

## Interaction of Ni(II) with 2,3-dihydroxybenzoic acid

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Received 8 July 2000; accepted 18 October 2000

### Abstract

The reaction of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with 2,3-dihydroxybenzoic acid = L in  $n\text{-PrOH}:\text{H}_2\text{O} = 1:1$  solution, produced the complex  $\{[\text{Ni}_5\text{L}_5(\text{OH})_7]\text{K}_4 \cdot 13\text{H}_2\text{O}\}_n$ . Its structure was investigated using elemental analysis, IR, UV–Vis, NMR and ES MS spectroscopy. The complex is unstable in aqueous solution and its decomposition scheme was proposed on the basis of NMR and ES MS spectra. This may contribute to the understanding of oxidative degradation of catecholic derivatives by Ni(II), as well as to other similar ones. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Ni(II) complexes; ES MS spectroscopy; 2,3-Dihydroxybenzoic acid; Catecholic derivatives; Oxidative degradation

### 1. Introduction

Metal complexes of 2,*x*-dihydroxybenzoic acids ( $x = 3, 4, 5, 6$ ) are suitable as models for the binding sites of humic acids with metals [1]. These ligands occur in three oxidation forms, viz. catechol, semiquinone and quinone. Various dihydroxybenzoic acid complexes with metals have been studied, e.g. the unusual seven-coordinated cadmium complex with 3,4-dihydroxybenzoic acid, viz.  $[\text{Cd}(3,4\text{-dhbH}_2)(\text{H}_2\text{O})_3] \cdot \text{HCl} \cdot (3,4\text{-dhbH}_3) \cdot 2.5\text{H}_2\text{O}$  [2], as well as manganese, iron and molybdenum complexes [3–5]. Crystal structure determinations have also been carried out for several metal complexes of 2,3-dhbH<sub>3</sub> as well as of other dihydroxybenzoic acids [6–9] or other similar ligands like 2,6-dimethoxybenzoic acid anion [10], 2,6-dihydroxybenzoic acid monoanion [11] or 2-nitroso-*o*-quinone [12]. For example, Ni complexes with catechol were of two types; either paramagnetic ones with the metal being octahedral or diamagnetic tetragonal ones with two semiquinone ligands [13].

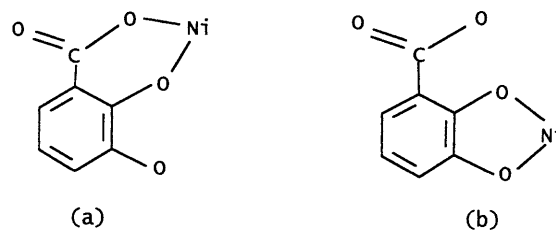
The oxidation–reduction behavior of catechol like ligands — either in the presence of metals or alone —

was studied and either paramagnetic complexes with semiquinone ligand or diamagnetic complexes were obtained [14,15].

The kinetics of the coordination and oxidation process for the system  $\text{Fe}-(2,3\text{-dhbH}_3)$  have been measured using the products as models of the naturally formed complex between Fe(III) and enterobactin and it was found that  $\text{Fe}(\text{dhbH})_2$  was formed, with the ligand binding to iron in its catecholate form [16,17].

The 1:2 complex of (2,3-dhb):Fe, with the ligand catechol-coordinated to the metal, causes degradation of dioxane–lignin up to 60% within 2 h. It was proposed that low-molecular weight compounds are involved in wood biodegradation [18].

The free ligands 2,*x*-dihydroxybenzoic acids are interesting in their own right. For example the ligand



Scheme 1. Salicylate (a) and catecholate (b) coordination of 2,3-dhbH<sub>3</sub> to Nickel(II).

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2,3-dhbH<sub>3</sub> was used as therapeutic metal-chelating agent and as an antitumor agent [19,20]. The ligand 3,4-dihydroxybenzoic acid was found more active than 2,3-dihydroxybenzoic acid against melanoma cells [21]. 2,3-dhbH<sub>3</sub> exhibited reduction of the inflammatory response in experimental phacoanalytic endophthalmitis thus being an effective antiflogistic agent [22]. The predominant ligand binding modes, viz. the salicylate versus the catecholate (Scheme 1), have also been studied [23,24]. Polymeric species are formed in water solutions of the systems Fe(III)–3,4-dhbH<sub>3</sub> and Mo(VI)–3,4-dhbH<sub>3</sub> [5,25–27], as indicated with ES MS, NMR and of other spectroscopic techniques.

In this paper we present the reaction of Ni(II) with 2,3-dhbH<sub>3</sub> in *n*-PrOH:H<sub>2</sub>O = 1:1 solution. The complex of formula  $\{[\text{Ni}_5\text{L}_5(\text{OH})_7]\text{K}_4 \cdot 13\text{H}_2\text{O}\}_n$ , L = 2,3-dihydroxybenzoic acid, was isolated and characterized using various spectroscopic techniques. The results give strong indications for the ligand's coordination behavior towards Ni(II).

## 2. Experimental

### 2.1. Materials and methods

The organic acid 2,3-dhbH<sub>3</sub> was obtained from Sigma and the chloride salt of Ni was obtained from Aldrich. All reagents were used with no further purification.

Solutions for <sup>1</sup>H NMR spectroscopy were prepared with D<sub>2</sub>O as a solvent and recorded on a Varian 300 MHz AM spectrometer with TSP used as an internal standard.

Infrared spectra were recorded in KBr pellets on a Perkin–Elmer 880 IR spectrophotometer over the region 4000–200 cm<sup>−1</sup>.

UV–Vis spectra in solutions were recorded on 0.1 cm cuvettes at the Hitachi U-2000 spectrophotometer.

ES MS spectra were received at the Fisons Instruments VG BIO-Q quadrupole mass spectrometer with the solution being injected via a Rheodyne injector valve directly through the 10 ml loop in the OCP-V4.06 QUATT 4000 spectrophotometer. Nitrogen was the nebulizing and drying gas and focus voltage was varied from 10 to 40 V while the skimmer voltage varied from 15 to 45 V. The capillary voltage was 3.00 kV and HV lens voltage was 0.46 kV. A total of 20–50 spectra were recorded each time to produce acceptable S/N ratios. The first focus voltages were varied from 10 to 40 V with corresponding change of the skimmer voltage (so that always  $V_f - V_s = 5$  V). Sample flow rate was 3 ml min<sup>−1</sup>, and acetonitrile was used as the mobile phase while the electrostatic ion source operated at atmospheric pressure. Elemental analyses were carried out at the National Hellenic Research Foundation in Athens, Greece.

### 2.2. Preparation of the complex

A total of 0.19 g of NiCl<sub>2</sub>·6H<sub>2</sub>O (= 0.75 mmol) were dissolved in 25 ml of *n*-PrOH and 0.25 g (= 1.62 mmol) of 2,3-dihydroxybenzoic acid were added. The green color of the solution was thus intensified. After stirring at room temperature (r.t.) in the presence of air for 12 h, a solution of 0.18 g KOH in 5 ml of H<sub>2</sub>O was added dropwise and within a few minutes an extra 20 ml of H<sub>2</sub>O were added (H<sub>2</sub>O:*n*-PrOH became finally 1:1), leading to a green precipitate. This was filtered, washed with 10 ml of a solution of H<sub>2</sub>O:*n*-PrOH = 1:1 and then with 10 ml of ether and, finally, dried in vacuum over CaCl<sub>2</sub> overnight. A total of 0.1 g of  $\{[\text{Ni}_5\text{L}_5(\text{OH})_7]\text{K}_4 \cdot 13\text{H}_2\text{O}\}_n$  (yield: 40.0%) were obtained. The compound was isolated as a light green solid soluble in water with simultaneous decomposition, producing a green solution with pH 7.8. Elemental analysis data are in close agreement with the proposed formula (%); C, 25.7(26.0); H, 2.1(2.2); K, 9.9 (10.0); Ni, 18.1 (18.1), with values in parentheses corresponding to theoretical calculated ones.

