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Research Article

Synthesis and Characterization of Chloridobis(dimethylglyoximato)4-(2-ferrocenylvinyl)pyridinecobalt(III): A New Heterobinuclear Cobaloxime

Sebastián Pizarro, Guillermo Saá, Francisco Gajardo, and Alvaro Delgadillo

Departamento de Química, Facultad de Ciencias, Universidad de La Serena, Casilla 599, Benavente 980, 1720170 La Serena, Chile

Correspondence should be addressed to Alvaro Delgadillo; adelgadillo@userena.cl

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The synthesis of a new heterobinuclear cobaloxime with 4-(2-ferrocenylvinyl)pyridine, fcvpy, is reported. The complex $[CoCl(dmgH)_2(fcvpy)]$, where $dmgH_2$ is dimethylglyoxime and dmgH is dimethylglyoximato, has been characterized by ^{1}H-NMR, UV-Vis, cyclic voltammetry, and elemental analysis. The cyclic voltammogram of this complex shows a fc/fc$^+$ reversible wave at +0.58 V versus Ag/AgCl, one irreversible wave, $E_{pc} = -0.54$ V versus Ag/AgCl, assigned to the reduction of Co(III) to Co(II), and two quasireversible processes at −1.02 V and −1.10 V versus Ag/AgCl associated with the reduction of Co(II). The complex showed ferrocene-ligand charge transfer bands at 334 nm and 505 nm. TDDFT/B3LYP/6-31G(d) calculations support this assignation.

1. Introduction

The cobaloximes, a family of pseudomacrocyclic bis(dialkylglyoximato)cobalt complexes, have been intensively studied over the past four decades since they are good models of vitamin B_{12} and related compounds [1]. Recently, the interest in these kinds of complexes has emerged again since they could be employed in proton electroreduction reactions for the production of dihydrogen [2–4] or the dehalogenation of organochloride volatile compounds [5, 6].

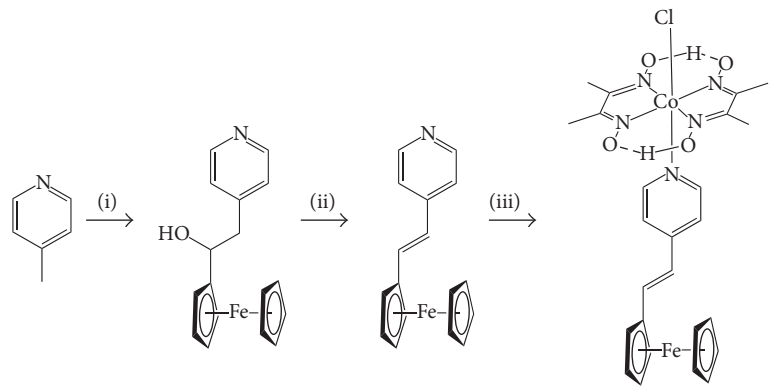
Usually, cobaloximes have the general formula $[CoL(D_{OX})_2B]$, where L is an anionic ligand to cobalt, B is an axial base *trans* to the anionic ligand, and D_{OX} is a monoanionic dioxime ligand. Generally, alteration of these building blocks has a great impact on the catalytic properties of the cobalt center. Several base ligands, B, were studied to understand the electronic and steric properties of the anionic L ligand [7–9]. In the same way, the substitution of the glyoxime equatorial ligands [10–12] was made in order to tune the electrochemical potentials of the cobalt center.

Despite the fact a large number of mononuclear cobaloxime complexes have been reported, the synthesis of binuclear cobaloxime complexes is relatively scarce. Bhuyan et al. have reported the preparation of homobinuclear cobaloximes using bidentate pyridyl bridge ligands [13, 14]. More recently, some heterobinuclear ruthenium [15, 16] and platinum [17] cobaloxime complexes have been synthesized for the photocatalytic hydrogen production.

Herein, we report the synthesis of a new cobaloxime where the pyridine axial ligand has been functionalized with a ferrocene unit. This new heterobinuclear complex was characterized using spectroscopic and electrochemical techniques to study the influence of the organometallic substituent on the electrochemical properties of the cobalt center.

2. Materials and Methods

2.1. Apparatus and Reagents. All reagents were from commercial sources and were used without further purification. 4-Methylpyridine (98%), ferrocenecarboxaldehyde (98%), phosphorus(V) oxychloride (99%), lithium diisopropylamide solution (2 M), and tetrahydrofuran (99.9%) were purchased from Aldrich; sodium sulphate (99%) was purchased from Merck.



