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Synthesis, characterization, and electrochemical behavior of a cobalt(II) salen-like complex

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ABSTRACT

A new tetradentate cobalt(II)-Schiff base complex has been synthesized via the reaction of the ligand 2,2'-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-((methyl(phenyl)amino)methyl)phenol) with a stoichiometric amount of cobalt(II) acetate tetrahydrate in absolute ethanol. This cobalt(II) complex has been characterized with the aid of several spectroscopic techniques (FT-IR, UV-Vis, and mass spectrometry) as well as by thermal (TGA and DTA) and elemental analysis. Cyclic voltammetry has been employed to examine the redox behavior of the cobalt(II) complex in dimethylformamide (DMF) containing 0.10 M tetra-*n*-butylammonium tetrafluoroborate (TBABF₄). In addition, the electrogenerated cobalt(I) form of the complex has been (a) employed as a catalyst for the reduction of 1-iododecane and (b) compared with the behavior of cobalt(I) salen. Finally, the cobalt(II) complex has been subjected to anodic electropolymerization onto the surface of a glassy carbon electrode in DMF containing 0.10 M tetra-*n*-butylammonium perchlorate (TBAP).

Keywords: Cobalt(II)-Schiff base complex, Cyclic voltammetry, Thermal analysis, Electrocatalytic reduction of primary alkyl iodide, Anodic formation of a cobalt-containing polymer on glassy carbon

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1. Introduction

Schiff bases continue to play a significant role in coordination chemistry [1], owing especially to the attractive chemical and physical properties of metal-Schiff base complexes [2]. Symmetrical Schiff bases, particularly tetradentate species (such as salen) with four donor heteroatoms, have been extensively studied [3], due to their ability to coordinate with and to stabilize many different metals in a variety of oxidation states. In addition, metal-Schiff base complexes can be employed to modify the surfaces of electrodes for anodic and cathodic processes [4–11]. Transition-metal complexes of tetradentate Schiff bases display a wide range of applications in the areas of catalysis [12] and electrocatalysis [13] and for the activation of small molecules such as carbon dioxide [14] and molecular oxygen [15].

Coordination chemistry of cobalt(II)-Schiff base complexes has been investigated in recent years [16]. Such complexes have been vigorously explored due to their ability to serve as homogeneous and heterogeneous catalysts for a number of oxidation and reduction reactions [17,18]. Additionally, electropolymerization of cobalt complexes has been explored as an effective method for the modification of electrode surfaces; such tailoring of an electrode surface by a symmetric cobalt(II)-Schiff base possessing an aniline moiety was first investigated by Horwitz and Murray [4].

Electrogenerated cobalt(I) salen has been employed as a homogeneous catalyst for the reduction of halogenated organic compounds, including iodoethane [19], benzyl chloride [3], 1,3-dibromopropane [5], 1,4-dibromobutane [5], 1,8-diiodooctane [6], and 2,6-bis(chloromethyl)pyridine [7]. For each of these systems, it was demonstrated that the electrogenerated cobalt(I) salen species attacks the substrate to

form an organocobalt(III) salen intermediate, which subsequently undergoes further reduction to afford the desired products.

As a continuation of our recent work [8] on the synthesis and study of a nickel(II) complex possessing a Schiff-base ligand, we describe herein the preparation, characterization, and electrochemical properties of a new tetradentate cobalt(II)-Schiff base complex bearing an aniline moiety. Scheme 1 depicts the key reaction between the ligand (1) and cobalt(II) acetate tetrahydrate that is involved in the synthesis of the complex (2). This complex has been characterized with the aid of a number of spectroscopic techniques (FTIR, UV–Vis, and mass spectrometry) as well as by means of elemental and thermal analysis. In addition, we probed the electrochemical behavior of 2 at glassy carbon cathodes with the aid of cyclic voltammetry, and an initial exploration of the catalytic reduction of 1-iododecane by the electrogenerated cobalt(I) analogue of 2 was conducted. Finally, the oxidative polymerization of 2 onto a glassy carbon electrode has been briefly investigated.

2. Experimental

2.1. Reagents and instrumentation

All chemicals for synthesis of the ligand (1) and its cobalt(II) complex (2) were obtained from commercial sources and were used without further purification. For electrochemical work, dimethylformamide (DMF, 99.9%, EMD Chemicals) was used as received. Tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) and tetra-*n*-butylammonium perchlorate (TBAP), used as supporting electrolytes, were recrystallized from water–methanol and stored in a vacuum oven at 70–80 °C for a minimum of 48 h to remove traces of water.