## 3. Results and discussion

For the reaction of Ni(II) with the ligand 2,3-dihydroxybenzoic acid in aqueous solution, the pK value of the Ni(II)–salicylate type of mode was reported to be 5, while for the Ni(II)–catecholate type of mode was 8 (Scheme 1) [26–28]. The ligand may be bound via both salicylate and catecholate type of modes in the conditions used for the preparation of the complex  $\{[\text{Ni}_5\text{L}_5(\text{OH})_7]\text{K}_4 \cdot 13\text{H}_2\text{O}\}_n$ .

IR data of the free ligand and its Ni(II) complex are presented in Table 1.

The  $\nu_{(\text{C}=\text{O})}$  and  $\nu_{(\text{C}=\text{C})}$  bands of the ligand appear at 1295 and 1470 cm<sup>−1</sup>, respectively (Table 1). The shape of the band at 1480 cm<sup>−1</sup> is indicative of a semiquinone ligand form coordinated to the Nickel atom [29–32]. The characteristic coordinated quinone  $\nu_{(\text{C}=\text{O})}$  band is present in the complex at 1600 cm<sup>−1</sup> [4]. The  $\nu_{\text{as}(\text{C}=\text{O})}$  band of the carboxylate group of the ligand is shifted to lower frequencies indicating its coordination to the metal. The difference  $\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$  of 155 cm<sup>−1</sup> indicate a rather monodentate binding of the metal to the carboxylate [33]. In the complex therefore, Ni(II) is simultaneously bound to the ligand, through either the carboxylate and the 2-oxygen or oxygen atoms at 2- and 3-positions. The slight shift of the skeletal vibrations of the ligand in the complex provides an additional evidence for its coordination to the metal.

The  $\epsilon$  value of a freshly prepared solution exhibits a band around 644 nm ( $\epsilon = 1.28 \times 10^3$ ) which has been assigned to an L to M charge transfer transition [26,32,34]. Metal coordination to the ligand (Scheme 1)

Table 1  
Characteristic IR data for the isolated Ni complex, in the solid state <sup>a</sup>

Compound	$\nu_{\text{as}}^{\text{b}}$	$\nu_{\text{s}}$	$\Delta\nu = \nu_{\text{as}} - \nu_{\text{s}}$	$\nu_{\text{C}=\text{C}}$	$\nu_{\text{C}=\text{O}}$	$V_{(\text{C}=\text{O})(\text{Q})}$	$V_{(\text{C}=\text{O})(\text{SQ})}$
	COO <sup>−</sup>	COO <sup>−</sup>	COO <sup>−</sup>				
2,3-dhbH <sub>3</sub>	1665s	1527m	138	1421s	1295s		
Complex	1550vs <sub>(coord)</sub>	1395s	155	1463s	1246mbr	1600	1480

<sup>a</sup> Values given in cm<sup>−1</sup>.

<sup>b</sup> Abbreviations: m, medium; s, strong; br, broad.

is indicated from the shift of the free ligand band at 306 to 320–330 nm in the complex [26].

### 3.1. NMR spectra

1D-<sup>1</sup>H HMR and 2D-COSY-NMR spectra as well as TOCSY-NMR spectra of the ligand and the complex were recorded (Table 2) in a freshly prepared solution in the presence of air, and at various time intervals afterwards. The aromatic ring protons of the free ligand appear at 7.44, 7.13 and 6.85 ppm, in the <sup>1</sup>H NMR spectra, of the freshly prepared solution.

These protons are upfield shifted in the coordinated ligand compared to those of the free ligand appearing at 7.32, 7.00 and 6.80 ppm, respectively. One uncoupled single band at 8.25 ppm is tentatively assigned to formic acid [35] formed upon ligand degradation (see also Section 3.2). Two h after complex dissolution in D<sub>2</sub>O and recording of the first spectra, degradation of the ligands starts being detectable, as it derives from several other NMR peaks, that start to appear. For example the uncoupled peak at 2.10 ppm, is of the same integral as the one at 8.25 ppm. The latter probably arises from the acetic acid formed (formic and acetic acid may be produced from the degradation of pyruvic acid observed at 2.80 ppm). Also, peaks at 1.30 and 4.25 ppm may be due to the presence of  $\alpha$ -hydroxypropionic acid possibly due to degradation of muconic acid and at 3.00 ppm to malonic acid. The presence of muconic acid is indicated from the peaks at 5.65, 6.20 and 7.80 ppm (Scheme 3). More peaks due to degradation products can be observed at 1.95, 2.20, 3.20, 3.55, 3.75 and 4.30 ppm, which were unassigned.

### 3.2. ES MS

In order to investigate the possible structure of the complex, we carried out ES MS of freshly prepared solutions of the complex in CH<sub>3</sub>CN and water. Ionization produces two groups of fractions, one detected in the cationic and one in the anionic ES MS mode, as presented in Table 3.

#### 3.2.1. Cationic mode of ES MS

In the cationic mode of ES MS, the two sets of bands are presented in the Fig. 1.

For low voltage at the focus lens (viz. 10 V) the ionization is softer, thus allowing the transfer of the intact ions existing in solution to the gas phase. This enables us to observe maximum  $m/z$  species, being the heptamer ion in the positive region of the spectra that corresponds to the formula [Ni<sub>7</sub>L<sub>7</sub>(OH<sub>2</sub>)<sub>4</sub>(OH)<sub>2</sub>(CH<sub>3</sub>CN)<sub>21</sub>]<sup>2+</sup> ( $m/z = 1209.5$  Da e<sup>−1</sup>) [36].

In solution we may have oligomeric species, like {[Ni<sub>5</sub>L<sub>5</sub>(OH)<sub>7</sub>]K<sub>4</sub>·13H<sub>2</sub>O}<sub>*n*</sub>. It is assumed that though the complex in the solid state is anionic, in solution the ligand oxidation leads to cationic species, like the heptamer ion above (Scheme 2).

In the more concentrated solutions hexameric or tetrameric species are also observed, e.g. [Ni<sub>6</sub>L<sub>6</sub>(OH)<sub>2</sub>-(OH<sub>2</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>7</sub>]<sup>2+</sup> ( $m/z = 818.9$  Da e<sup>−1</sup>), or [Ni<sub>4</sub>L<sub>4</sub>(CH<sub>3</sub>CN)<sub>14</sub>]<sup>+</sup> ( $m/z = 706.7$  Da e<sup>−1</sup>). As the solvolysis is a dynamic procedure, similar solvated species have also been observed at the ES MS of other complexes, e.g. of [CrO<sub>3</sub>(RCOO)<sub>6</sub>L<sub>3</sub>]<sup>+</sup>, R = H, CH<sub>3</sub>, etc. L = H<sub>2</sub>O, py, MeOH [37] or of ferric dihydroxamate complexes [38]. In addition, solvated catecholate complexes with various transition metals are usual and several of them have been isolated in the solid state [14].

In more dilute solutions (concentrations in the range of 10<sup>−3</sup> M) and higher focus voltage (20–40 V), the area below  $m/z = 600$  Da e<sup>−1</sup> fragments corresponding to less polymeric complex cations like [Ni<sub>2</sub>L(CH<sub>3</sub>CN)<sub>3</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>+</sup> ( $m/z = 428.8$  Da e<sup>−1</sup>) or

Table 2  
<sup>1</sup>H NMR spectral data for 2,3-dhbH<sub>3</sub> and its Ni complex <sup>a</sup>

Compound	pH	$\delta\text{H}_{\alpha}$	$\delta\text{H}_{\gamma}$	$\delta\text{H}_{\beta}$	$\Delta\delta' = \delta_{\text{compl}} - \delta_{\text{pr. ligand}}$
2,3-dhbH <sub>3</sub>	2.5	7.44	7.13	6.85	H <sub><math>\alpha</math></sub> : 0.12
2,3-dhbH <sub>3</sub>	6.0	7.39	7.05	6.81	H <sub><math>\gamma</math></sub> : 0.13
Complex <sup>b</sup>	7.4	7.32	7.00	6.80	H <sub><math>\beta</math></sub> : 0.05

