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Synthesis and Characterization of a New Cobaloxime-Terpyridine Compound

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Abstract: A new cobaloxime was synthesized by the reaction of cobalt chloride and diphenylglyoxime in methanol, followed by the addition of 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine, pytpy. This complex was characterized by UV–Vis spectroscopy, ^{1}H-NMR spectroscopy, cyclic voltammetry, and single-crystal X-ray diffraction analysis. In cyclic voltammetry experiments an irreversible reduction wave assigned to Co(III)/Co(II) at Ecp = −0.31 V vs. Ag/AgCl and a quasi-reversible process assigned to the Co(II)/Co(I) reduction at −0.72 V vs. Ag/AgCl were observed. The crystal of the complex belongs to the triclinic space group P1 with a = 12.4698(6) Å, b = 14.1285(8) Å, c = 15.5801(8) Å, α = 109.681(4)°, β = 112.975(4)°, γ = 81.67(96.414(4)°3)°, V = 2284.0(2) Å^3, Z = 2, Dc = 1.408 mg·m^{-3}, μ = 0.66 mm^{-1}, F(000) = 996, and final R1 = 0.0564, ωR2 = 0.1502.

Keywords: cobalt; cobaloxime; cyclic voltammetry; terpyridine; X-ray structure

1. Introduction

The cobaloximes are a family of vic-dioxime cobalt complexes known from a long time [1]. The interest on these compounds has emerged recently due to their ability to catalyze the reduction of protons at low overpotentials in non-aqueous solvents [2–4]. Several mechanisms for the production of dihydrogen has been proposed [5,6], most of them consider the presence of cobalt in a low oxidation state.

Since the most common oxidation potentials for these complexes are +3 and +2, a reduction process must happen before the proton reduction occurs. To accomplish the reduction of the cobalt center, a number of methods have been employed, electrochemical [7] and photochemical reductions [8] have been reported.

In several studies, the cobaloxime moiety has been bound to a photosensitizer in order to reduce the cobalt center by a photoinduced electron transfer [9,10]. The synthesis of photosensitizers bearing a cobaloxime unit could be sometimes laborious, therefore the design and preparation of new cobaloximes which could be easily introduced in the structure of metallic photosensitizers are attractive.

In this work, we show the preparation as well the electrochemical, spectroscopic, and structural characterization of a novel cobaloxime which could be used as a ligand in the formation of polynuclear coordination compounds that could be potentially used in the photocatalytic generation of dihydrogen.

2. Results and Discussion

2.1. Synthesis

The 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine ligand was synthesized by modifying procedures described in the literature. The synthesis was performed by condensation between 4-pyridinecarboxaldehyde and two equivalents of 2-acetylpyridine in the presence of a sodium methoxide solution, finally condensation of the product was conducted with ammonium acetate to obtain the desired ligand with high yields.

The complex [CoCl(dpg)($dpgH_2$)(pytpy)], where $dpgH_2$ is diphenylglyoxime, dpg is diphenylglyoxamate and pytpy is 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine, was prepared in a two-step synthesis by the reaction of cobalt chloride and diphenylglyoxime in methanol, followed by the addition of pytpy as shown in Figure 1.