Purity of the synthesized Schiff base (1) was checked by means of TLC with glass plates, precoated with silica gel (60F, Merck). High-resolution mass spectra (HRMS) for both 1 and the cobalt(II) complex (2) were acquired via electrospray ionization–mass spectrometry (ESI–MS) with the aid of a Bruker APEX-2 instrument. Perkin-Elmer 1000 and Unicam UV-300 spectrophotometers were employed, respectively, to record FT–IR and UV-visible spectra. Using a EuroVector EA3000 elemental analyzer, we determined the C, H, and N content of 2; the results agreed with the calculated percentages to within $\pm 0.4\%$. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for both 1 and 2 were carried out with a Perkin-Elmer instrument; measurements were done at a heating rate of 10 °C min⁻¹ under a dry nitrogen atmosphere at a flow rate of 50 mL min⁻¹ over the temperature range of 20–1000 °C.

2.2. Electrochemistry

Procedures and data acquisition methods for cyclic voltammetry have been described in previous publications [20,21]. Cyclic voltammetry experiments were carried out in a one-compartment (undivided) cell described in an earlier paper [20]. We fabricated a planar, circular glassy carbon working electrode, with a geometric area of 0.071 cm², by press-fitting a short piece of glassy carbon rod (Grade GC-20, 3.0-mm-diameter, Tokai Electrode Manufacturing Company, Tokyo, Japan) into the end of a machined Teflon tube; electrical contact to this working electrode was made via a 3.0-mm-diameter stainless-steel pole that extended upward through the tube. A coil of platinum wire served as the auxiliary (counter) electrode. Our reference electrode consisted of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride, which has a potential of

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-0.76 V vs. an aqueous saturated calomel electrode (SCE) at 25 °C [22–24]; however, all potentials in this paper have been converted to the SCE scale.

2.3. Synthesis of the cobalt(II) complex of 2,2'-((1E,1'E)-(ethane-1,2diylbis(azanylylidene))bis(ethan-1-yl-1-ylidene))bis(4-

((methyl(phenyl)amino)methyl)phenol)

Preparation of the Schiff-base ligand $(H_2L, 1)$ was carried out by means of the method described in a previous publication [8]. Synthesis of the cobalt(II) complex of this Schiff base was accomplished according to the following procedure: 200 mg (0.374 mmol) of 1 was dissolved in 10 mL of absolute ethanol, and the solution was transferred to a 50-mL three-necked flask fitted with a reflux condenser. After an ethanolic solution (10 mL) of 93 mg (0.374 mmol) of cobalt(II) acetate tetrahydrate was added dropwise to the solution of the ligand, the stirred mixture was refluxed 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 green precipitate was collected by filtration, washed with ethanol, and dried under reduced pressure for several hours to afford the desired complex (2) in 56% yield before being characterized: (a) UV-Vis: $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M⁻¹ cm⁻¹]: $\lambda_{max(1)}$ (235), $\varepsilon_{max(1)}$ [11830]; $\lambda_{max(2)}$ (256), $\varepsilon_{max(2)}$ [4750]; $\lambda_{max(3)}$ (361), $\varepsilon_{max(3)}$ [1410]; (b) IR (KBr): v_x $(cm^{-1}): v_{C-H(aliph)}$ (2900–3000), $v_{C=N}$ (1576), v_{CH_2-N} (1302), v_{C-O} (1370), v_{Ni-O} (525). v_{Ni-N} (478); (c) HRMS (ESI) *m/z*: calcd. for C₃₄H₃₆CoN₄NaO₂: [M + Na]⁺ 614.20680, found 614.20657; (d) anal. calculated for $C_{38}H_{46}CoN_4O_8$ (*i.e.*, Co(II)L + 2 CH₃COO + 2 H₂O): C, 61.20; H, 6.22; N, 7.51, found: C, 61.49; H, 6.08; N, 7.33. Repeated efforts to grow a single crystal of 2, suitable for structural analysis, were unsuccessful.

3.1. Chemistry

Synthesis of the Schiff base (1) was accomplished as described in a previous publication [8]. Depicted in Scheme 1 is the reaction used to prepare the desired cobalt(II)-Schiff base complex (2), the structure of which was confirmed with the aid of several spectroscopic techniques, including UV-Vis, FT-IR, and mass spectrometry.