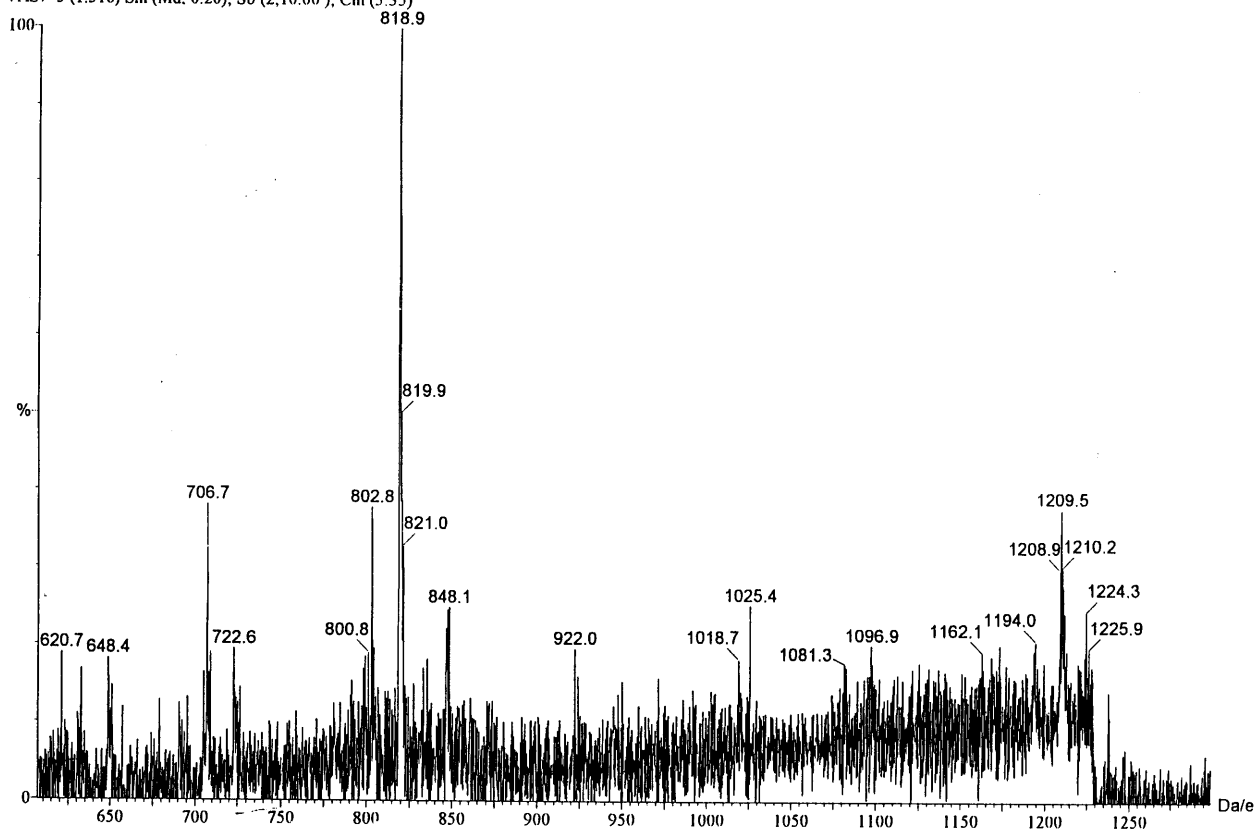
<sup>a</sup> Values of the chemical shifts given in ppm.

<sup>b</sup> Freshly prepared solid, just after dissolution in D<sub>2</sub>O.

## Ni DHB ESP+

(A)

VAS7 5 (1.316) Sm (Md, 0.20); Sb (2,10.00); Cm (5:35)



## Ni DHB ESP+

(B)

VAS6 9 (1.851) Sm (Md, 0.20); Sb (2,10.00); Cm (4:26)

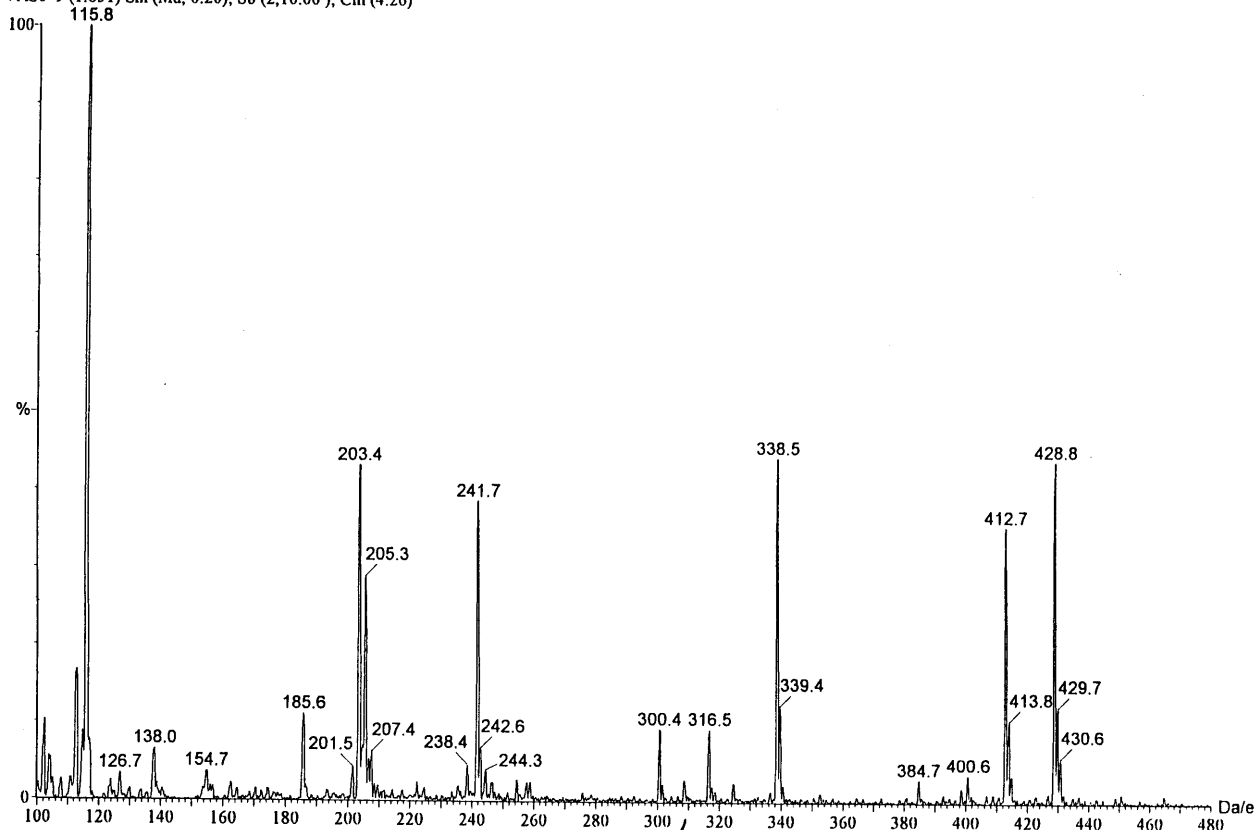
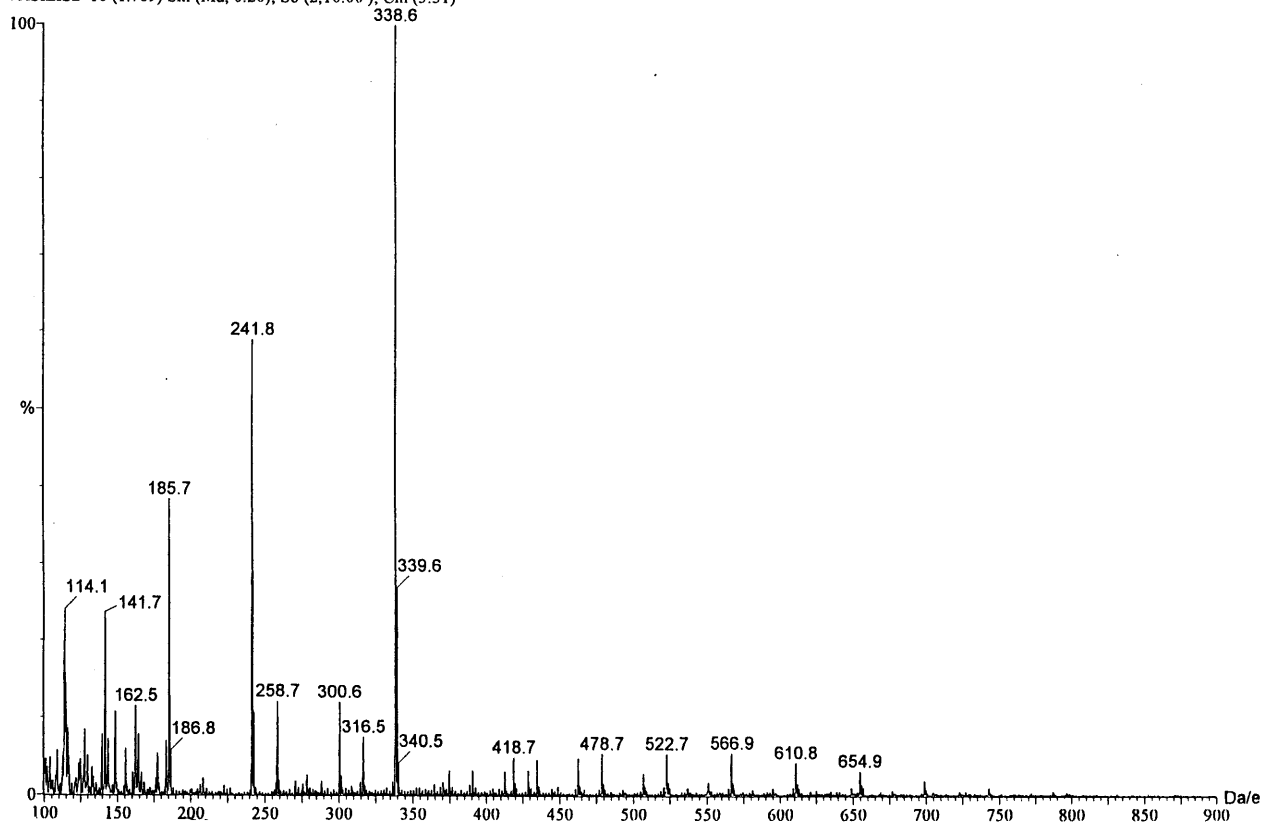


