign the bands of

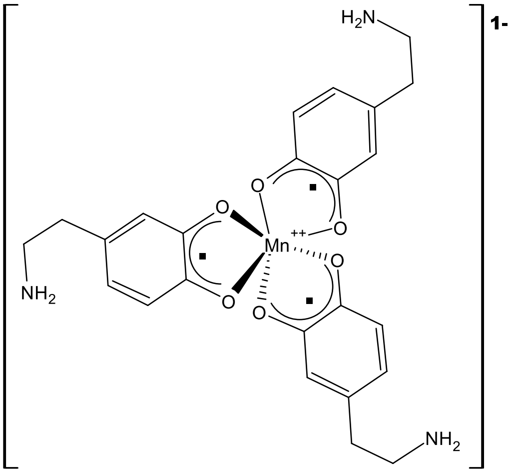

Fig. 6. Proposed structure for the anion complex

these dioxolene complexes. It is well known that the frequencies for the C–O bond are observed between $\bar{\nu} = 1630$–1640 for *M–Q*, 1400–1500 for *M–SQ*, and 1250–1275 cm^{-1} for *M-Cat* complexes [14]. Therefore the most intense *Raman* band at ca. $\bar{\nu} = 1360\,\text{cm}^{-1}$ could be assigned to a C–O stretching with major C_1–C_2 character (C_1 and C_2 are the carbons bonded to oxygens) remaining close to that assigned for the *M–SQ* ($\bar{\nu} = 1400\,\text{cm}^{-1}$). It is difficult to specify the C–O contribution to this mode, but it is reasonable to use this mode and the absence of the intense *Raman* band at ca. $\bar{\nu} = 1480\,\text{cm}^{-1}$ to characterize the ligands as an *o*-semiquinone radical anion. We can tentatively assign the resonance *Raman* band observed at ca. $\bar{\nu} = 1580\,\text{cm}^{-1}$ to a ring stretching, and the band at $\bar{\nu} = 1250\,\text{cm}^{-1}$ to a ring deformation with major C–O character also observed at ca. $\bar{\nu} = 1250\,\text{cm}^{-1}$ as a characteristic for the *M–SQ* complexes. The broad bands in the $\bar{\nu} = 400$–$750\,\text{cm}^{-1}$ region can be assigned to deformations associated with the five-membered ring chelate including the manganese ion, the oxygens and the C_1–C_2 bond. The absence of a strong *Raman* resonance band at ca. $\bar{\nu} = 1440\,\text{cm}^{-1}$ assigned as $\nu(\text{C=N}^+)$ for all chrome substances, such as aminochrome, indicates that cyclization of the aminoethyl side chain did not occur. Finally, based on the observations made, a structure of the anion complex is proposed as presented in Fig. 6.

Conclusion

The results showed that MnO_2 oxidized dopamine or *L-dopa* in aqueous solution, even in the presence of sodium thiosulphate that is known to be a strong reducing agent. Highly stable Mn(II) complexes were generated in this process that could be precipitated with cetyltrimethylammonium bromide. The complexes obtained were characterized as [*CTA*][(Mn)(*SQ*)$_3$] and showed an octahedral-type structure, where the *SQ* ligands are the dopamine-*o*-semiquinone or *L-dopa-o*-semiquinone anionic radicals, products of the dopamine or *L-dopa* oxidation. These complexes maintain the stable *SQ* radical ligands when in contact with air, unlike other complexes of the same type. The thermal analysis of the complexes derived from dopamine and *L-dopa* indicated that the two decompose according to the same mechanism.

The similarity of the proposed structures and decomposition mechanisms indicated that the two catecholamines show the same performance in oxidative processes in reducing aqueous media.

Experimental

The analytical degree reagents used were sodium thiosulphate ($Na_2S_2O_3$, Aldrich 99%), 3-hydroxytyrosine (*L-dopa*, $C_9H_{11}NO_4$, Sigma); 4-(2-aminoethyl)benzene-1,2-diol (dopamine, $C_8H_{11}NO_2$, Sigma), manganese oxide (MnO_2, Aldrich 99%), cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, Fluka Chemika), chloroform (Nuclear).

Preparation of the Complexes [CTA][Mn(II)(L-dopa-SQ)$_3$] and [CTA][Mn(II)(dopamine-SQ)$_3$]

The complexes were prepared by mixing $Na_2S_2O_3$ (0.265 g) in ultra pure water (0.200 dm^{-3}), followed by adding *L-dopa* or dopamine (0.1 g) and MnO_2 (0.0230 g) under constant agitation for 24 h. After this period the solution presented an intensive blue color. The solution was then allowed to settle and the supernatant was filtered through a sintered glass crucible with fine porosity to eliminate MnO_2 suspended in this solution. A solution prepared with cetyltrimethylammonium bromide (*CTAB*) (0.2 g) in water (0.020 dm^3) was added dropwise and stirred until a dark blue precipitate formed. The precipitate formed was filtered through a sintered glass crucible, washed thoroughly with ultra pure water, and kept in a desiccator at 25°C. The excess of *CTAB* and soluble Na^+, $S_2O_3{}^{2-}$ and Mn^{2+} ions, that might have contaminated the precipitate, were removed in this process. The black-blue solid obtained decomposes in acetone. The complex could not be crystallized from chloroform by slow evaporation. Elemental analyses (C, H, N, Mn) were conducted using the Elemental Analyser Perkin Elmer 2400 CHN; their results were found to be in good agreement ($\pm 0.2\%$) with the calculated values.

Physical Measurements

The *Raman* spectra were obtained by a *Raman* Jobin-Yvon spectrometer with $\lambda = 488$ nm exciting radiation, $\bar{\nu} = 7$ cm^{-1} resolution, and 150 mW laser power. The base lines were corrected due to fluorescence and smoothing was performed to improve the signal/noise ratio. The infrared spectra were obtained using a Perkin-Elmer 2000 FT-IR spectrometer. The mass losses (TG) were obtained in a T. A. Instruments TG 2950, High Resolution device, with N_2 atmosphere and a heating rate of 10°C/min. EPR experiments were performed at the X-band (9.5 GHz) microwave frequency and with a magnetic field modulation of 100 kHz using a VARIAN E-109 apparatus at room temperature. The microwave frequency was accurately read with a Hewlett Packard frequency counter, model HP 5352B. The data were acquired with a PC microcomputer using software for data acquisition developed at the Institute of Physics of the University of São Paulo, Brazil. To calculate the vibrational frequencies a semi-empirical model, PM3, was used with a PC Spartan Pro-1.0.3 software (Wavefunction, Inc.).

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