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Synthesis, characterization, and electrochemical study of a new tetradentate nickel(II)-Schiff base complex derived from ethylenediamine and 5′-(*N*-methyl-*N*-phenylaminomethyl)-2′-hydroxyacetophenone

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ABSTRACT

A tetradentate Schiff base ligand (**3**) has been synthesized via the reaction of 5′-(*N*-methyl-*N*-phenylaminomethyl)-2′-hydroxyacetophenone (**2**) with a stoichiometric amount of ethylenediamine in absolute ethanol. Compound **2** was prepared by reaction of 5′-chloromethyl-2′-hydroxyacetophenone (**1**) with *N*-methylaniline, in the presence of sodium bicarbonate in tetrahydrofuran. Compound **1**, on the other hand, was obtained through a reaction between a hydrochloric acid–formaldehyde mixture and 2′-hydroxyacetophenone. Refluxing a mixture of the Schiff base (**3**) and a stoichiometric amount of nickel(II) acetate tetrahydrate in absolute ethanol at 50 °C under a nitrogen atmosphere afforded the expected tetradentate nickel(II)-Schiff base coordination compound (**4**). Compounds **1**–**4** have been characterized with the aid of a number of techniques: UV–Vis spectrophotometry; FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry; and elemental analysis. Cyclic voltammetry has been employed to investigate the redox behavior of compound **4** as well as the ability of the electrogenerated nickel(I) form of **4** to catalyze the reduction of 1-iodooctane.

1. Introduction

There has been considerable effort in recent years to prepare new Schiff bases (imines) similar in their structures to porphyrins; these compounds are well known as good ligands to coordinate metal ions [1]. Their transition-metal complexes have been found to be useful as antibacterial [2] and anticancer [3,4] agents, as efficient drugs in the arena of pharmacology [5], as excellent homogeneous- and heterogeneous-phase catalysts [6], as precursors for electrocatalytic processes [7–10], and as chemical sensors [11]. Symmetrical Schiff bases, particularly tetradentate species (such as salen) with four donor heteroatoms, have been extensively studied in the literature [12], due to their ability to stabilize many different metals in various oxidation states. In addition, metal-Schiff base complexes are efficient as electrode modifiers for anodic oxidation or cathodic reduction [10,13–18].

Electropolymerization of redox-active entities, such as metal complexes, is an effective way to modify the surface of an electrode. Accordingly, metal-Schiff base complexes could be used, together with monomers such as aniline, pyrrole, and thiophene, to form, via anodic oxidation, polymer-coated electrodes, with imbibed electroactive metal centers for a variety of applications in the fields of electrocatalysis and electroanalysis. Alternatively, it is possible to use a symmetrical metal-Schiff base complex, structurally modified with aniline-like moieties on the periphery of the ligand, that can be electropolymerized as a conducting film onto the surface of an electrode; this strategy was first employed by Horwitz and Murray [19] to prepare films from aniline-modified salen complexes of nickel(II), cobalt(II) and manganese(II). This latter approach, where metal complexes bearing electropolymerizable moieties such as aniline and pyrrole are used for the preparation of modified electrodes, is now being actively pursued in one of our laboratories. As part of this research effort [20–22], we describe in this report the synthesis, characterization, and electrochemical behavior of a new tetradentate nickel(II)-Schiff base complex (**4**) bearing an aniline moiety. An overview of the reactions involved in the synthesis of this new complex is presented in Scheme 1. A roster of spectroscopic techniques has been employed to characterize the nickel(II) complex as well as the Schiff base ligand (**3**) and its two building blocks—5′-chloromethyl-2′-hydroxyacetophenone (**1**)