Fig. 1. The cationic fractions produced in the ES MS. (A) Fresh solution in  $\text{CH}_3\text{CN}$ , focus: 10 V; (B) fresh solution in  $\text{CH}_3\text{CN}$ , focus: 20 V; (C) fresh solution in  $\text{CH}_3\text{CN}$ , focus: 40 V; (D) solution in  $\text{CH}_3\text{CN}$  remained 2 days in the presence of air, focus: 40 V; (E) fresh solution in water (pH 7.4), focus: 10 V.

**Nickel, DHB positive ions...**

VASILIS2 16 (1.769) Sm (Md, 0.20); Sb (2,10.00); Cm (5:31)

(C)



MAIRH2 17 (1.510) Sb (2,10.00); Sm (Md, 0.20); Cm (2:82)

(D)

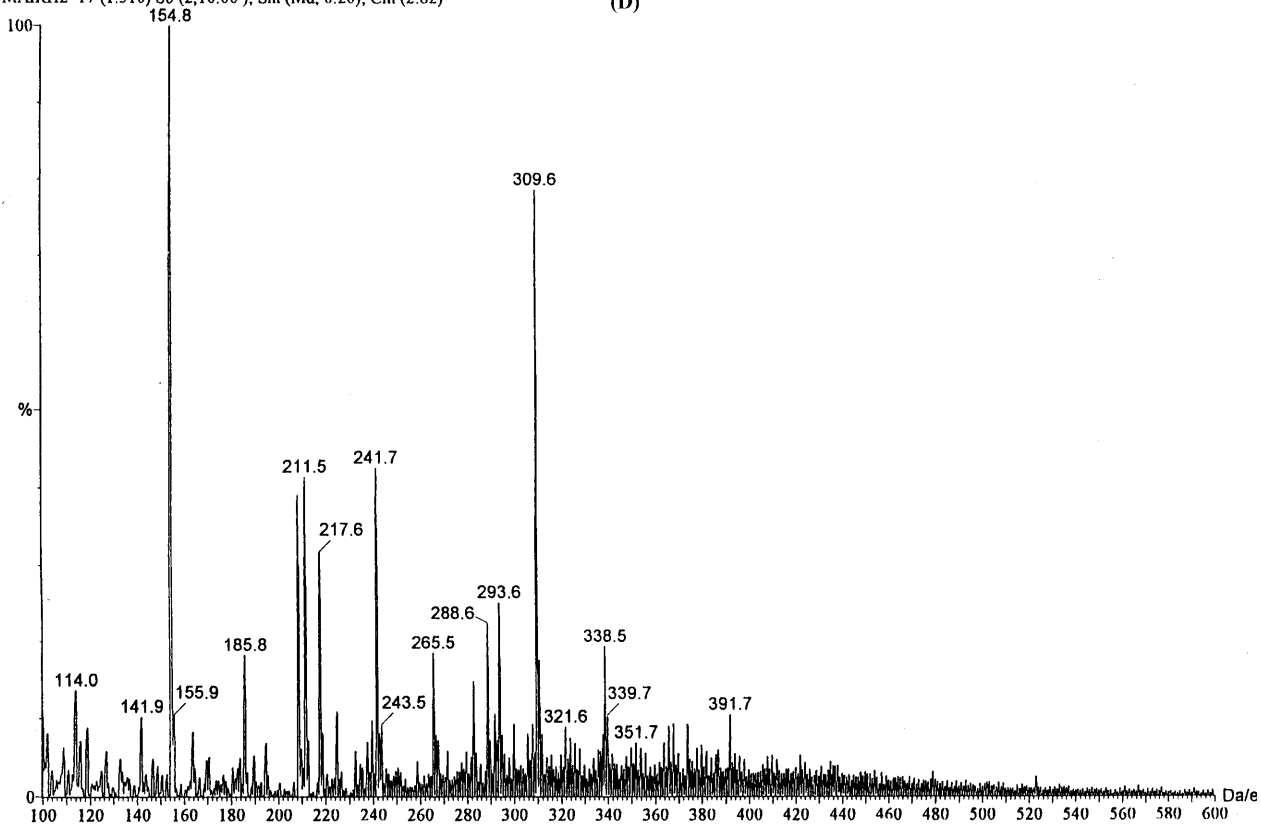


Fig. 1. (Continued)

