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New mixed ligand saccharin complexes with o-phenylenediamine Schiff base and antioxidant investigations

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In this study, four new mixed-ligand saccharin complexes with 2-[[(2-Aminophenyl)imino]methyl]-6-methoxy phenol Schiff base and metal saccharinates (nickel, copper, zinc and cadmium) have been prepared and characterized with various methods including elemental analysis, FT-IR spectroscopy, UV-visible absorption spectroscopy, NMR spectroscopy, QTOF-LC/MS spectroscopy. All methods have confirmed the inclusion of the Schiff base obtained by condensation of o-phenylendiamine and o-vanillin into the metal saccharinates. Besides, DPPH scavenging activities and metal chelating abilities of all complexes have been determined and compared to well-known antioxidant standards (Butylated hydroxyanisole, Butylated hydroxytoluene and α-Tocopherol) along with starting metal saccharinates. According to the results, nickel complex has exhibited the best DPPH scavenging activity, while copper complex has the highest ferrous ion chelating ability.

Keywords: Schiff base, Mixed-ligand saccharin complexes, Antioxidant assays, o-phenylenediamine

Schiff bases, reported first time in 1864 by Hugo Schiff, are a compound group having wide using areas varying from polymer, dye, pharmaceutical and food industry to agrochemical and sensor applications[1-13]. In addition to easy synthesis, the structural stability and versatility induced gaining wide prevalence of imine compounds. Among its various features, bioactivity of Schiff bases especially comes to the forefront in consequence of interactions and hydrogen bonds between the azomethine group and certain sites in the cell structure. Also, electrons in sp^2 hybrid orbitals of azomethine nitrogen play a crucial role for chelating ability in addition to biological applications[14]. Especially, the presence of donor atoms such as oxygen, nitrogen and sulfur which are close to the azomethine group gives the Schiff base excellent chelating ability[15].

Sometimes, various ligands are used to ease the coordination of Schiff bases to metal ions and these type of coordination compounds are named as mixed-ligand complexes. Metal saccharinates can be used along with Schiff bases for this purpose. Although saccharin has been extensively used as an artificial sweetener since 1885, it was accused of being carcinogenic and banned for use in the 1970s[16]. After saccharin was acquitted of assertion of being carcinogenic, it began to attract much attention of coordination chemists. The underlying reason of this interest is that saccharine possesses three potential donor centers: two sulfonyl oxygens, one carbonyl oxygen and an imino nitrogen. Thanks to these donor centers, saccharine can act as a mono- or bidentate ligand[17,18].

Aqua ligands within metal saccharinates having $[M(Sac)_2(H_2O)_4]$ general formula can easily interchange with various ligand moieties. For this reason, there is a lot of work in the literature about mixed-ligand metal saccharin complexes with organic ligands, on the other hand Schiff bases have not been included in such structures, frequently. In the studies including Schiff base ligands, thiocarbazide derivative ligands coordinating by NNS or NOS donor atoms to metal saccharinates were used, mainly[19-24]. In addition to structural characterizations in these studies, antibacterial and cytotoxicity studies were generally performed. Apart from these thiocarbazide ligands, different Schiff bases have also been involved in the structure of mixed-ligand saccharin complexes on occasion[25-28].

In this study, four new mixed ligand metal saccharin complexes were prepared by using metal saccharinates (nickel, copper, zinc and cadmium) and 2-[[(2-Aminophenyl)imino]methyl]-6-methoxyphenol Schiff base (Fig. 1). Obtained compounds were characterized by elemental analysis, FT-IR spectroscopy, UV-visible absorption spectroscopy,