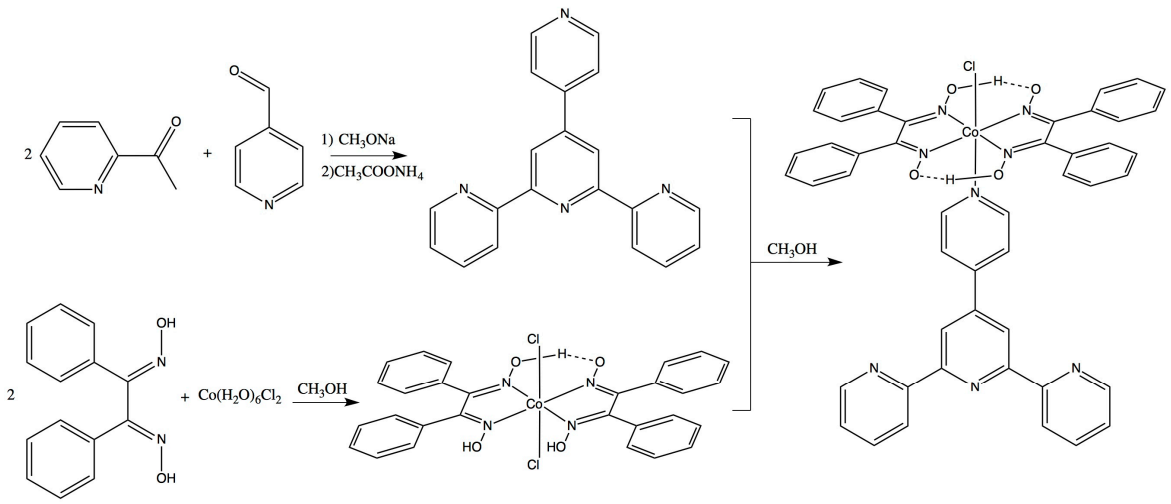

Figure 1. Synthetic route to prepare the [CoCl($dpgH)_2$(pytpy)] complex.

2.2. ^{1}H-NMR

Figure 2 shows the proton magnetic resonance spectrum for [CoCl($dpgH)_2$(pytpy)] recorded in DMSO-d6. In this spectrum, we observe a pair of signals with a chemical shift of 7.23 and 7.34 ppm which make up the equivalent of 8 and 12 protons respectively, assigned to protons 1 and 2 corresponding to the phenyl rings in the ligand dpgH. At the lower field of the signals corresponding to the pytpy ligand. With a chemical displacement of 8.25 and 8.50 ppm, integrating the equivalent of two protons assigned to hydrogens 4 and 3 respectively correspond to the protons of the pyridine ring that is directly bound to the cobalt center. The protons 9, 6, and 5 appear in a very low field, specifically 8.67, 8.75, and 8.77 ppm, this is due to the anisotropic currents generated by the pyridine rings. Finally, with a chemical displacement of 7.55 and 8.05 ppm that comprises an equivalent of two protons for each, this signal is assigned to hydrogens 8 and 7.

2.3. UV–Vis Spectroscopy

Figure 3 shows the UV–Vis spectra registered in dichloromethane solution, the maximum wavelength of highest intensity band is observed at 270 nm, followed by two unresolved bands at ca. 330 nm and 400 nm, respectively. These bands are ascribed to terpyridine based $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

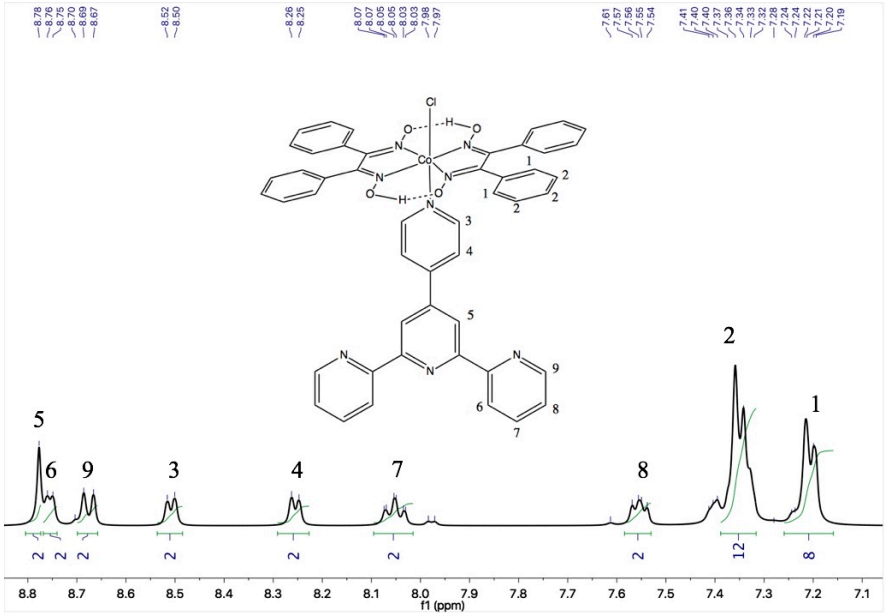

Figure 2. ^{1}H-NMR spectrum for [CoCl(dpgH)$_2$(pytpy)] recorded in DMSO-d6. The insertion of this figure shows the structure of the complex and the numbering of the protons used for the assignment of the signals.