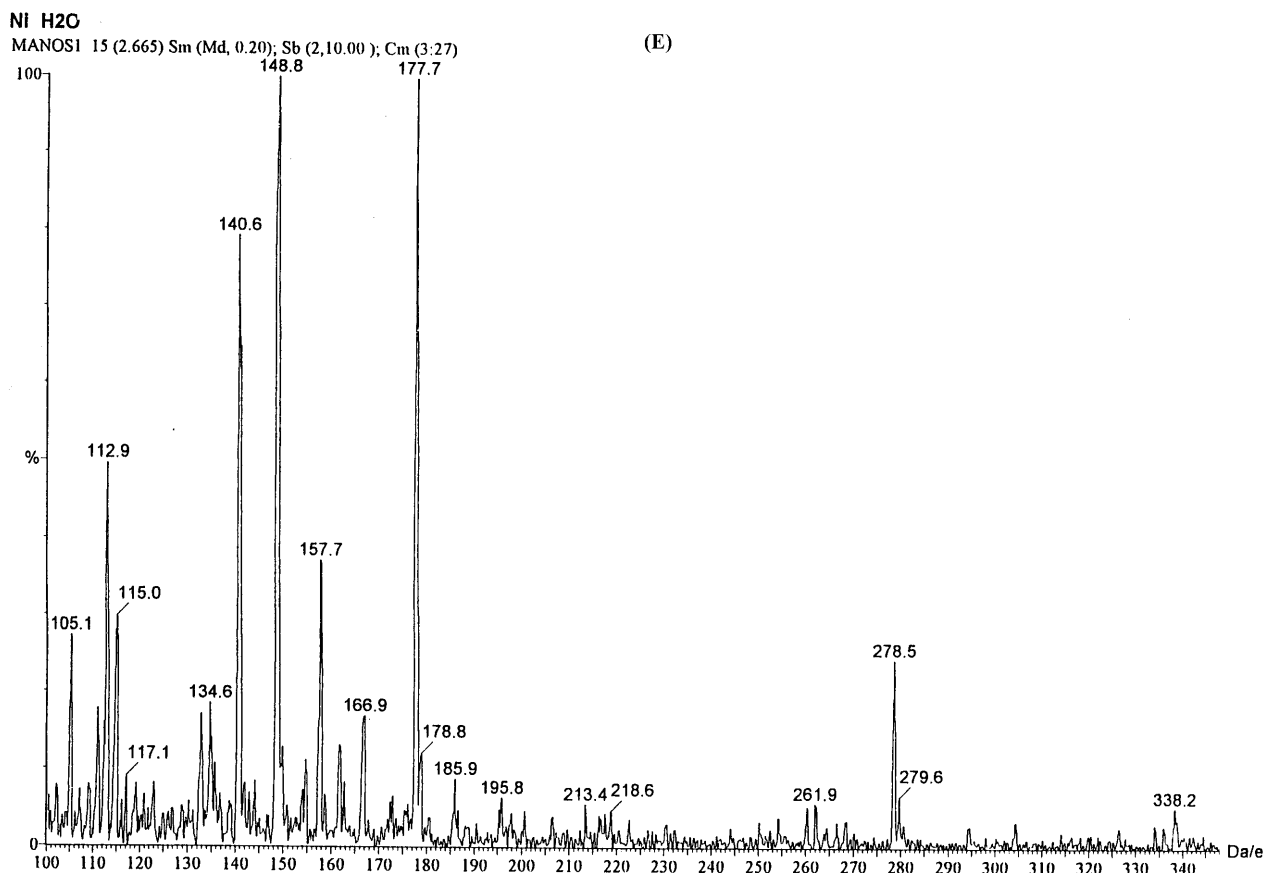


Fig. 1. (Continued)

$[\text{Ni}_2\text{L}(\text{CH}_3\text{CN})_3(\text{OH})]^{2+}$  ( $m/z = 203.4 \text{ Da e}^{-1}$ ) were detected. Monomeric species as the solvated  $[\text{Ni}(\text{CH}_3\text{CN})_3(\text{OH}_2)]^+ \cdot \text{CH}_3\text{CN}$  ( $m/z = 241.7 \text{ Da e}^{-1}$ ),  $[\text{NiL}(\text{OH})_2(\text{OH}_2)_2]^+ \cdot (\text{OH}_2)_3$  ( $m/z = 338.5 \text{ Da e}^{-1}$ ), dimeric ones like the species  $[\text{Ni}_2\text{L}(\text{OH})(\text{CH}_3\text{CN})_3]^{2+}$  ( $m/z = 203.4 \text{ Da e}^{-1}$ ) or the molecular ion of the ligand ( $m/z = 154.8 \text{ Da e}^{-1}$ ) were further observed (Table 3).

When the complex was dissolved in  $\text{CH}_3\text{CN}$ , initially polymer solvolysis takes place followed by decomposition leading to less polymeric and then to monomeric products. Finally, ligand liberation and degradation to aliphatic organic compounds is obvious from all spectra obtained (Table 3). Only ligand bands are present in the ES MS spectrum which was obtained after leaving the solution to stand for 6 days in  $\text{CH}_3\text{CN}$  solutions at room temperature, in the presence of air and focus voltage of 40 V, in the positive region (Table 3).

The bands at  $m/z = 154.8 \text{ Da e}^{-1}$  correspond to the free ligand ( $M_w = 154.12$ ), while the group of bands at  $m/z = 338.5 \text{ Da e}^{-1}$  is assigned to the species  $[\text{Ni}(\text{2,3-dhb})(\text{HO})_2(\text{OH}_2)_2]^+ \cdot (\text{OH}_2)_3$  (Fig. 1(d,c)).

Several species are produced by the decomposition of the ligand itself. Thus, a decrease of  $m/z$  by  $14 \text{ Da e}^{-1}$

units corresponds to a  $-\text{CH}_2-$  loss, by  $18 \text{ Da e}^{-1}$  to a  $-\text{OH}_2$  loss, by  $44 \text{ Da e}^{-1}$  units to a  $-\text{CO}_2$  loss and by  $16 \text{ Da e}^{-1}$  units to a  $-\text{O}$  loss (e.g. oxygen loss from muconic acid to produce the corresponding aldehyde, Fig. 1(c): bands from  $654.9$  to  $418.7 \text{ Da e}^{-1}$ ). In  $\text{CH}_3\text{CN}$  solution we obtain a fragment at  $m/z = 654.9$  which is  $[\text{NiL}_3(\text{CH}_3\text{CN})_3(\text{H}_2\text{O})]$ . From this, several other species occur with a  $m/z$  difference of  $44 \text{ Da e}^{-1}$ , indicating subsequent decarboxylation reactions ( $-\text{CO}_2$ ) including ring opening. Further degradation leads to species at  $434 \text{ Da e}^{-1}$  which may be an intermediate. Similar degradation is observed for the species with  $m/z = 506.9$  leading to species with  $m/z = 418.7$  (Fig. 1(c)).

The more stable species is  $[\text{NiL}(\text{OH})_2(\text{OH}_2)_2]^+ \cdot (\text{OH}_2)_3$  ( $m/z = 338.5 \text{ Da e}^{-1}$ ), with an Ni-to-ligand ratio of 1:1, which may involve formation of peroxo-groups as in the case of vanadium complexes [4] and ferric complexes in dioxygenases [39]. The fragment at  $m/z = 185.7$  is also important as it can be assigned to oxygenated ligand species ( $\text{L}-\text{O}_2$ ). The presence of a peak at  $m/z = 141.7$ , corresponding to hydrated catechol and the one at  $114.1 \text{ Da e}^{-1}$  is assigned to

Table 3

Electrospray mass spectrometric (ES MS) data for Ni-2,3-dhb complex in CH<sub>3</sub>CN, H<sub>2</sub>O

Focus voltage (V)	Skimmer voltage (V)	Ions observed ( $m/z$ , in Da $e^{-1}$ )	Time (h) <sup>a</sup>	Solvent
<i>Positive ion mode</i>				
10	15	[Ni <sub>7</sub> L <sub>7</sub> (OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>4</sub> (CH <sub>3</sub> CN) <sub>21</sub> ] <sup>2+</sup> (1209.5)	0.5	CH <sub>3</sub> CN
10	15	[Ni <sub>6</sub> L <sub>6</sub> (OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (CH <sub>3</sub> CN) <sub>7</sub> ] <sup>2+</sup> (818.9)	0.5	CH <sub>3</sub> CN
10	15	[Ni <sub>4</sub> L <sub>4</sub> (CH <sub>3</sub> CN) <sub>14</sub> ] <sup>2+</sup> (706.7) <sup>c</sup>	0.5	CH <sub>3</sub> CN
20	25	[Ni <sub>2</sub> L(CH <sub>3</sub> CN) <sub>3</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup> (428.8)	0.5	CH <sub>3</sub> CN
20	25	[NiL(OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup> (OH <sub>2</sub> ) <sub>3</sub> (338.5)	0.5	CH <sub>3</sub> CN
20	25	[Ni(CH <sub>3</sub> CN) <sub>3</sub> (OH)] <sup>+</sup> ·CH <sub>3</sub> CN (241.7)	0.5	CH <sub>3</sub> CN
20	25	[NiL(CH <sub>3</sub> CN) <sub>3</sub> (OH)] <sup>+</sup> (407.94)	0.5	CH <sub>3</sub> CN
20	25	OH-CH <sub>2</sub> -CH <sub>2</sub> -CH=CH-CH <sub>2</sub> CH <sub>2</sub> -OH (114.1)	0.5	CH <sub>3</sub> CN
40	45	[NiL <sub>3</sub> (CH <sub>3</sub> CN) <sub>3</sub> (H <sub>2</sub> O)] <sup>+</sup> (654.9)	0.5	CH <sub>3</sub> CN
40	45	[NiL(OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup> ·(OH <sub>2</sub> ) <sub>3</sub> (338.5)	0.5	CH <sub>3</sub> CN
40	45	[Ni(CH <sub>3</sub> CN) <sub>3</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>2+</sup> ·CH <sub>3</sub> CN (241.7) <sup>c</sup>	0.5, 48	CH <sub>3</sub> CN
40	45	[Ni <sub>2</sub> L(CH <sub>3</sub> CN) <sub>3</sub> (OH)] <sup>2+</sup> (203.4)	48	CH <sub>3</sub> CN
40	45	L (154.8) <sup>b</sup>	48	CH <sub>3</sub> CN
40	45	L <sub>2</sub> (309.6)	144	CH <sub>3</sub> CN
40	45	L <sup>+</sup> (154.07) <sup>c</sup>	144	CH <sub>3</sub> CN
10	15	[NiL(OH) <sub>2</sub> (OH <sub>2</sub> )] <sup>0</sup> (OH <sub>2</sub> ) (278.5)	0.5	H <sub>2</sub> O
10	15	HOOC-CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -CH(OH)-COOH (177.7)	0.5	H <sub>2</sub> O
10	15	HOOC-CH <sub>2</sub> -CH(OH)-CH <sub>2</sub> -CH <sub>2</sub> -COOH (157.7)	0.5	H <sub>2</sub> O
10	15	HOOC-CH=CH-CH=CH-COOH (140.6)	0.5	H <sub>2</sub> O
<i>Negative ion mode</i>				
20	25	[NiL(OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>-</sup> (OH <sub>2</sub> ) <sub>3</sub> (338.7)	0.5	CH <sub>3</sub> CN
20	25	L <sup>-</sup> (152.7) <sup>c</sup>	0.5	CH <sub>3</sub> CN
30	35	[NiL(OH) <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> ] <sup>-</sup> (OH <sub>2</sub> ) <sub>3</sub> (338.7)	0.5	CH <sub>3</sub> CN
30	35	[Ni <sub>4</sub> L <sub>2</sub> (OH) <sub>6</sub> (CH <sub>3</sub> CN)] <sup>4-</sup> (170.9)	0.5	CH <sub>3</sub> CN
30	35	L <sup>-</sup> (152.7) <sup>c</sup>	0.5	CH <sub>3</sub> CN, H <sub>2</sub> O
40	45	[Ni <sub>4</sub> L <sub>2</sub> (OH) <sub>6</sub> (CH <sub>3</sub> CN)] <sup>4-</sup> (170.9) <sup>c</sup>	0.5	CH <sub>3</sub> CN
10	15	O=HC-CH <sub>2</sub> -CH=CH-CH <sub>2</sub> -COO <sup>-</sup> (126.7)	0.5	H <sub>2</sub> O