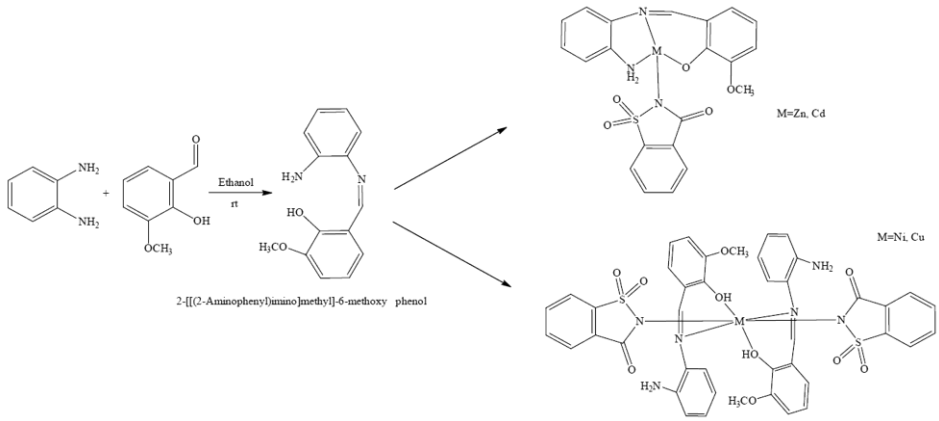


Fig. 1 — Reaction scheme and proposed structures for the complexes

^{1}H- and ^{13}C-NMR spectroscopy, QTOF-LC/MS. Besides, antioxidant properties of new compounds were determined by 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging activity and metal chelating ability assays. Antioxidant capacities of the complexes were determined and compared to the standard antioxidants (Butylated hydroxyanisole (BHA), Butylated hydroxytoluene (BHT) and α-Tocopherol) in antioxidant tests.

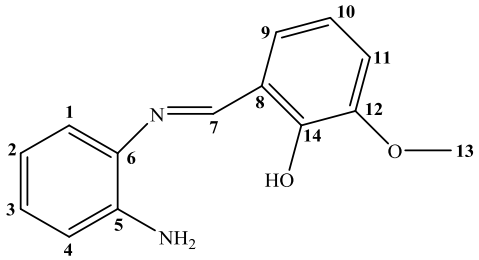
Materials and Methods

Sodium saccharinate, copper(II) acetate dihydrate, nickel(II) acetate tetrahydrate, zinc(II) acetate dihydrate, cadmium(II) acetate dihydrate, o-phenylenediamine, o-vanillin, p-toluenesulfonic acid and ethanol were purchased from commercial sources and used without further purification. FT-IR spectra were recorded on a Jasco FT-IR 4700 spectrometer in the range of 400-4000 cm^{-1}. The UV-visible absorption spectra of the complexes in dimethyl sulfoxide (DMSO) solvent (10^{-3} M) were measured on a Perkin-Elmer Lambda-35 UV-Vis spectrophotometer between 200-800 nm wavelength range. C, H, N analyses were recorded on a Elementar Vario Micro Cube elemental analyzer. ^{1}H- and ^{13}C-NMR spectra of the Schiff base was measured using AC Bruker 400 MHz NMR spectrometer in $CDCl_3$ and DMSO-d_6 at ambient temperature. Mass spectra were obtained by using Agilent 6530 Accurate-Mass QTOF-LC/MS spectrometer.

Synthetic Procedures

2-[[(2-Aminophenyl)imino]methyl]-6-methoxy phenol

To the ethanolic solution (30 mL) of o-phenylendiamine (1 g, 9.25 mmol), o-vanillin (1 eq, 1.4 g) in 20 mL ethanol was added dropwise in the presence of p-toluenesulfonic acid monohydrate as catalyst at room temperature. When o-vanillin was added, the colorless solution started to turn into orange and an intense precipitate was formed. After the reaction mixture was stirred for a couple of hours, the orange precipitate was filtered and washed with ethanol. The chemical structure of the compound is given below.



M. p. 127 °C, Anal. Calc. for $C_{14}H_{14}N_2O_2$(%): C, 69.41; H, 5.82; N, 11.56 Found (%): C, 69.50; H, 5.70; N, 11.63. IR (cm^{-1}): 3462 (O-H), 3362 (N-H), 3058, 3011 (C-H arom.), 1596 (C=N), 1249 (C-O). ^{1}H NMR ($CDCl_3$, ppm): 12.98 (s, 1H, -OH), 8.85 (s, 1H, -CH=N-), 7.28-6.64 (m, 7H, -CH aromatic), 5.06 (s, 2H, -NH_2), 3.84 (s, 3H, -OCH_3). ^{13}C NMR ($CDCl_3$, ppm): 161.84(C_7), 150.94 (C_{14}), 148.41 (C_{12}), 140.96 (C_5), 134.79 (C_6), 128.31 (C_3), 123.72 (C_1), 119.49 (C_9), 118.79 (C_2), 118.78 (C_8), 118.25 (C_4), 115.91 (C_{10}), 114.69 (C_{11}), 56.20 (C_{13}).