Scheme 1: Synthesis of the compounds used in this study: (i) LDA and THF, (ii) $POCl_3$, and (iii) $[CoCl_2(dmgH_2)(dmgH)]$.

$[CoCl(dmgH)_2(py)]$ [18] and $[CoCl_2(dmgH)(dmgH_2)]$ [19] were synthesized as reported in the literature. Solvents were HPLC grade and were used as received with the exception of tetrahydrofuran (THF) which was dried and distilled from sodium.

Absorption spectra were measured on a Spekol UV-Vis 1200 spectrophotometer. Electrochemical measurements were performed using a Princeton Applied Research PG 580 potentiostat and a classical three-electrode setup consistent on vitreous carbon flat disk working electrode (3 mm diameter), a Pt wire auxiliary electrode, and an Ag/AgCl reference electrode. ^{1}H-NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer using $CDCl_3$. Chemical shifts are expressed in parts per million (δ/ppm) downfield from tetramethylsilane (TMS). Elemental analyses were performed on a Fisons Instrument Analyzer, model EA1108/CHNS-O, with PC NCR system 3225.

All molecular geometries were calculated by density functional theory (DFT) with the B3LYP functional and the 6-31G(d) basis set. Tighter convergence criteria were specified, to ensure finding the exact geometrical minima. Frequencies were calculated and checked to make sure that all of them were positive. Solvent environment effects were described by using the polarizable continuum model (PCM) with the integral equation formalism variant for acetonitrile. The adiabatic approximation of time dependent DFT was used to solve for 30 singlet excited states. All calculations were done in Gaussian 09W [20].

2.2. 1-Ferrocenyl-2-(pyridine-4-yl)ethanol. 1 cm^3 of 4-methylpyridine (10.27 mmol) was dissolved in 20 cm^3 of dry THF. The solution was cooled in liquid nitrogen ethanol bath. To the chilled solution 5.2 cm^3 of lithium diisopropyl amide, LDA 2.0 M was added. The solution formed was stirred for one hour; the liquid nitrogen ethanol bath was then changed for an ice bath and 2.2 g of ferrocene carboxaldehyde (5 mmol) in 15 cm^3 of dry THF was added. The solution was stirred overnight, subsequently quenched with water, and extracted four times with chloroform (15 cm^3). The organic phase was dried with anhydrous sodium sulphate and the solvent was eliminated. The solid obtained was used without further purification.

2.3. 4-(2-Ferrocenylvinyl)pyridine. 2.6 g of 1-ferrocenyl-2-(pyridine-4-yl)ethanol (1.22 mmol) and 3 cm^3 of phosphorous oxychloride were dissolved in pyridine; the resulting solution was refluxed for 5 hours. Afterwards, the solution was cooled, poured onto water, and then extracted four times with chloroform (15 cm^3). The organic phase was dried with anhydrous sodium sulphate and the solvent was eliminated. The solid obtained was recrystallized from acetonitrile. Yield 90%. UV-Vis (CH_3CN, nm) 266, 311, 379, 466. ^{1}H-NMR 400 MHz ($CDCl_3$ ppm) 8.5 (d, 2H pyridine ring); 7.3 (d, 2H pyridine ring); 7.1 (d, 1H vinyl); 6.6 (d, 1H vinyl); 4.5 (s, 2H substituted cp ring); 4.3 (s, 2H substituted cp ring); 4.1 (s, 5H cp ring). Elemental analysis calculated (%) for $C_{17}H_{15}FeN$: C 70.61; H 5.23; N 4.84 Found C 70.34; H 5.63; N 4.37.

2.4. Chloro(4-(2-ferrocenylvinyl)pyridine)bis(dimethylglyoximato)cobalt(III) $[CoCl(dmgH)_2(fcvpy)]$. 0.10 g (0.27 mmol) of $[Co(dmgH)(dmgH_2)Cl_2]$ and 0.08 g (0.27 mmol) of 4-(2-ferrocenylvinyl)pyridine in 50 cm^3 of ethanol were heated to reflux for 2 hours. The solvent was evaporated and the resulting solid purified using silica gel chromatography. Yield 55%. UV-Vis (CH_3CN, nm) 335, 503. ^{1}H-RMN 400 MHz ($CDCl_3$ ppm) 8.06 (d, 2H pyridine ring); 7.16 (d, 1H vinyl); 7.12 (d, 2H pyridine ring); 6.44 (d, 1H vinyl); 4.49 (s, 2H substituted cp ring); 4.43 (s, 2H substituted cp ring); 4.12 (s, 5H cp ring); 2.41 (s, 12H CH_3 dioxime). Elemental analysis calculated (%) for $C_{25}H_{29}ClCoFeN_5O_4$: C 48.92; H 4.76; N 11.41 Found C 48.69; H 5.01; N 11.18.