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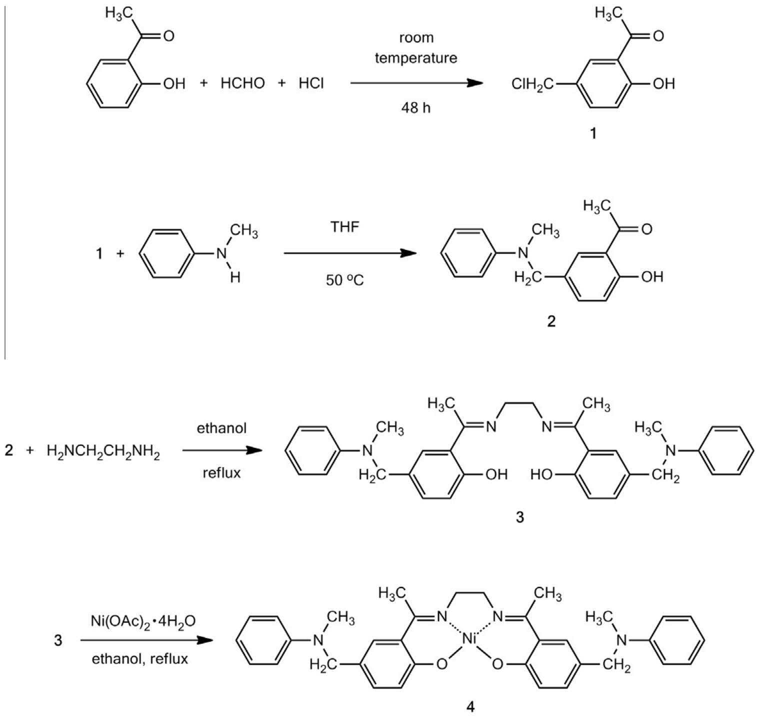

Scheme 1.

and 5′-(*N*-methyl-*N*-phenylaminomethyl)-2′-hydroxyacetophenone (**2**). Finally, we have conducted an initial exploration of the electrochemical behavior of **4** and of the catalytic reduction of a primary alkyl iodide (1-iodooctane) by the electrogenerated nickel(I) analogue of **4**.

2. Experimental

2.1. Reagents and instrumentation

For the syntheses described later in this experimental section, all chemicals were obtained from commercial sources and were used as received without further purification. For the cyclic voltammetry studies, dimethylformamide (DMF, EMD Chemicals, 99.9%) was employed as the solvent; tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$, GFS Chemicals, 98%), used as the supporting electrolyte, was recrystallized from water–methanol and thoroughly dried by continuous storage in a vacuum oven at 80 °C; 1-iodooctane (Aldrich, 98%) was chosen as the substrate to test the catalytic properties of the electrogenerated nickel(I) form of **4**; and zero-grade argon (Air Products) was used to deaerate all solutions.

Purity of the synthesized compounds (**1**–**4**) was checked by means of thin-layer chromatography (TLC); glass plates, precoated with silica gel (60F, Merck), were used. Uncorrected melting points were measured in open-capillary tubes on a Kofler bench (model WME) apparatus. All new compounds were analyzed for C, H, and N with the aid of a EuroVector EA3000 elemental analyzer, and the observed results agreed with the calculated percentages to within ±0.4%. Using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard, we obtained ^{1}H and ^{13}C NMR spectra with a Bruker 400-MHz spectrometer; chemical shifts are expressed in ppm. We recorded FT-IR spectra as KBr disks on a Perkin-Elmer 1000 spectrophotometer, and UV–Vis spectra were obtained with the aid of a UNICAM UV-300 instrument with DMF solutions (1-cm cell).

High-resolution mass spectra (HRMS) were acquired with an electrospray ion-trap (ESI) technique by collision-induced dissociation on a Bruker APEX-4 (7 Tesla) instrument. Samples were dissolved in acetonitrile and diluted in a spray solution (methanol–water 1:1 v/v with 0.1% formic acid); the mobile phase was pumped at 2 mL min^{-1}. Mass calibration was achieved with monoprotonated arginine clusters in the mass range *m*/*z* 175–871.