Mixed Ligand Saccharin Complexes [M(Sac)$_2$(NNO)$_2$] (M=Ni(1) and Cu(2)) and [M(Sac)(NNO)] (M=Zn(3) and Cd(4))

First, metal saccharinates with the general formula of $[M(Sac)_2(H_2O)_4].2H_2O$ (M= Ni(**1**), Cu(**2**), Zn(**3**), Cd(**4**)) were synthesized according to the literature[29,30]. Mixed ligand saccharin complexes were prepared by treatment of the Schiff base with metal saccharinates. For this aim, ethanolic solution of the Schiff base was added by stirring to the metal saccharinate solved in hot water. After a couple of

hours mixing and heating, precipitation carried out. The precipitate was filtered, washed with ethanol and dried in air.

$[Ni(Sac)_2(NNO)_2]$ (1) M. p. 225 °C (decomp.), Anal. Calc. for $C_{42}H_{36}N_6NiO_{10}S_2$(%): C, 55.58; H, 4.00; N, 9.26 Found (%): C, 55.72; H, 3.90; N, 9.42. IR (cm^{-1}): 3336 (O-H), 3455, 3406 (N-H), 3057 (C-H arom.), 1609 (C=O), 1580 (C=N), 1245 (S=O asym), 1143 (S=O sym).

$[Cu(Sac)_2(NNO)_2]$ (2) M. p. 290 °C (decomp.), Anal. Calc. for $C_{42}H_{36}N_6CuO_{10}S_2$(%): C, 55.29; H, 3.98; N, 9.21 Found (%): C, 55.41; H, 4.12; N, 9.50. IR (cm^{-1}): 3253 (O-H), 3465 (N-H), 3070, 3019 (C-H arom.), 1605 (C=O), 1582 (C=N), 1248 (S=O asym), 1152 (S=O sym).

[Zn(Sac)(NNO)] (3) M. p. 347 °C (decomp.), Anal. Calc. for $C_{21}H_{17}N_3O_5SZn$(%): C, 51.60; H, 3.51; N, 8.60 Found (%): C, 51.48; H, 3.75; N, 8.91. IR (cm^{-1}): 3334 (N-H), 3094, 3063, 3036 (C-H arom.), 1606 (C=O), 1582 (C=N), 1238 (S=O asym), 1136 (S=O sym). ^{1}H NMR (DMSO-d_6, ppm): 9.02 (s, 1H, -CH=N-), 7.90 (m, 2H, $H_{Schiff\ base}$), 7.68 (m, 4H, $H_{Saccharine}$), 7.39 (m, 2H, $H_{Schiff\ base}$), 7.06 (d, 1H, $H_{Schiff\ base}$), 6.88 (d, 1H, $H_{Schiff\ base}$), 6.48 (t, 2H, $H_{Schiff\ base}$), 3.76 (s, 3H, -OCH_3). ^{13}C NMR (DMSO-d_6, ppm): 168.01 (C=O), 163.36 (C=N), 152.63 (C_{arom}-OCH_3), 145.04 (C_{arom}-O^-), 139.78 (C_{arom}-NH_2), 134.06 (C_{arom}-SO_2), 132.56 (C_{arom}-CN), 132.24, 127.91, 127.80, 123.34, 119.90, 119.23, 116.94, 114.41, 112.81, 55.74 (O-CH_3).

[Cd(Sac)(NNO)] (4) M. p 283 °C (decomp.), Anal. Calc. for $C_{21}H_{17}CdN_3O_5S$(%): C, 47.07; H, 3.20; N, 7.84 Found (%): C, 47.21; H, 3.38; N, 8.00. IR (cm^{-1}): 3325 (N-H), 3059, 3012 (C-H arom.), 1620 (C=O), 1581 (C=N), 1278 (S=O asym), 1143 (S=O sym). ^{1}H NMR (DMSO-d_6, ppm): 8.70 (s, 1H, -CH=N-), 7.63 (m, 4H, $H_{Saccharine}$), 7.25 (m, 7H, $H_{Schiff\ base}$), 5.30 (s, 2H, -NH_2), 3.91 (s, 3H, -OCH_3). ^{13}C NMR (DMSO-d_6, ppm): 168.41 (C=O), 166.03 (C=N), 145.64 (C_{arom}-OCH_3), 136.92 (C_{arom}-O^-), 135.10 (C_{arom}-NH_2), 132.12 (C_{arom}-SO_2), 131.58 (C_{arom}-CN), 128.74, 126.86, 125.26, 124.44, 123.02, 120.56, 119.62, 119.22, 114.00, 56.99 (O-CH_3).