3.2. Spectroscopy

It is possible to explain the IR spectrum of the cobalt(II)-Schiff base complex (2) by comparison with spectral data for similar structures [9] and of the Schiff base itself [8]. Absorption in the region from 2900 to 3000 cm⁻¹ is due to the $v_{C-H(aliph)}$ vibration. There is a shift in the frequency of the azomethine band ($v_{C=N}$) from 1616 to 1576 cm⁻¹, which indicates that the nitrogen atom of the azomethine group is coordinated to cobalt(II). This bathochromic shift can be explained by the increase in electron delocalization through the newly coordinated metal center [10,11]. Moreover, the v_{CH_2-N} absorption band is shifted to higher wavenumbers (1295–1302 cm⁻¹), due to coordination of the metal ion through the nitrogen atoms of the azomethine groups [25]. In addition, the new bands at 470–490 cm⁻¹ and 530–550 cm⁻¹ can be assigned to Co–N [26] and Co–O [27] vibrations, respectively, confirming the tetradentate coordination of cobalt(II) to the ligand [28]. Finally, a broad absorption band centered at 3436 cm⁻¹ can be assigned to cobalt(II) [29].

In DMSO the electronic absorption spectrum of the cobalt(II) complex exhibits an intense band centered at 256 nm, assigned to $n-\pi^*$ transitions of the

azomethine group, whereas a second band, observed at 361 nm, corresponds to ligand-to-metal charge transfer [30].

A FAB-mass spectrum of the cobalt(II) complex displayed the following major signals: m/z = 614.2070 (observed), 614.2068 (calculated), $[M + Na]^+$ (42%); 485.1517 (observed), 485.1514 (calculated), $[M - C_7H_8N]^+$ (100%); and 107.0728 (observed), 107.0735 (calculated), $[C_7H_9N]^+$ (28%). In addition, a peak, identical in magnitude to that seen at m/z 485.1517, was detected at m/z 1205.4218 (observed), 1205.4238 (calculated), suggesting the presence of a binuclear form of the complex with an accompanying sodium, *i.e.*, $[2M + Na]^+$.

3.3. Thermal analysis

In the present study, thermal analyses (both TGA and DTA) were performed to obtain information about the stabilities of **1** and **2** as well as to establish the presence of water molecules either inside or outside the inner coordination sphere of cobalt(II). To perform these measurements, the temperature was increased from ambient to 950 °C, at a rate of 10 °C min⁻¹ under a nitrogen atmosphere, and the resulting TGA and DTA curves for **1** and **2** are depicted in Fig. 1 and Fig. 2, respectively. In addition, mass losses obtained from the TGA curves are compiled in Table 1, together with species proposed to account for these mass losses, which shows that observed and calculated values are in good agreement. For the ligand (1), the TGA curve revealed a mass loss of 38.46% (calculated 39.70%) over the temperature range of 200–332 °C, which can be attributed to loss of two fragments (C₇H₈N) derived from *N*-methylaniline. In the temperature range of 332–532 °C, the ligand loses a C₉H₉O fragment, as indicated by a mass loss of 24.61% (calculated 24.91%). For the cobalt(II) complex (**2**), two water molecules of hydration are lost in the temperature range of 128–186 °C, but any water molecules coordinated directly to

cobalt(II) would be eliminated at higher temperatures [31]. As seen for higher temperatures in Table 1, the complex undergoes further decomposition in several steps with the loss of one or more fragments (acetate, *N*-methylaniline, C_7H_5O , and C_5H_9N), which eventually leads to production of cobalt oxides.

3.4. Cyclic voltammetric behavior of the cobalt(II) complex

Displayed in Fig. 3 is a cyclic voltammogram recorded at a scan rate of 100 mV s⁻¹ for reduction of a 1.25 mM solution of the cobalt(II) complex alone in oxygen-free DMF containing 0.10 M TBABF₄ at a freshly polished glassy carbon electrode. For this cyclic voltammogram, the most important feature is the reversible cobalt(II)–cobalt(I) redox couple with a cathodic peak potential (E_{pc}) of -1.39 V, an anodic peak potential (E_{pa}) of -1.28 V, and a peak separation ($\Delta E_p = E_{pa} - E_{pc}$) of 110 mV. These observations are comparable to those observed in an earlier study [19] of the reversible one-electron reduction of cobalt(II) salen ($E_{pc} = -1.32$ V, $E_{pa} = -1.23$ V, $\Delta E_p = 90$ mV) under similar experimental conditions. At more negative potentials, one sees a small irreversible cathodic peak ($E_{pc} = -1.74$ V) and a second much larger cathodic peak ($E_{pc} = -2.66$ V), both of which we attribute to reduction of the ligand; indeed these two features are observed when a cyclic voltammogram is recorded for the ligand by itself in the solvent–supporting electrolyte. Moreover, the cyclic voltammetric characteristics of the cobalt(II) complex are remarkably similar to those of the corresponding nickel(II) complex that were reported previously [8].