2.2. Synthesis of 5′-chloromethyl-2′-hydroxyacetophenone (1)

We prepared **1** according to a procedure described by Wulff and Akelah [23] that involved addition of 17 g (0.125 mol) of 2′-hydroxyacetophenone, in small portions with stirring, to 75 mL of concentrated hydrochloric acid containing 6.75 g (0.225 mol) of paraformaldehyde. This reaction mixture was maintained at room temperature with stirring for 48 h until a precipitate formed. Then the solid product was collected by suction filtration, washed with an aqueous solution of sodium bicarbonate (0.5%), washed with water, dried, and recrystallized from a toluene–petroleum ether mixture. Yield: 18.5 g (80%) of white crystals; M.p.: 100–102 °C. Its purity was checked by means of TLC with silica-gel plates; the eluent was a dichloromethane–ethanol mixture (95/5, v/v). UV–Vis (DMF) $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1} cm^{-1}]: $\lambda_{max(1)}$ (265), $\varepsilon_{max(1)}$ [603]; $\lambda_{max(2)}$ (327), $\varepsilon_{max(2)}$ [1139]. IR (KBr) ν_x (cm^{-1}): ν_{C-OH} (3426), $\nu_{C-H(aliphatic)}$ (2951–3013), $\nu_{C=O}$ (1640), ν_{CH2-Cl} (1255), ν_{C-Cl} (819). ^{1}H NMR ($CDCl_3$) δ (ppm): 12.33 (s, 1H, OH), 7.37 (m, 3H), 4.69 (s, 2H), 2.66 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 204.3, 161.1, 137.3, 132.3, 128.9, 120.8, 118.6, 46.3, 28.4. HRMS (ESI) *m*/*z*: calcd. for $C_9H_9{}^{35}ClNaO_2$ $[M+Na]^+$ 207.01888, found 207.01833; calcd. for $C_9H_9{}^{37}ClNaO_2$ $[M+Na]^+$ 209.01593, found 209.01538.

2.3. Synthesis of 5′-(N-methyl-N-phenylaminomethyl)-2′-hydroxyacetophenone (2)

To a mixture of 13 g (0.071 mol) of **1** and 6.5 g (0.077 mol) of $NaHCO_3$ in 20 mL of THF, placed in a three-necked flask fitted with a condenser, was added, dropwise, 7.5 g (0.070 mol) of *N*-methylaniline, dissolved in 10 mL of THF. This mixture was heated to 50 °C and maintained at this temperature with stirring and under nitrogen for at least 2 h. Then the suspension, containing solid NaCl, was filtered and washed with diethyl ether, and the solvent was removed under reduced pressure. We recrystallized the resulting pale yellow solid from a mixture of toluene and petroleum ether to obtain **2**; its purity was checked by means of TLC on silica-gel plates, with a dichloromethane–pentane mixture (7/3, v/v) as eluent. Yield: 9.5 g (46%); M.p.: 82 °C. UV–Vis (DMF) $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1} cm^{-1}]: $\lambda_{max(1)}$ (270), $\varepsilon_{max(1)}$ [1500]; $\lambda_{max(2)}$ (307), $\varepsilon_{max(2)}$ [1231]; $\lambda_{max(3)}$ (343), $\varepsilon_{max(3)}$ [1065]. IR (KBr) ν_x (cm^{-1}): ν_{C-OH} (3425), $\nu_{C-H(aliphatic)}$ (2827–3048), $\nu_{C=O}$ (1641), ν_{CH2-N} (1306), ν_{N-CH3} (512). ^1H NMR ($CDCl_3$) δ (ppm): 12.15 (s, 1H, OH), 7.14 (m, 8H), 4.45 (s, 2H), 2.97 (s, 3H), 2.54 (s, 3H). ^{13}C NMR ($CDCl_3$) δ (ppm): 204.6 (CO), 161.7 (CO), 150.0, 135.5, 129.5, 128.9, 119.8, 118.9, 117.4, 113.1, 56.4, 38.6, 28.8. HRMS (ESI) *m*/*z*: calcd. for $C_{16}H_{17}NO_2$ $[M]^+$ 255.12593, found 255.12536.