3. Results and Discussion

3.1. Synthesis. The ligand 4-(2-ferrocenylvinyl)pyridine, fcvpy, was synthesized in two steps as is illustrated in Scheme 1. The first step consisted in the lithiation of 4-methylpyridine with lithium diisopropylamide which reacted subsequently with ferrocenecarboxaldehyde to form 1-ferrocenyl-2-(pyridine-4-yl)ethanol. The second step was the dehydration of the former compound with phosphorous oxychloride to obtain the desired ligand with high yields. A similar procedure was previously described by Yang et al. [21] but

Table 1: Spectroscopic and electrochemical properties of 4-(2-ferrocenylvinyl)pyridine, fcvpy, and $[CoCl(dmgH)_2(fcvpy)]$.

	λ_{abs}(nm)[b]	$E_{1/2}$ fc^+/fc (V versus Ag/AgCl)	E_{pc} Co(III/II) (V versus Ag/AgCl)	$E_{1/2}$ Co(II/I) (V versus Ag/AgCl)
Ferrocene[a]	420	0.41	—	—
fcvpy	310, 460	0.48	—	—
$[CoCl(dmgH)_2py]$[a]	255	—	−0.64	−1.03
$[CoCl(dmgH)_2(fcvpy)]$	334, 505	0.58	−0.54	−1.02

[a]Ferrocene and $[CoCl(dmgH)_2py]$ are included as reference. [b]Measured in CH_3CN solution.

employing a different dehydration agent. Finally, the 4-(2-ferrocenylvinyl)pyridine ligand reacts straightforwardly with $[Co(dmgH)(dmgH_2)Cl_2]$ to form the complex of interest.

Figure S1 (in Supplementary Material, page 3, available online at http://dx.doi.org/10.1155/2016/1385236) shows the 400 MHz ^{1}H-NMR spectra of the cobaloxime with 4-(2-ferrocenylvinyl)pyridine recorded in $CDCl_3$. A set of two doublets at 8.06 ppm and 7.12 ppm are observed and assigned to the protons of the pyridine ring. The chemical shifts for these protons are displaced to higher field in contrast to the uncoordinated ligand, fcvpy (8.5 ppm and 7.3 ppm), evidencing the coordination to the cobalt center. On the other hand, the AB system of the ethene bridge shows relatively low field (7.16 and 6.44 ppm) with a coupling constant, J_{AB} = 15.4 Hz, which indicates a *trans* geometry for the ligand. The inset in Figure S1 shows the characteristic pattern of proton signals for the monosubstituted and the unsubstituted cyclopentadiene rings [22]. The protons of the methyl groups corresponding to the dimethylglyoximate ligand appear at 2.41 ppm; the integration of these signals is in completely concordance with the structure depicted in Figure S1 (supplementary material, page 3). Chemical shifts for the oxime protons were not observed in the −2.0–18.0 ppm interval used in the NMR experiments.

The spectroscopic and electrochemical data of the compounds under study as well as reference compounds for comparison are presented in Table 1. The electronic spectra of the uncoordinated fcvpy ligand as well as the new cobaloxime are shown in Figure 1. Both compounds present low energy absorption bands, which have been reported in other compounds featuring a ferrocenyl moiety coupled to an organic acceptor region [23]. These bands could be catalogued as ferrocene to ligand charge transfer bands.

In order to support the assignation of the electronic transitions, computational calculations were made. Initially, the geometry of the ligand, fcvpy, as well as the cobaloxime was optimized in gas phase using the DFT/B3LYP/6-31G(d) level of theory.

Figures S2 and S3 (supplementary material, pages 3 and 4) show the optimized geometries of the free ferrocenylvinyl pyridine and the cobaloxime. In both the ligand and the complex, the computed C-C bond lengths in the cyclopentadienyl rings (cp) of the ferrocenes are in the range 1.42–1.43 Å that agrees with the experimental data of relatively similar compounds [24].