Antioxidant Activity Studies

DPPH scavenging activity studies

DPPH scavenging activities of the prepared complexes were determined by the Blois' method with slight modifications[31]. For this aim, 1 mL of 0.1 mM DPPH in methanol was added to methanolic solutions of samples at different concentrations ranging from 5 to 80 ppm and then shaken strongly. After incubation in the dark for 30 min, the absorbance of the solutions was measured at 517 nm (A_{sample}). BHA, BHT and α-tocopherol used as positive controls were exposed to the same procedure ($A_{control}$). The inhibition activities were calculated by the following equation (Eqn. 1):

$$\% \text{ Inhibition} = \left(1 - A_{sample}/A_{control}\right) \times 100 \quad \ldots (1)$$

Ferrous ion chelating activity studies

The chelating abilities of the complexes towards ferrous ion were measured by using the method as given by Dinis et al.[32]. 200 µL ferrozine was added to the methanolic samples with the varying concentrations from 5 to 15 ppm in pursuit of the addition of 50 µL $FeCl_2$. Then, the mixtures were shaken strongly. After incubation in the dark for 30 min, the absorbance of the solutions was measured at 562 nm. BHA, BHT and α-tocopherol used as positive controls were exposed to the same procedure. The inhibition activities were calculated by using Eqn. 1.

Result and Discussions

Four new mixed ligand saccharin complexes were synthesized by interchanging aqua ligands in metal saccharinates with an o-vanillin Schiff base. The Schiff base and the complexes were air and moisture stable at ambient conditions. While the Schiff base was soluble in common alcohols like ethanol, methanol, etc., all of the obtained complexes had low solubility in methanol and ethanol but good solubility in DMSO. The possible structural formulas were proposed for the complexes in compliance with elemental analysis, FT-IR, NMR (^{1}H- and ^{13}C-), UV-visible absorption and QTOF-LC/MS spectral data.

FT-IR and UV-visible absorption studies

The FT-IR spectra of **4** and its starting materials (the Schiff base and cadmium saccharinate) were depicted in Fig. 2. Besides, the characteristic FT-IR

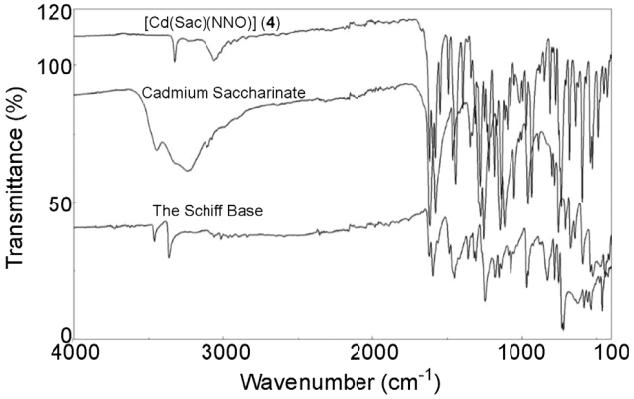


Fig. 2 — FT-IR spectra of complex **4** along with its starting materials

Table 1 — The characteristic bands observed in the Schiff base, metal saccharinates and mixed ligand complexes

Compound	FT-IR bands, ν (cm^{-1})					
	νOH	νNH	νC=N	νC=O	$\nu_{as}SO_2$	$\nu_{s}SO_2$
The Schiff base	3462	3362	1596	-	-	-
Nickel saccharinate	3700-3200	-	-	1616	1258	1149
$[Ni(Sac)_2(NNO)_2]$ (**1**)	3336	3455, 3406	1580	1609	1245	1143
Copper saccharinate	3700-3300	-	-	1612	1299	1160
$[Cu(Sac)_2(NNO)_2]$ (**2**)	3253	3465	1582	1605	1248	1152
Zinc saccharinate	3700-3200	-	-	1616	1258	1149
[Zn(Sac)(NNO)] (**3**)	-	3334	1582	1606	1238	1136
Cadmium saccharinate	3600-3100	-	-	1616	1280	1149
[Cd(Sac)(NNO)] (**4**)	-	3325	1581	1620	1278	1143