2.4. Synthesis of substituted salen ligand (3)

Schiff base 3 (a modified salen ligand) was synthesized according to a procedure slightly modified from that described in the literature [19]. To a solution of 7.0 g (27.5 mmol) of **2** in 30 mL of absolute ethanol in a 100-mL three-necked flask fitted with a condenser was slowly added a solution of 0.823 g (13.7 mmol) of ethylenediamine in 20 mL of absolute ethanol. This mixture was heated to 50 °C with stirring and under a nitrogen atmosphere for 2 h, after which the resulting precipitate was filtered, washed with diethyl ether, and dried under reduced pressure to afford compound **3** as a yellow solid. Yield: 4.26 g (58%); M.p.: 156 °C. Its purity was checked with the aid of TLC; silica-gel plates were used and a dichloromethane–ethyl acetate mixture (8/2, v/v) served as eluent. UV–Vis (DMF) $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1} cm^{-1}]: $\lambda_{max(1)}$ (272), $\varepsilon_{max(1)}$ [2950]; $\lambda_{max(2)}$ (311), $\varepsilon_{max(2)}$ [2050]; $\lambda_{max(3)}$ (392), $\varepsilon_{max(3)}$ [989]. IR (KBr) ν_x (cm^{-1}): ν_{C-OH} (3416), $\nu_{C-H(aliphatic)}$ (2922), $\nu_{C=N}$ (1616), ν_{CH2-N} (1295), ν_{N-CH3} (488). ^1H NMR ($CDCl_3$) δ (ppm): 14.15 (s, 2H, OH), 6.74–7.27 (m, 16H), 4.42 (s, 4H), 3.93 (s, 4H), 2.93 (s, 6H), 2.29 (s, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 172.8 (CO), 162.4 (CO), 150.2, 131.6, 129.4, 127.6, 126.7, 119.5, 118.8, 117.0, 113.1, 56.4, 50.5, 38.4, 15.0. HRMS (ESI) *m*/*z*: calcd. for $C_{34}H_{38}N_4NaO_2$ $[M+Na]^+$ 557.28925, found 557.28879.

A single crystal of ligand **3** was obtained by slow evaporation from an ethanol–methylene chloride (8/2, v/v) solvent mixture. Fig. 1 depicts the molecular geometry of **3** with displacement ellipsoids drawn at the 50% probability level; H atoms are represented as small spheres of arbitrary radii, and only the non-H atoms of the asymmetric unit are labeled.

2.5. Synthesis of the nickel(II) compound (4)

To prepare the desired nickel(II) salt (**4**), 200 mg (0.374 mmol) of the ligand (**3**) was dissolved in 10 mL of absolute ethanol and the solution was transferred to a 50-mL three-necked flask fitted with a condenser. To the flask was added, dropwise, an ethanolic solution (10 mL) of 93 mg (0.374 mmol) of nickel(II) acetate tetrahydrate. Then the stirred mixture was heated to reflux under a nitrogen atmosphere for 20 h. After being cooled to room temperature, the solution was reduced to half of its original volume and was stored in a refrigerator overnight. Finally, the brown precipitate of **4** was collected by filtration, washed with ethanol, and dried under reduced pressure for several hours to yield 138 mg (63%) of the desired compound. M.p.: >250 °C. UV–Vis (DMF) $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1} cm^{-1}]: $\lambda_{max(1)}$ (269), $\varepsilon_{max(1)}$ [280]; $\lambda_{max(2)}$ (309), $\varepsilon_{max(2)}$ [1110]; $\lambda_{max(3)}$ (413), $\varepsilon_{max(3)}$ [443]; $\lambda_{max(4)}$ (449), $\varepsilon_{max(4)}$ [180]. IR (KBr) ν_x (cm^{-1}): $\nu_{C-H(aliphatic)}$ 3163–3280, $\nu_{C=N}$ 1589, ν_{CH2-N} 1306, ν_{C-O} 1328, ν_{Ni-O} 521, ν_{Ni-N} 498. ^1H NMR ($CDCl_3$) δ (ppm): 6.68–7.26 (m, 16H), 4.25 (s, 4H), 3.35 (s, 4H), 2.84 (s, 6H), 2.01 (s, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 168.2, 163.4, 150.1, 131.6, 129.1, 126.7, 124.2, 122.8, 121.1, 116.7, 112.8, 56.4, 54.6, 38.1, 18.1. HRMS (ESI) *m*/*z*: calcd. for $C_{34}H_{37}N_4NiO_2$ $[M+H]^+$ 591.22700, found 591.22568. *Anal.* Calc. for $C_{34}H_{36}N_4NiO_2$: C, 69.05; H, 6.14; N, 9.47. Found: C, 68.87; H, 6.08; N, 9.35%. Repeated efforts to obtain a single crystal of **4**, suitable for structural analysis, were unsuccessful.