In the $[CoCl(dmgH)_2(fcvpy)]$ complex (see Figure S3 of supplementary material), the Co(III) ion is coordinated to two coplanar dimethylglyoximate ligands and a chloride

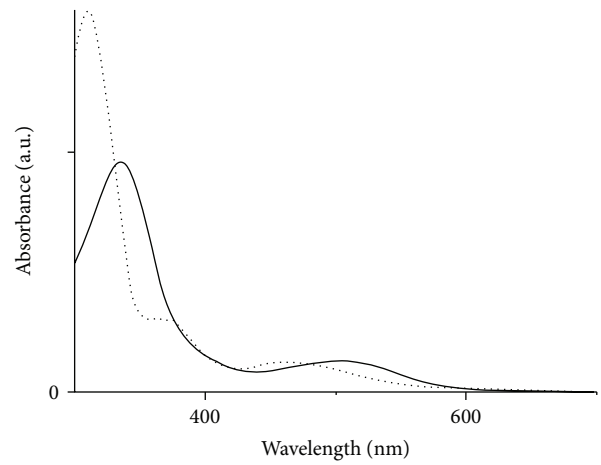


Figure 1: Electronic absorption spectra of 4-(2-ferrocenylvinyl)pyridine (dotted line) and $[CoCl(dmgH)_2(fcvpy)]$ solid line.

trans to the fcvpy ligand. The calculated Co-N_{fcvpy} distance, 1.976 Å, and CoCl distance, 2.265 Å, are slightly higher than the experimental values reported for the $[CoCl(dmgH)_2py]$, 1.959 Å for Co-N_{py} and 2.229 for CoCl [25].

Subsequently, TDDFT/B3LYP/6-31G(d) calculations were performed including the IEFPCM model to simulate an acetonitrile environment. Maximum wavelength, oscillator frequency, major contributions, and representative surfaces, for both 4-(2-ferrocenylvinyl)pyridine (Tables TS1 and TS2) and the $[CoCl(dmgH)_2(fcvpy)]$ complex (Tables TS3 and TS4), are resumed on the supplementary material.

Figures S4 and S5 (supplementary material) show their calculated spectra; they correlate well with the strong absorptions of the UV region and with the less intense absorptions of the visible region associated with the ferrocenyl moiety.

A bathochromic shift of these bands is observed upon coordination of the fcvpy ligand to the cobalt center; this is in agreement with the expected stabilization of the π^* orbitals of the pyridine ring.

The calculations indicate that, in both compounds, the lowest energy bands can be assigned to transitions between mainly nonbonding metal orbitals of the ferrocene moiety, for example, the HOMO, to empty π^* orbitals of the pyridine ring. Figure 2 shows the molecular orbital surfaces involved in these transitions.

The cyclic voltammogram of $[CoCl(dmgH)_2(fcvpy)]$ recorded in acetonitrile is shown in Figure 3. A reversible