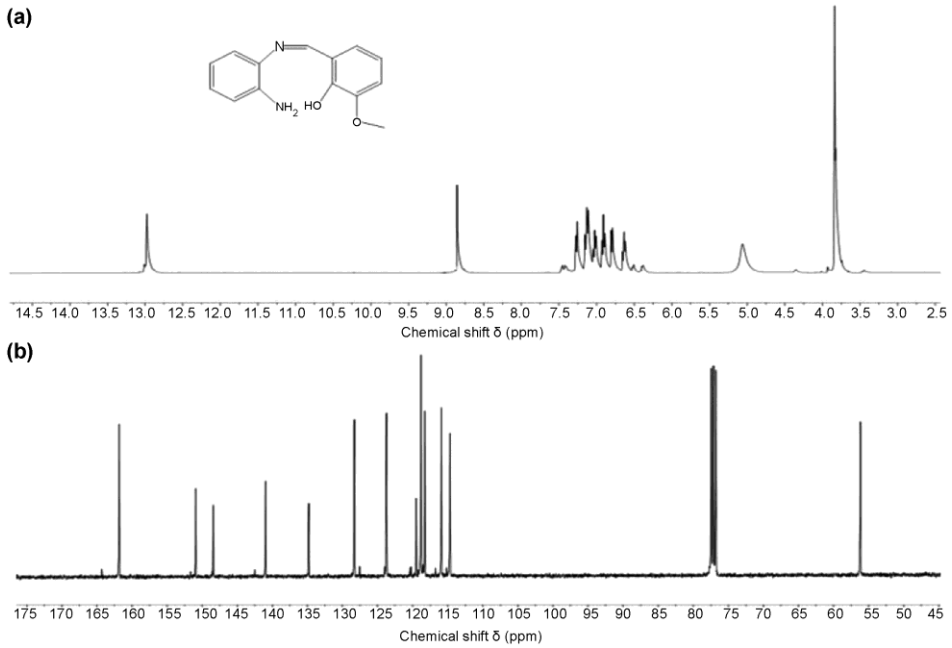


Fig. 3 — (a) ^{1}H- and (b) ^{13}C-NMR spectra of Schiff base

bands of all synthesized complex structures and their starting compounds were summarized in Table 1. The characteristic peaks belonging to metal saccharinates and the Schiff base were also observed in similar frequencies in the spectra of mixed ligand complexes except for two absorption bands. First, broad and strong bands over 3000 cm^{-1} originating from aqua ligands in metal saccharinates disappeared in the spectra of mixed ligand complexes because of interchanging the Schiff base with aqua ligands. The other band disappearing upon coordination was the O-H stretching vibration of the Schiff base at 3462 cm^{-1} indicating deprotonation of these hydroxyl groups for **3** and **4**. Other characteristic vibration bands were appeared with shifts in their positions (Table 1). νC=N stretches of the mixed ligand complexes shifted to lower wave numbers in keeping with the literature[22]. In addition to the existence of the characteristic FT-IR peaks of the Schiff base, $\nu_{as}SO_2$, $\nu_{s}SO_2$ and νC=O bands proved saccharin ligand existence within mixed ligand complexes.

In the UV-visible absorption spectra of **1** and **2** measured in DMSO, two different type transitions were observed: one of them n-π and π-π* intraligand transitions (268 and 300 nm for **1**; 260 and 323 nm for **2**) and the other one d-d transitions (378 and 490 nm for **1**; 439 nm for **2**). When it comes to the other two complexes, two UV bands were observed assigned as intraligand transitions (π-π* 259 and n-π 309 nm for **3**; π-π* 259 and n-π 303 nm for **4**). Besides, charge transfer bands appeared at 417 nm for both complex structures.

^{1}H- and ^{13}C-NMR spectral studies

2-[[(2-Aminophenyl)imino]methyl]-6-methoxy phenol

NMR spectra of the Schiff base was recorded in $CDCl_3$ and shown in Fig. 3. While methoxy group