2.6. Electrochemical study of the behavior of 4

Cyclic voltammograms were acquired with a Princeton Applied Research Corporation (PARC) model 2273 multipurpose electrochemical instrument operated by PowerSuite® software (PowerSuite®-2.58, PowerSuite® I/O Library-2.43.0, and PowerSuiteCV®–2.46) with data processing in OriginPro 8.6. We constructed a planar, circular working electrode with a geometric area of 0.077 cm^2 by press-fitting a short length of 3-mm-diameter glassy carbon rod (Grade GC-20, Tokai Electrode Manufacturing Co., Tokyo, Japan) into the end of a machined Teflon tube; electrical connection to the carbon was made by a 3-mm-diameter stainless-steel rod that contacted the cathode material and extended upward through the tube. Before each cyclic voltammogram was recorded, the working electrode was cleaned on a Master-Tex (Buehler) polishing pad with an aqueous suspension of 0.05-μm alumina, after which the electrode was rinsed ultrasonically in DMF and wiped dry before being inserted into the electrochemical cell. All potentials are reported with respect to a reference electrode that consisted of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride [24–26]; this electrode has a potential of −0.76 V versus an aqueous saturated calomel electrode (SCE) at 25 °C. A description of the cell used for cyclic voltammetry can

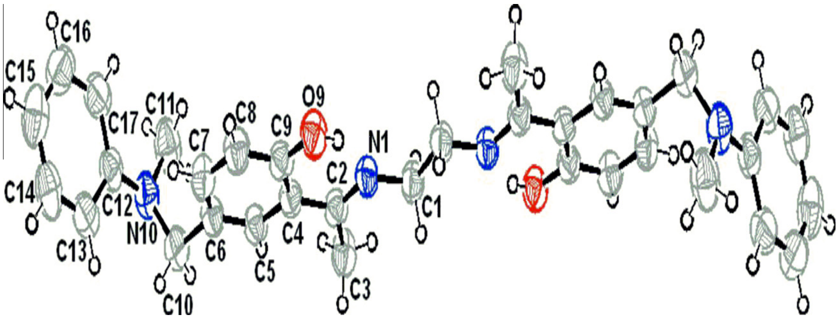

Fig. 1. ORTEP diagram for the substituted salen ligand (**3**).

be found in an earlier paper [27]; this single-compartment, three-electrode cell incorporates a platinum wire auxiliary (counter) electrode, along with the aforementioned working and reference electrodes.

3. Results and discussion

3.1. Chemistry

Syntheses of compounds **1**–**4** were carried out via known chemical reactions, as depicted in Scheme 1. Compound **1** was prepared according to published procedures that basically involved a reaction between 2′-hydroxyacetophenone, paraformaldehyde, and hydrochloric acid. Compound **2** was synthesized by alkylation of *N*-methylaniline with compound **1**. Reaction of compound **2** with ethylenediamine afforded the modified salen ligand **3** which, upon treatment with nickel(II) acetate tetrahydrate, produced **4**. Purities of compounds **1**–**3** were checked with the aid of TLC (with appropriate mobile phases being mentioned in the experimental section) and confirmed by determinations of their melting points. Structural features of the compounds (including **4**) were substantiated by means of various spectroscopic techniques, including UV–Vis, IR, NMR, and HRMS data, and an elemental analysis of **4** was carried out.

For all four compounds (**1**–**4**), the ^{1}H NMR and ^{13}C NMR spectral features are in full agreement with the suggested structures; the ^{1}H NMR spectra for compounds **1**–**3** showed signals corresponding to methylene, aromatic, and OH protons, and DEPT experiments were employed to differentiate secondary and quaternary carbons from primary and tertiary carbons. Moreover, infrared spectra for the prepared compounds showed absorption bands characteristic of C=O groups, along with other absorptions correlated to the assigned structures. Additional support for the proposed structures came from mass spectral data; mass spectra of the synthesized compounds are in complete agreement with the assigned structures and showed the expected molecular ions (M$^+$) as suggested by their molecular formulas. Details of some spectral data are given below.

3.2. FT-IR spectra

Compounds **1**–**3** exhibit a broad absorption band in the region from 3300 to 3800 cm^{-1} that can be assigned to an intramolecular hydrogen bond arising from the presence of hydroxyl groups in their molecular structures. Absorption bands observed at 1640 and 1641 cm^{-1} are attributed to C=O stretching vibrations for compounds **1** and **2**, respectively, whereas the stretching vibration for the CH$_2$–Cl moiety of **1** appears at 819 cm^{-1}; this last band is absent from the spectrum of **2**, which has an absorption band at 1306 cm^{-1} due to the newly formed CH$_2$–N bond [28]. A significant shift of the carbonyl group frequency to lower energy for both **1** and **2**, in comparison with that of acetophenone (1720 cm^{-1}), can be attributed to the stronger dipole–dipole interactions between the phenolic proton and the carbonyl group. In addition, this scenario could explain the significant displacement of the chemical shift for the phenolic proton ($\delta_{\text{Ar–OH}}$) from 7.54 (phenol) to about 12–15 ppm for 2′-hydroxyacetophenone and its analogues; this behavior is well discussed for the ^{1}H NMR spectra of similar structures [29–31].