<sup>a</sup> Refers to the time the solution was kept in the presence of air at room temperature before the measurement.<sup>b</sup> L = 2,3-dhb.<sup>c</sup> Other more species, due to decomposition, were observed with lower  $m/z$  ratios.

muconic alcohol, being the product of reduction of muconic acid (Fig. 1(c,d)).

The spectrum in water (Fig. 1(e)) also indicate the presence of a monomeric neutral Ni(II) complex with  $m/z = 278.5$  Da  $e^{-1}$ , namely [NiL(OH)<sub>2</sub>(OH<sub>2</sub>)]<sup>0</sup>·(OH<sub>2</sub>), with the ligand being in its quinone form. The band present at  $m/z = 177.7$  Da  $e^{-1}$  corresponds to doubly hydrated muconic acid, the one at  $m/z = 157.7$  Da  $e^{-1}$  to the monohydrated muconic acid and the one at  $m/z = 140.6$  is assigned to muconic acid.

### 3.2.2. Anionic mode of ES MS

For the anionic species spectra in acetonitrile (Fig. 2) several species were again observed. Among them, the one with maximum  $m/z$  ratio is [Ni<sub>4</sub>L<sub>2</sub>(OH)<sub>6</sub>(CH<sub>3</sub>CN)]<sup>4-</sup> ( $m/z = 170.5$  Da  $e^{-1}$ ) and the monomeric species like [NiL(OH)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]<sup>-</sup>(OH<sub>2</sub>)<sub>3</sub> ( $m/z = 338.7$  Da  $e^{-1}$ ) are observed. More peaks are present, in accordance with ligand decomposition. Initially, one hydroxyl-group is lost from the free ligand ( $m/z = 152.7$  Da  $e^{-1}$ ) giving fragments at  $m/z = 136.4$

Da  $e^{-1}$  followed by subsequent loss of one-by-one of the methylenic groups of the aromatic ring. The anionic fraction, in acetonitrile, at  $m/z = 126.6$  Da  $e^{-1}$  corresponds to the muconic acid aldehyde monoanion, while the one with  $m/z = 108.9$  Da  $e^{-1}$  corresponds to the decarboxylated ligand (viz. to *o*-catechol).

It should be noted that aliphatic organic species with  $m/z$  lower than 100 observed in the <sup>1</sup>H NMR spectra of the complex in water and assigned to degradation products of 2,3-dihydroxybenzoic acid, like pyruvic acid (CH<sub>3</sub>COCOOH) and malonic acid (HOOC-CH<sub>2</sub>-COOH) as well as several other products detected in the 2-D experiments, cannot be detected at the ES MS in this region ( $m/z < 100$  Da  $e^{-1}$ ) because several solvent peaks interfere resulting in very complicated spectra with several overlapping bands. The only species produced by the ligand degradation which is observable by both techniques is muconic acid (Scheme 3). Based on the above data, the following complex degradation scheme may be proposed (Scheme 3).