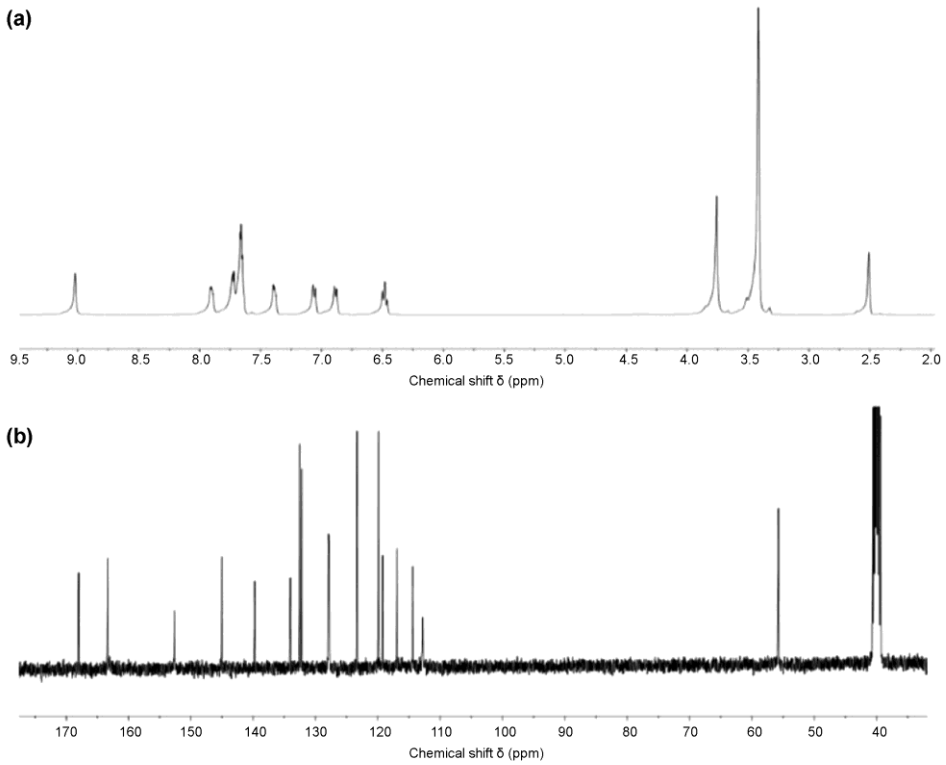


Fig. 4 — (a) ^{1}H- and (b) ^{13}C-NMR spectra of complex **3**

protons were observed at 3.84 ppm, the singlets at 5.06 and 12.98 ppm were attributable to protons of NH_2 and OH donor groups, respectively. Aromatic ring protons were appeared in the range of 7.28-6.64 ppm as expected. Besides, the singlet at 8.85 ppm was assigned to the azomethine proton. When it comes to the ^{13}C-NMR spectra, the resonance appeared as the most downfield peak belonged to the azomethine carbon. In addition, the peak at 56.20 ppm resulted from methoxy carbons. The other resonances in the spectrum apart from aromatic carbons attached to hydroxy, methoxy and amino groups (150.94, 148.40 and 140.96, respectively) were the ones expected for remaining aromatic carbons.

[Zn(Sac)(NNO)] (3)

The NMR spectra of the zinc complex recorded in d-DMSO were depicted in Fig. 4. The singlet peaks at 9.02 and 3.76 ppm were determined to belong to the azomethine and methoxy protons, respectively. Aromatic ring protons of the Schiff base and saccharin were observed in the range of 6.45 and 7.90 ppm. The multiplet between 7.64 and 7.74 ppm characterized as saccharin ring protons. The aromatic protons of the Schiff base appeared as doublets and triplets.

[Cd(Sac)(NNO)] (4)

The NMR spectra measured in DMSO as shown in Fig. 5 belongs to the mixed ligand cadmium saccharin complex **4**. The singlet peaks observed at 8.70 and 3.91 ppm were identified as the azomethine and methoxy protons, respectively. As distinct from complex **3**, the singlet at 5.30 ppm can be attributed to the amino group attached to the phenyl ring in the Schiff base. Aromatic ring protons of the Schiff base and saccharin were observed in the range of 7.12 and 7.67 ppm as overlapped.

Mass spectral studies

QTOF-LC/MS spectra of all complexes were consistent with proposed formulas. In the mass spectra of **1** and **2**, similar peaks (433 for Ni complex **1** and 438 for Cu complex **2**) corresponding to [M(NNO)(Sac)-OH-OCH_3] were observed with high intensities. The molecular peaks at 890 for **1** and 897 (M+2) for **2** were found in the spectra of mixed ligand saccharin complexes (Fig. 6a). The peak at 243 in the mass spectra of **3** and **4** can be assigned as deprotonate Schiff base ligand (M+2). While the mass spectra of **3** exhibited molecule ion peak at 488, the molecule ion peak was observed at 507 (M+2) subsequent to cleavage of OCH_3 fragment in the mass spectra of **4** (Fig. 6b).