In the IR spectrum for the nickel(II) complex (**4**), the azomethine band is shifted to a lower frequency (1589 cm^{-1}), which indicates that the nitrogen atom of the azomethine group is coordinated to the metal ion. This bathochromic effect can be explained by the increase in the electronic delocalization through the newly coordinated metal center in **4** [29,30,32–34]. Moreover, the ($\nu_{\text{C–O}}$) absorption band shifts to higher wavenumbers (1275–1295 cm^{-1}). These two observations are due to coordination of the metal cation through the oxygen atoms of ionized hydroxyl groups and the nitrogen atoms of azomethine groups [35,36]. In addition, the new bands at 498 and 521 cm^{-1} confirm the nature of the metal–ligand bonding; these bands are assigned to Ni(II)–N and Ni(II)–O vibrations, respectively [37,38].

3.3. Electronic spectra

Typical absorption bands of aromatic moieties were observed for **1** and **2**. Compound **1** shows two absorption bands at 265 and 327 nm, whereas three bands at 270, 307 and 337 nm (the last being a shoulder) appear for **2**. In both cases, the first two bands correspond to phenyl-ring electronic transitions [39], whereas the third band for compound **2** was assigned to an n → π* transition [40]. As for the other two compounds (**3** and **4**), the former displays three bands at 250, 309, and 414 nm, and the latter exhibits four bands of which the first three are similar to those of the ligand. As for the fourth band at 449 nm for **4**, it was assigned to the Soret band [40], suggesting that nickel(II) is effectively coordinated to the ligand, as previously shown by IR data [35,36].

3.4. NMR spectra

There is good agreement between the ^{1}H NMR spectra of the prepared compounds and their assigned structures. Spectra for **1**, **2**, and **3** reveal a downfield singlet signal in the range 14.15–12.15 ppm that is due to the phenolic protons [29–31]. This deshielding effect is ascribed to the formation of intramolecular hydrogen bonds [31,41,42]. Aromatic protons of the four compounds appear as complex multiplets between 6.86 and 7.37 ppm. Due to the difference in electronegativity between chlorine and nitrogen atoms, the singlet for the methylene group shifts from 4.69 ppm for the CH$_2$–Cl moiety in **2** to 4.45 ppm for the CH$_2$–N moiety in **1**. Protons of methyl groups linked to an imine function, i.e., N=C–CH$_3$, resonate as singlets with almost the same chemical shifts, 2.93 ppm for **3** and 2.84 ppm for **4**. Signals for phenolic protons are not observed for the nickel complex (**4**), suggesting that both phenoxy groups bind with the nickel ion as anions.

In the ^{13}C NMR spectra for compounds **1** and **2**, one sees peaks associated with the different types of carbons. Carbon-atom resonances at 204.6–150.0 ppm are associated with carbonyl, phenoxy, and anilinic groups, whereas aromatic carbon atoms resonate in the 137.0–113.1 ppm range. In the spectrum for **3**, signals for the aliphatic carbon atoms appear at 56.4–26.8 ppm. For **3** and **4**, the ^{13}C NMR spectra are similar to that of **2**, because their molecular structures are symmetrical and derive from compound **2** and ethylenediamine. Carbon atoms associated with phenoxy groups are more downfield and appear at 172.8 and 168.2 ppm, respectively, and the carbon atoms of azomethine groups are observed at 162.4 ppm for **3** and at 163.4 ppm for **4**. Aromatic and aliphatic carbon atoms resonate at almost the same chemical shifts of the same carbons in compounds **1** and **2**. These results are in good agreement with the spectra of similar compounds described in the literature [31,37,38].