We have investigated the electrochemical behavior of the cobalt(II) complex with emphasis on the reversible cobalt(II)–cobalt(I) redox couple in the region of potentials around –1.30 V. As the scan rate (v) was increased from 50 to 500 mV s⁻¹, the peak separation (ΔE_p) became larger, as expected, increasing from 110 to 310 mV, which indicates that the electron-transfer process is intrinsically sluggish. A plot of

the cathodic peak current (I_{pc}) versus $v^{1/2}$ was linear, revealing that reduction of the cobalt(II) complex is a diffusion-controlled process.

3.5. Cyclic voltammetric behavior of the cobalt(II) complex in the presence of 1-iododecane

When the cobalt(II) complex (1.25 mM) was reduced at a freshly polished glassy carbon electrode in the presence of 2.00 mM 1-iododecane in DMF-0.10 M TBABF₄, the cyclic voltammograms shown in curve B of Fig. 4 was recorded. Comparison of curve A (obtained in the absence of 1-iododecane) with curve B reveals that the cathodic peak for reduction of the cobalt(II) complex does not increase substantially in size, but does shift from -1.39 to -1.30 V, which is attributable to the interaction between the electrogenerated cobalt(I) complex and 1-iododecane to afford a decylcobalt(III) species [19]; in addition, the anodic peak for reoxidation of the cobalt(I) complex disappears. A large irreversible peak, due to reduction of the decylcobalt(III) intermediate is seen at a more negative potential As illustrated in curve C of Fig. 4, raising the concentration of (-1.81 V). 1-iododecane to 5.00 mM causes an increase in current for the peak at -1.81 V, but does not alter the size or potential of the peak at -1.30 V; these observations mimic closely those reported in earlier work dealing with the cobalt(I) salen-catalyzed reduction of iodoethane [19].

3.6. Electrooxidative formation of a polymer-coated electrode

Anodic polymerization of the cobalt complex onto the surface of a freshly polished glassy carbon electrode was explored by sequential scanning of the potential from 0 V to +1.5 V and then to -1.8 V vs. SCE. Shown in Fig. 5 are the first 10 consecutive scans recorded, without interruption, at 100 mV s⁻¹ for such an

experiment with a 2.00 mM solution of the cobalt(II) complex in DMF containing 0.10 M TBAP. For the first potential cycle, depicted by the dotted curve in Fig. 5, one sees a pair of anodic waves at approximately ± 1.0 and ± 1.4 V that we associate, respectively, with oxidation of cobalt(II) to cobalt(III) and with oxidative polymerization of the salen-like ligand to produce a film on the surface of the glassy carbon electrode; these voltammetric features appear to resemble those described in earlier studies of the anodic polymerization of nickel(II) salen onto glassy carbon surfaces [32–34]. For the subsequent negative-going portion of this first cycle (dotted curve), a cathodic shoulder at -1.2 V and a Gaussian-shaped peak at -1.6 V are observed; interestingly, however, and unlike the previously described behavior [34] of an anodically formed poly[nickel(III) salen] film, no cathodic peaks are seen anywhere in the potential region from +1.5 to -0.5 V in Fig. 5. Our suggested interpretation of the cathodic response in the region of potentials from -0.5 to -1.8 V is that there is sequential reduction of polymer-bound cobalt(III) to polymer-bound cobalt(II), followed by reduction of the soluble cobalt(II)-Schiff base species (2) and then by reduction of polymer-bound cobalt(II) to cobalt(I). As the potential is scanned from -1.8 to -1.0 V, some reoxidation of cobalt(I) to cobalt(II) must occur before the start of the second complete potential scan. From the second to the tenth scan in Fig. 5, there is very little change in the appearance of the cyclic voltammetric response; indeed the only notable difference is the 200-mV shift of the most cathodic peak to a less negative potential.