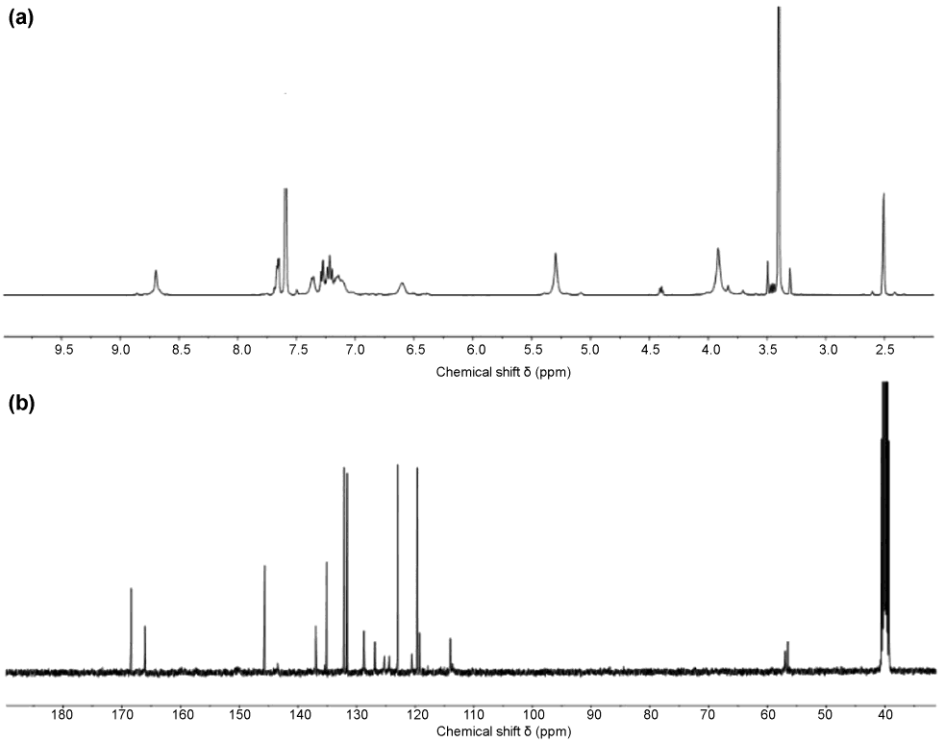


Fig. 5 — (a) ^{1}H- and (b) ^{13}C-NMR spectra of complex **4**

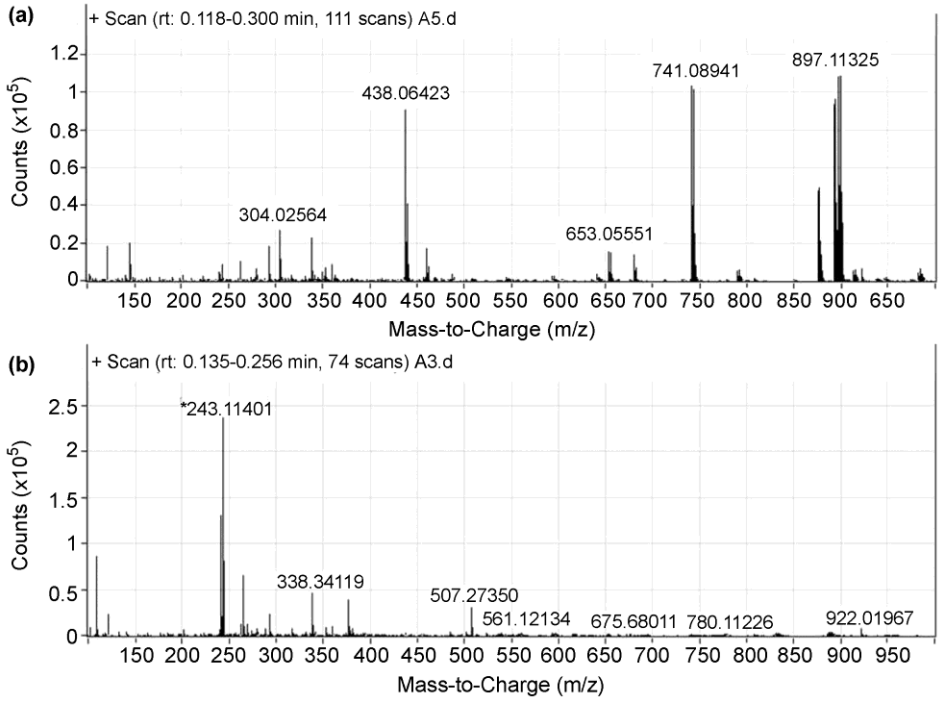


Fig. 6 — QTOF-LC/MS spectrum of complex (a) **2** and (b) **4**

Antioxidant activity studies

Antioxidant activities of the synthesized complexes were expressed by the IC50 value which is the concentration that can scavenge 50% of free radicals. Calculated IC50 values of the compounds were compared with well-known positive controls BHA, BHT and α-Tocopherol. IC50 values of the complexes and positive controls were tabulated in

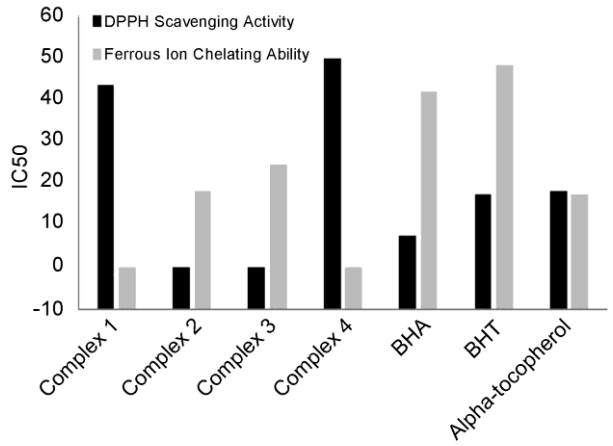


Fig. 7 — DPPH scavenging and ferrous ion chelating abilities of the synthesized compounds and positive controls

Table 2 — IC50 values of the test compounds for DPPH scavenging and ferrous ion chelating assays

Test compound	IC50	
	DPPH scavenging	Ferrous ion chelating
Complex 1	43, 50	not determined
Complex 2	not determined	18, 09
Complex 3	not determined	24, 31
Complex 4	49, 61	not determined
BHA	7, 46	41, 73
BHT	17, 32	48, 01
Alpha-tocopherol	17, 95	17, 28

Fig. 7. While copper (**2**) and zinc (**3**) complexes did not scavenge any DPPH free radicals, nickel (**1**) and cadmium (**4**) complexes did not exhibit the ferrous ion chelating ability. On the other hand, remaining two complexes showed a great chelating ability towards ferrous ions even greater than BHA and BHT (IC50 values 18.09 for **2** and 24.31 for **3**) (Table 2). However, parent metal saccharinates may be responsible for this important metal chelating activity (IC50 values 10.99 for copper saccharinate and 12.61 for zinc saccharinate). When it comes to DPPH scavenging activities, good antioxidant capacities were observed for the mixed ligand complexes in comparison with starting metal saccharinates which did not exhibit any activities to scavenge DPPH (IC50 values 43.50 for **1** and 49.61 for **5**).

Conclusions

In brief, a Schiff base ligand synthesized from o-phenylendiamine and o-vanillin was converted to mixed ligand metal saccharine complexes by mixing with four metal saccharinates in this study. According to the results of spectroscopic characterization methods, elemental analysis, QTOF-LC/MS, two different molecular structures were proposed for synthesized complexes. Complex **1** and **2** were suggested having an octahedral geometry with two Schiff base ligands and two saccharinates. When it comes to **3** and **4**, tetrahedral structure with one deprotonate Schiff base and one saccharinate was proposed. In the absorption spectra of the complexes, intraligand transitions were observed. In addition, **1** and **2** exhibited d-d transitions while **3** and **4** showed charge transfer transitions. Antioxidant capacities of the prepared complexes were determined by DPPH scavenging and ferrous ion chelating methods. While complex **1** and **4** did not exhibit any ferrous ion chelating activity, they had good DPPH scavenging activity. On the other hand, complex **2** and **3** could not scavenge any DPPH molecule as they showed high ferrous ion chelating activity even higher than antioxidant standards BHA and BHT. Although the differences between the antioxidant properties of the complexes may arise from various reasons, they may be related to the changes in the coordination capability of the central metal ions.

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