3.5. Cyclic voltammetric behavior of the nickel(II) complex (**4**)

Shown in Fig. 2 is a cyclic voltammogram recorded at a scan rate of 100 mV s^{-1} for reduction of a 2.0 mM solution of **4** in oxygen-free DMF containing 0.10 M TBABF$_4$ at a freshly polished glassy carbon electrode. A central feature of this cyclic voltammogram is the reversible nickel(II)–nickel(I) redox couple with a cathodic peak potential (E_{pc}) of −1.05 V and an anodic peak potential (E_{pa}) of −0.97 V ; this 80-mV peak separation ($\Delta E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$) is identical to that observed for the reversible one-electron

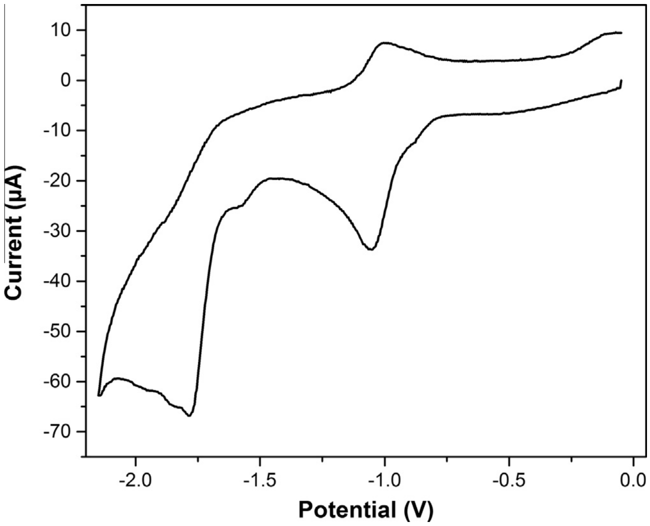

Fig. 2. Cyclic voltammogram recorded at 100 mV s^{-1} for reduction of a 2.0 mM solution of **4** at a glassy carbon electrode (area = 0.077 cm^2) in oxygen-free DMF–0.10 M TBABF$_4$. Scan goes from ca. 0 to −2.24 to 0 V.

reduction of nickel(II) salen under similar experimental conditions [43]. At potentials more negative than −1.50 V, there are several irreversible cathodic peaks that we believe are associated with reduction of the ligand. In addition, on the rising portion of the cathodic peak for reduction of **4** is a small prepeak, the origin of which we have not yet elucidated.

We undertook a more detailed examination of the electrochemistry of **4** by focusing on the reversible nickel(II)–nickel(I) redox couple in the region of potentials close to −1.00 V. Over a range of scan rates (v) from 50 to 5000 mV s^{-1}, we found that the peak current ratio, I_{pa}/I_{pc}, for the nickel(II)–nickel(I) couple was 1.00 ± 0.04, indicating that the nickel(I) intermediate is stable on this cyclic voltammetric time scale. For the same range of scan rates, the average values for the cathodic and anodic peak potentials were $E_{pc} = -1.08 \pm 0.03$ V and $E_{pa} = -0.96 \pm 0.01$ V, respectively. As the scan rate is increased, the peak separation becomes larger, as expected, which is a reflection of intrinsic sluggishness of the electron-transfer process. Finally, a plot of I_{pc} versus $v^{1/2}$ was linear, revealing that reduction of **4** is a diffusion-controlled process. As a part of future work, it would be interesting to determine the energy difference between the metal-centered and ligand-centered one-electron reduction of **4**, as a further comparison of its behavior with respect to nickel(II) salen [43].

*3.6. Cyclic voltammetric behavior of the nickel(II) complex (**4**) in the absence and presence of 1-iodooctane*

A set of cyclic voltammograms obtained at a scan rate of 100 mV s^{-1} with a freshly polished glassy carbon electrode for the reduction of a 2.0 mM solution of **4** in oxygen-free DMF–0.10 M TBABF$_4$ in the absence and presence of 1-iodooctane is depicted in Fig. 3. We show just the region of potentials for which the nickel(II) species is electroactive. In the absence of 1-iodooctane (curve A, Fig. 3), the reversible one-electron nickel(II)–nickel(I) process is observed; as described earlier, the cathodic peak potential (E_{pc}) and the anodic peak potential (E_{pa}) are −1.05 and −0.97 V, respectively, and the ratio of anodic and cathodic peak currents (I_{pa}/I_{pc}) is close to unity. As mentioned above, there is a small cathodic hump that precedes the main peak for reduction of the nickel(II) species as well as an anodic hump that follows the main peak for oxidation of the nickel(I) species, but neither hump can be explained at this time.