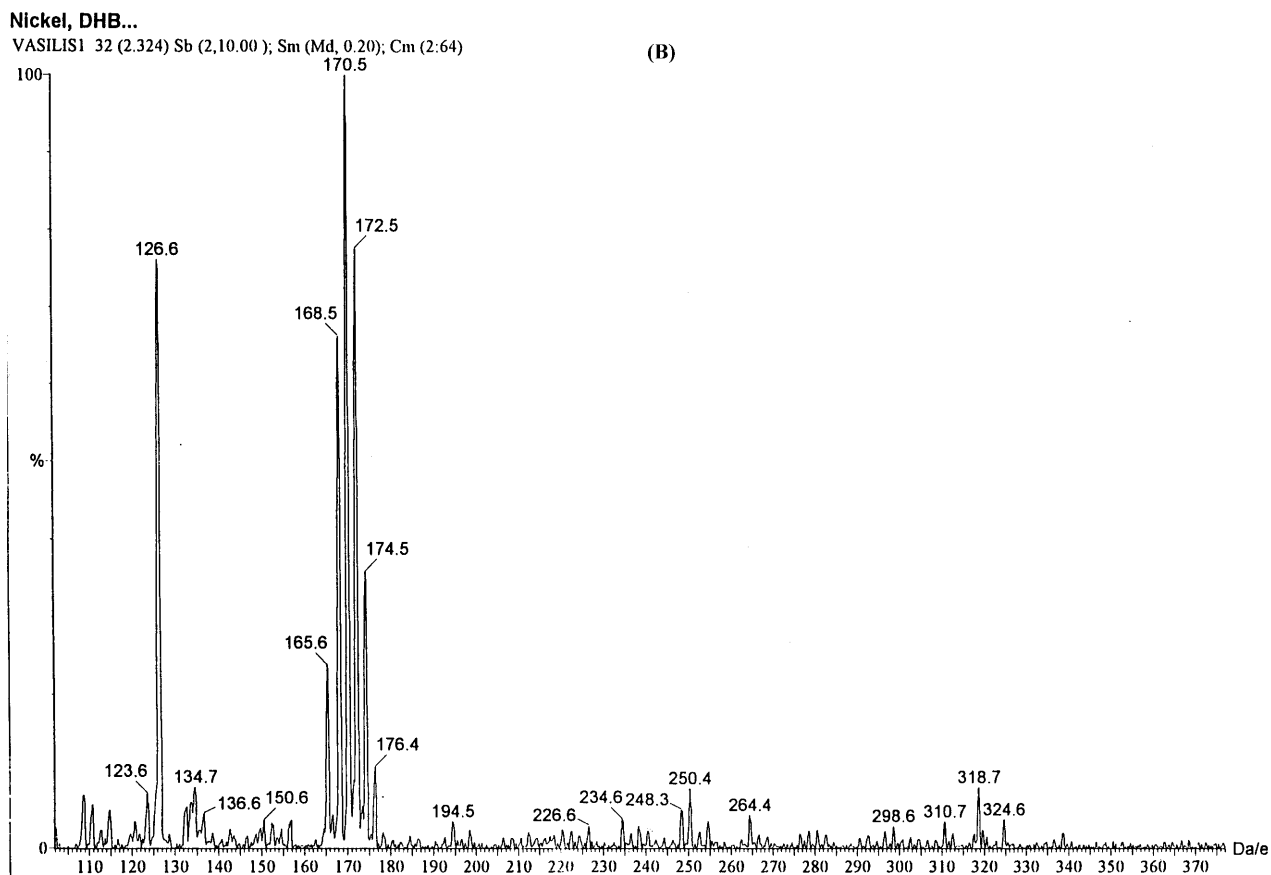
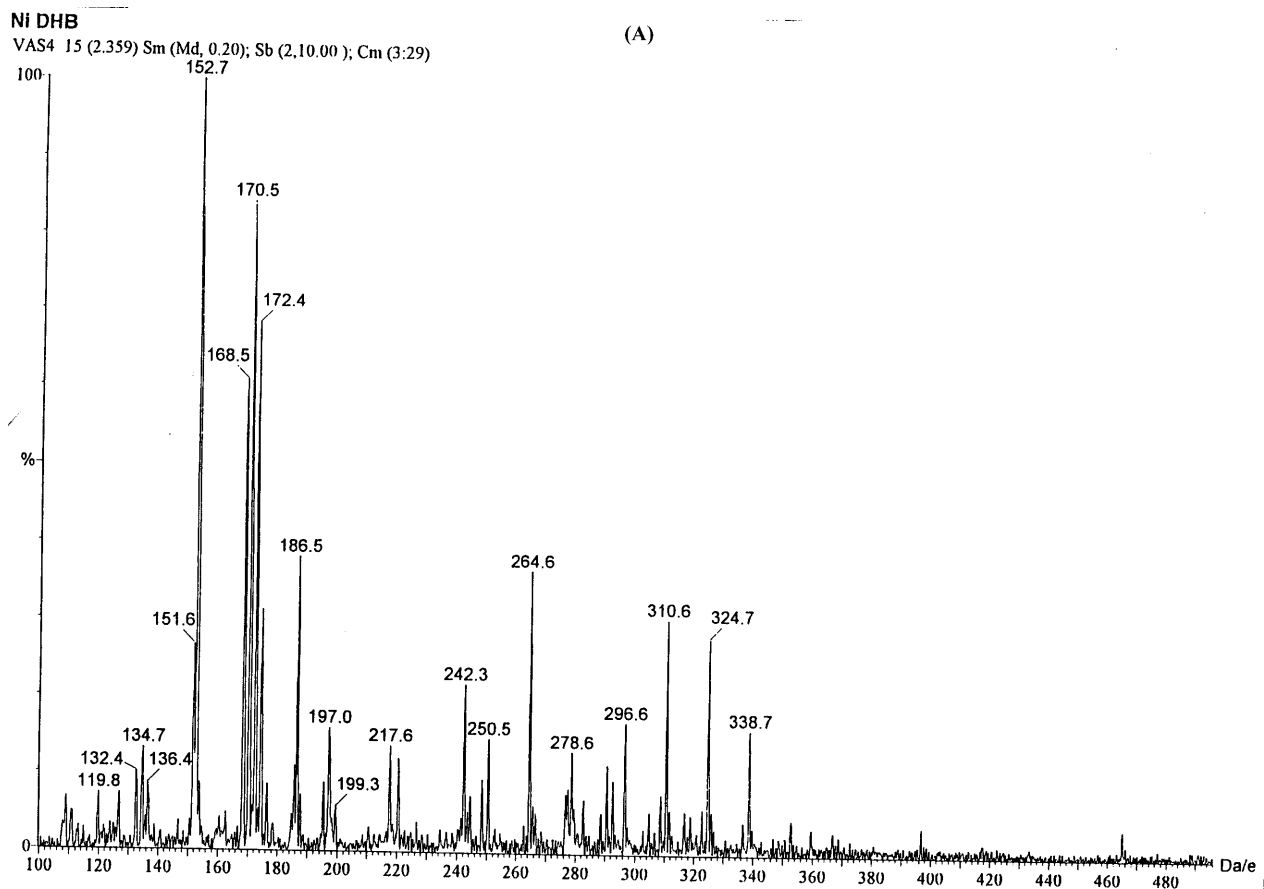


Fig. 2. The anionic species produced in the ES MS, in  $\text{CH}_3\text{CN}$ . (A) Fresh solution, focus: 20 V; (B) fresh solution, focus: 40 V; (C) solution remained 6 days in the presence of air, focus: 40 V.



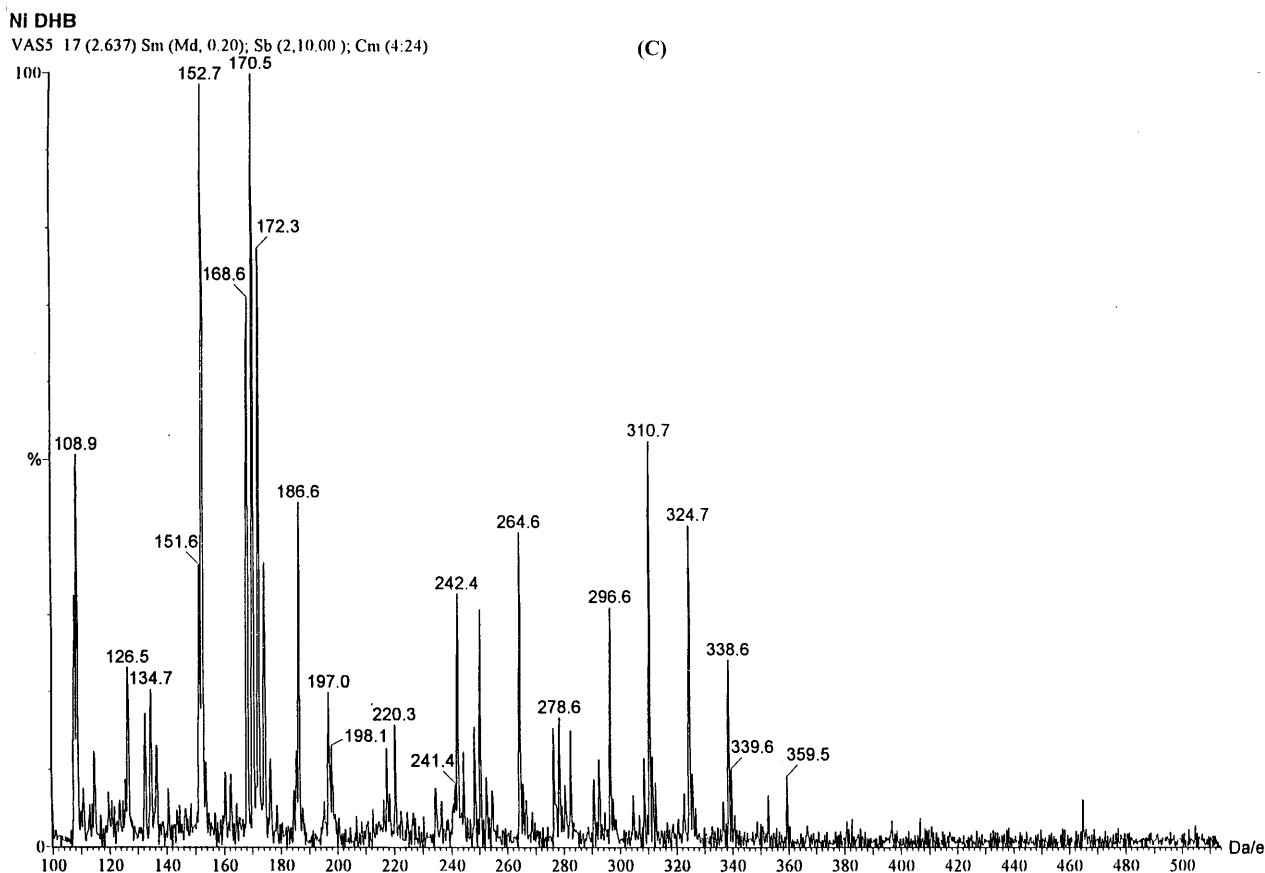


Fig. 2. (Continued)

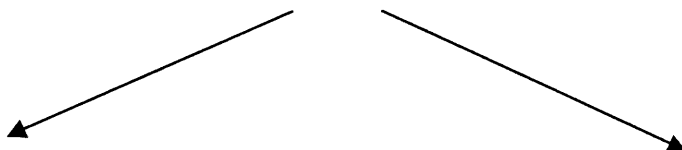
A similar degradation mechanism has been proposed for the reaction of vanadium with 3,4-dihydroxyphenyl-ethanoic acid in alcoholic solution [39]. Several degradation species were also detected in the ES MS in the case of polymeric Mo-complexes with 3,4-dihydroxybenzoic acid [5]. It should be noted that degradation reactions are also known to take place between several metal ions and dihydroxybenzoates and related ligands [40–46] that are quite similar (leading to the same products) to several biodegradation reactions that are carried out in nature by microorganisms<sup>1</sup>.