4. Conclusions

In this work, we have synthesized a novel complex of cobalt(II) with a salenlike ligand that bears two pendant anilinic moieties. This new compound has been characterized with the aid of FT-IR, UV-Vis, and mass spectrometric techniques, along with elemental and thermal analyses. At a glassy carbon electrode in DMF containing 0.10 M TBABF₄ as supporting electrolyte, the cobalt(II) complex displays reversible one-electron reduction to the corresponding cobalt(I) species. In the presence of 1-iododecane, the cobalt(I) form of the complex serves as an electrogenerated catalyst for reduction of the alkyl iodide. We believe the catalytic process involves formation of a decylcobalt(III) intermediate which is subsequently reduced at a more negative potential to a decylcobalt(II) monoanion; the latter decomposes to regenerate the active cobalt(I) catalyst and to give a decyl radical that leads to three products (*n*-eicosane, *n*-decane, and 1-decene). Because the parent cobalt(II) complex possesses anodically polymerizable anilinic substituents, we believe that it should be possible to construct modified electrodes for use as sensors and for heterogeneous catalysis.

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CAPTIONS FOR SCHEME AND FIGURES

Scheme 1. Reaction of Schiff base (1) with cobalt(II) acetate tetrahydrate in ethanol to afford the cobalt(II)-Schiff base complex (2).

Fig. 1. Thermogravimetric analysis (TGA, upper panel) and differential thermal analysis (DTA, lower panel) curves for the ligand (1).

Fig. 2. Thermogravimetric analysis (TGA, upper panel) and differential thermal analysis (DTA, lower panel) curves for the cobalt(II) complex (**2**).

Fig. 3. Cyclic voltammogram recorded at 100 mV s⁻¹ for reduction of a 1.25 mM solution of the cobalt(II)-Schiff base complex (**2**) with a freshly polished glassy carbon electrode (area = 0.071 cm^2) in oxygen-free DMF containing 0.10 M TBABF₄. Scan goes from -0.75 to -2.80 to -0.75 V vs. SCE.

Fig. 4. Cyclic voltammograms recorded at 100 mV s⁻¹ for a 1.25 mM solution of the cobalt(II)-Schiff base complex (**2**) with a freshly polished glassy carbon electrode (area = 0.071 cm^2) in oxygen-free DMF containing 0.10 M TBABF₄ and different concentrations of 1-iododecane: (A) no 1-iododecane; (B) 2.00 mM 1-iododecane; (C) 5.00 mM 1-iododecane. Scan A goes from -0.75 to -2.00 to -0.75 V vs. SCE; scan B goes from -0.75 to -2.20 to -0.75 V vs. SCE; scan C goes from -0.75 to -1.93 to -0.75 V vs. SCE.

CAPTIONS FOR SCHEME AND FIGURES (continued)

Fig. 5. Cyclic voltammetric electropolymerization at a scan rate of 100 mV s⁻¹ of the cobalt(II) complex (2.00 mM) in DMF containing 0.10 M TBAP at a freshly polished glassy carbon electrode (area = 0.071 cm^2). Note that the first of 10 consecutive scans is denoted by the dotted curve, and the arrow indicates that each successive scan begins at 0 V, goes to +1.50 V, then to -1.80 V, and back to 0 V vs. SCE.







Figure 3 Ourari, Messall, Ouennoughi, Aggoun, Bouzerafa, Mubarak, Strawsine, and Peters "Synthesis, characterization, and electrochemical behavior of a cobalt(II) salen-like complex" 10 0 -10 -20 Current (µA) -30 -40 -50 -60 -70 -80 -2.5 -2.0 -1.5 -1.0 Potential (V) RCU





Table 1

Ourari, Messall, Ouennoughi, Aggoun, Bouzerafa, Mubarak, Strawsine, and Peters "Synthesis, characterization, and electrochemical behavior of a cobalt(II) salen-like complex"

Table 1

Results of thermogravimetric analysis (TGA) of the ligand (1) and its cobalt(II) complex (2).

	Compound	Temperature range (°C)	Mass loss (%)		Proposed species lost
			Observed	Calculated	
	1	200–332	38.46	39.70	$2 C_7 H_8 N$
		332–532	24.61	24.91	C ₉ H ₉ O
	2	128–186	5.07	4.83	$2 H_2O$
		186–350	30.35	30.19	2 OAc + <i>N</i> -methylaniline
		350-473	14.64	14.36	N-methylaniline
		473–640	14.64	14.10	C ₇ H ₅ O
		640-820	11.42	11.15	C ₅ H ₉ N
P					

Graphical abstract

A new cobalt(II)-Schiff base complex has been prepared and characterized; its electrochemistry has been investigated, catalytic reduction of 1-iododecane by the corresponding electrogenerated cobalt(I) species has been probed, and the complex has been anodically polymerized onto glassy carbon.