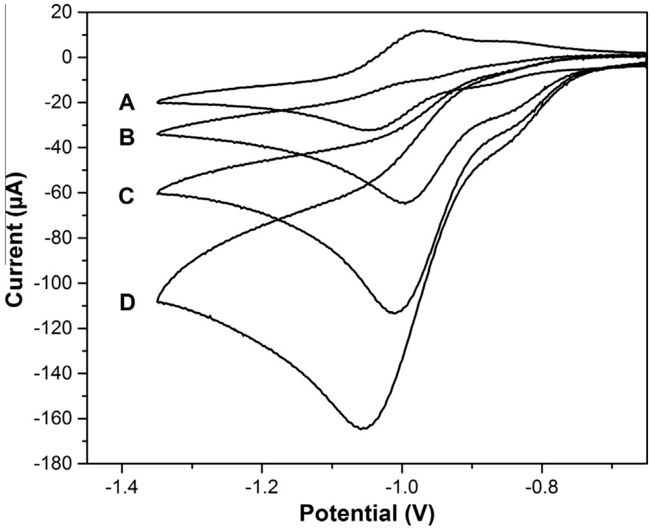

Fig. 3. Cyclic voltammograms for reduction of a 2.0 mM solution of **4** at a glassy carbon electrode (area = 0.077 cm^2) in oxygen-free DMF–0.10 M TBABF$_4$ containing (A) 0 mM, (B) 2.0 mM, (C) 5.0 mM, and (D) 10.0 mM 1-iodooctane. Scans go from −0.65 to −1.35 to −0.65 V.

It should be mentioned here that direct reduction of 1-iodooctane (in the absence of **4**) at a freshly polished glassy carbon electrode in DMF-0.10 M TBABF$_4$ and at a scan rate of 100 mV s^{-1} shows a single irreversible cathodic peak with a peak potential of −1.38 V [43]. Therefore, direct reduction of the alkyl iodide cannot occur at potentials involved in the reduction of **4**.

When 1-iodooctane is added to the system (curves B–D, Fig. 3), the cyclic voltammetric behavior of the nickel(II) species is altered; the cathodic peak current is enhanced (due to the nickel(I)-catalyzed reduction of the alkyl iodide) and the anodic peak disappears; however, the increase in the cathodic peak current is not proportional to the concentration of 1-iodooctane, a phenomenon that is also observed with nickel(II) salen.

One significant difference is observed when cyclic voltammograms for the nickel(II) salen–1-iodooctane and **4**–1-iodooctane systems are compared. In previous research [43–45], it was discovered that, when nickel(II) salen undergoes one-electron reduction at a glassy carbon cathode in the presence of 1-iodooctane, a ligand-reduced form of nickel(II) salen is produced which reacts with 1-iodooctane such that an imide (C═N) bond of the ligand is octylated; the resulting alkylated nickel(II) salen shows a new cathodic peak at a potential more negative than that for reduction of unmodified nickel(II) salen, and the alkylated nickel(II) salen is less effective as a precursor for catalytic reduction of the alkyl iodide. In contrast, we have not yet seen any voltammetric evidence that the reduced form of **4** undergoes any octylation, so **4** may prove to be a more robust catalyst precursor than nickel(II) salen, because each imino (C═N) bond of the ligand of **4** is sterically protected by a methyl substituent. This phenomenon merits more attention in a future study.

4. Conclusions

In this work, we have synthesized and characterized four compounds, one among them being a Schiff-base ligand (**3**), possessing in its molecular structure an aniline moiety, that might be used as an electropolymerizable monomer to fabricate surface-modified electrodes. In addition, the nickel(II) complex (**4**) of this monomer was synthesized and characterized; its cyclic voltammetric behavior has been investigated, and the corresponding electrogenerated nickel(I) complex has been shown to catalyze the reduction of

1-iodooctane. Furthermore, anodically formed films of this nickel complex might be effective for the mediated electroreduction of alkyl halides. Finally, the new ligand might be useful for the preparation of other transition-metal complexes that could be advantageously exploited as solid-phase (modified) electrodes for heterogeneous catalysis, electrocatalysis, analysis, sensors, and biosensors. Such work is now in progress.

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