#### 4. Conclusions

From the above results it is concluded that when Ni(II) reacts with 2,3-dihydroxybenzoic acid an

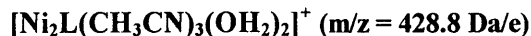
oligomeric complex is formed corresponding to the formula  $\{[\text{Ni}_5\text{L}_5(\text{OH})_7]\text{K}_4 \cdot 13\text{H}_2\text{O}\}_n$ , possibly containing three quinone and two semiquinone ligands with salicylate and/or catecholate coordination modes, bridging the Ni atoms. This complex is diamagnetic because of the intramolecular interaction of the two semiquinone radicals of the anion, leading to their electron spin coupling, exhibiting no total paramagnetism at room temperature [15] (temperature of recording NMR spectra). It should be noted that even monomeric semiquinone complexes with tetrahedral Ni are diamagnetic [46]. The aqueous solution study of this complex with the aid of NMR and ESMS provides evidence for a polymeric complex formation. Finally the proposed degradation mechanism aims to contribute to the research on the mechanism of oxidative degradation of catecholic derivatives catalyzed by Ni(II) as well as to the research on degradation and bio-degradation of phenolic derivatives through decarboxylation and peroxo complex formation, leading to acetic and formic acids as final products.

<sup>1</sup> For extended information see 'University of Minnesota Biocatalysis/Biodegradation Database', at <http://www.labmed.umn.edu/umbdd/aboutBBD.html>.



Year	Value	Count
1630	30.23	10
1631	20.29	5
1632	78.59	10
1633	52.87	10
1634	100.00	10
1635	65.34	10
1636	84.59	10
1637	52.68	10
1638	53.91	10
1639	31.87	10
1640	27.60	10
1641	15.51	10
1642	11.78	10
1643	6.30	10
1644	4.29	10
1645	2.18	10
1646	1.35	10
1647	0.66	10
1648	0.37	10

2414	18.41	*****
2415	55.71	*****
2416	56.82	*****
2417	92.33	*****
2418	84.80	*****
2419	100.00	*****
2420	83.08	*****
2421	80.09	*****
2422	60.87	*****
2423	50.85	*****
2424	35.76	*****
2425	26.73	*****
2426	17.54	*****
2427	11.97	*****
2428	7.37	****
2429	4.65	***
2430	2.70	**
2431	1.58	*
2432	0.87	*

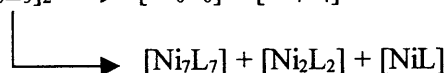


Year	Value	Significance
1412	55.10	
1413	38.19	
1414	100.00	
1415	67.06	
1416	87.79	
1417	54.59	
1418	51.47	
1419	29.40	
1420	22.83	
1421	12.16	
1422	8.09	
1423	4.03	*
1424	2.35	*
1425	1.09	*

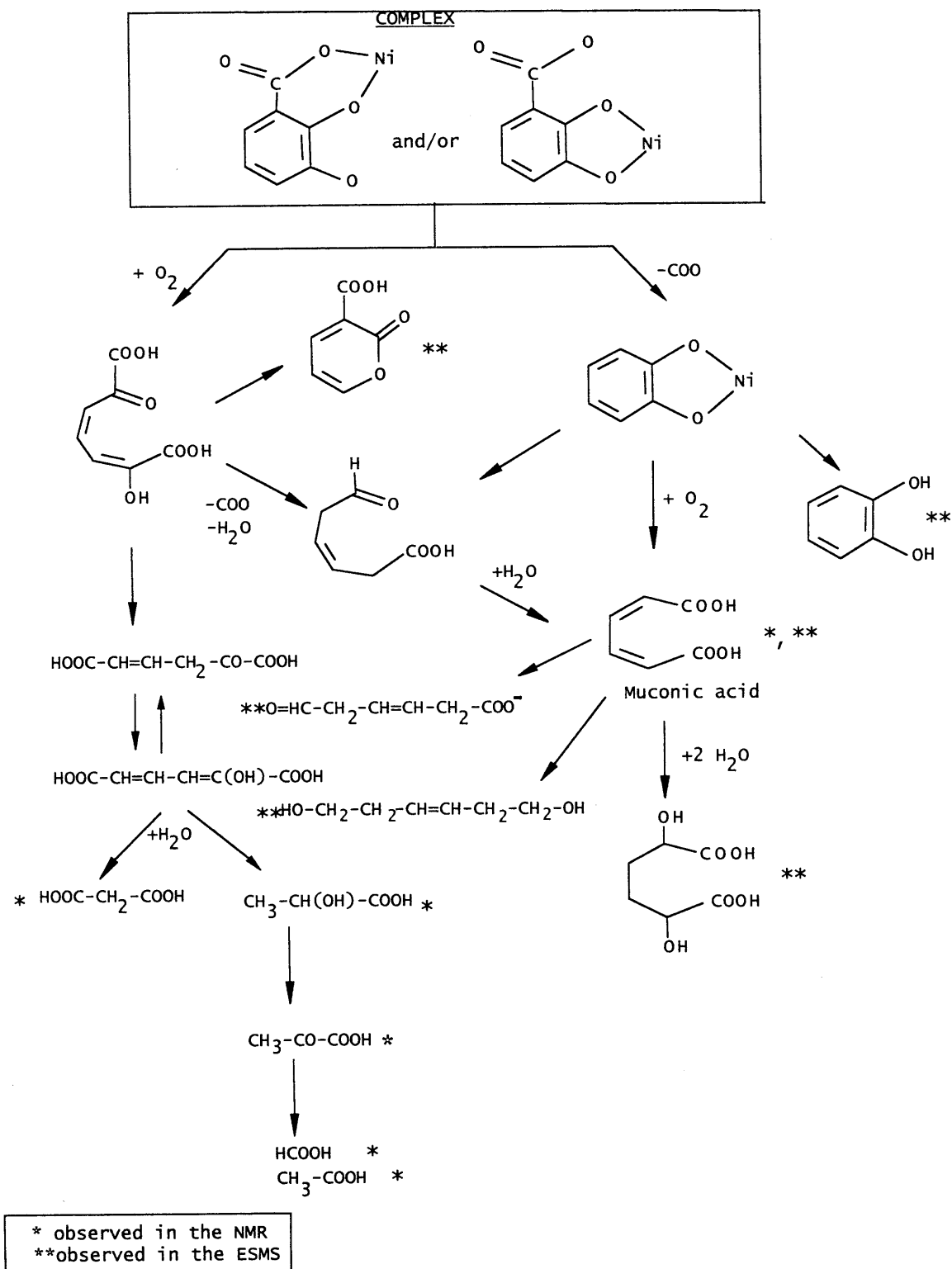
428	100.00	.....
429	16.16	.....
430	79.73	.....
431	16.25	.....
432	28.20	.....
433	5.79	***
434	8.26	.....
435	1.48	*
436	1.74	*
437	0.33	



Iteration	Value	Plot
338	100.00	.....
339	8.55	.....
340	41.21	.....
341	5.26	.....
342	6.57	.....
343	0.58	.....
344	1.75	.....
345	0.15	.....

$$[\text{Ni}_5\text{L}_5]_2 \longrightarrow [\text{Ni}_6\text{L}_6] + [\text{Ni}_4\text{L}_4]$$


Scheme 2. Degradation of the complex in H<sub>2</sub>O. Molecular weights of all the species formed are given in parentheses. All species are observed in the ES MS.



Scheme 3. Proposed degradation scheme for the complex.

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