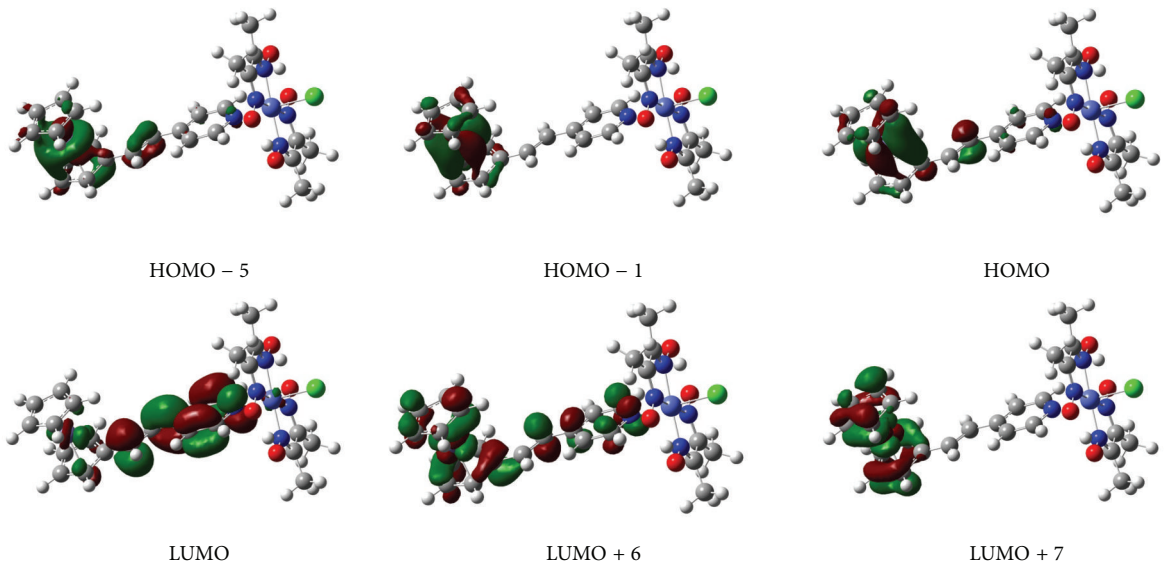


Figure 2: Surfaces of the molecular orbitals involved in the transitions of the $[CoCl(dmgH)_2(fcvpy)]$ absorption spectrum.

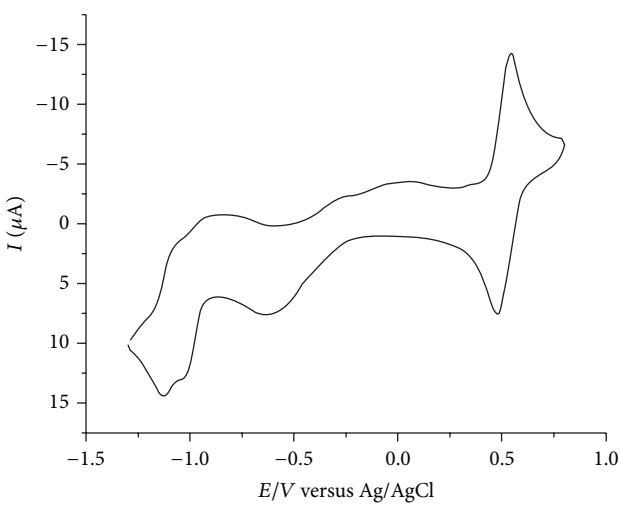


Figure 3: Cyclic voltammogram of $[CoCl(dmgH)_2(fcvpy)]$ recorded in acetonitrile solution of n-Bu_4NPF_6 (0.1 mol dm^{-3}) on a glassy carbon electrode at 100 mVs^{-1}.

wave can be observed at +0.58 V versus Ag/AgCl which is assigned to the fc/fc$^+$ couple. This half-wave potential is displaced to more positive values than the uncoordinated ligand (+0.48 V versus Ag/AgCl) and ferrocene (+0.41 V versus Ag/AgCl) denoting the electron withdrawal character of the pyridine region.

Also, one irreversible wave, E_{pc} = −0.54 V versus Ag/AgCl, is observed, assigned to the reduction of Co(III) to Co(II) followed by two quasireversible processes at −1.02 V and −1.10 V versus Ag/AgCl, respectively. The presence of these two waves differs from the behavior reported for similar cobaloximes where usually only one reversible wave assigned to the Co(II)/Co(I) couple is observed [26]. We postulate that the behavior observed is due to a side reaction which could involve the polymerization or the isomerization of the vinylpyridine moiety which has been reported for compounds with a relatively similar structure [27]. After several cycles, just a single quasireversible wave is observed. These cyclic voltammograms are shown in the supplementary data, Figures S6 and S7, respectively (supplementary material).

The results shown above suggest a small interaction between the metallic centers, if any. Nevertheless, the presence of charge transfer bands resulting from the inclusion of ferrocene to the axial ligand could be exploited to obtain, by a photochemical way, a cobalt center in a lower oxidation state which could be potentially used in catalytic applications.

4. Conclusions

In conclusion, a new heterobinuclear complex $[CoCl(dmgH)_2(fcvpy)]$ was prepared by direct reaction between 4-(2-ferrocenylvinyl)pyridine and $[Co(dmgH)(dmgH_2)Cl_2]$. This cobaloxime shows absorption bands in the visible region assigned to charge transfers between the ferrocene moiety and the pyridine region of the fcvpy ligand.

The electrochemical experiments showed that the redox potential of the ferrocenyl moiety is displaced to more positive potentials by coordination to the cobalt center, but compared with the $[CoCl(dmgH)_2(fcvpy)]$ complex, the inclusion of the ferrocenyl moiety on the axial pyridine ring has no significant influence on the reduction potentials of the cobalt center.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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