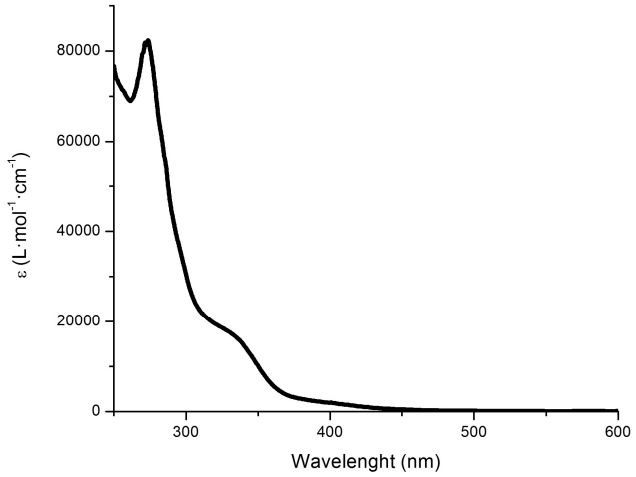

Figure 3. UV–Vis spectra for [CoCl(dpgH)$_2$(pytpy)] recorded in dichloromethane.

2.4. Electrochemistry

The electrochemical properties of the complex were investigated using cyclic voltammetry. Figure 4 shows the cyclic voltammogram of the complex registered in a 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) DMF solution.

An irreversible reduction wave assigned to the Co(III)/Co(II) is observed at Ecp = −0.31 V vs. Ag/AgCl, this wave is broad and unresolved due to the equilibrium associated with the axial chloride lost. A quasi-reversible process assigned to the Co(II)/Co(I) reduction is observed at −0.72 V vs. Ag/AgCl, this last process is termed quasi-reversible since the separation of the cathodic and anodic peak potential is ΔE = 0.08 V. Finally, an anodic irreversible process is observed at Eap = 0.1 V vs. Ag/AgCl and assigned to the Co(II)/Co(III) oxidation. A similar electrochemical behavior has been reported for other cobaloximes with different dioxime ligands [11]. Table 1 resumes the electrochemical data obtained for [CoCl(dpgH)$_2$(pytpy)] together with those of reference compounds for comparison.

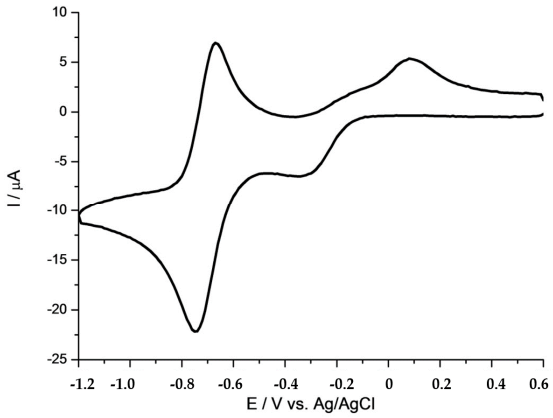

Figure 4. Cyclic voltammogram of $[CoCl(dpgH)_2(pytpy)]$ taken at 0.1 V/s in DMF 0.1 M $TBAPF_6$ using a vitreous carbon working electrode. Fc+/Fc vs. Ag/AgCl = 0.55 V in DMF [12].

Table 1. Electrochemical data of $[CoCl(dpgH)_2(pytpy)]$ and $[CoCl(dpgH)_2(py)]$.

Compound	E_{pc} $Co^{III/II}$ (V)	$E_{1/2}$ $Co^{II/I}$ (V)
$[CoCl(dpgH)_2(py)]$ #	−0.43	−0.71
$[CoCl(dpgH)_2(pytpy)]$	−0.32	−0.72

All data were measured in 0.1 M $TBAPF_6$ DMF solution using a vitreous carbon working electrode (0.07 cm^2)
py is pyridine. Fc+/Fc vs. Ag/AgCl = 0.55 V in DMF [12].

The cathodic peak assigned to the CoIII/II reduction in the $[CoCl(dpgH)_2(pytpy)]$ is observed at more positive potentials than the parent complex $[CoCl(dpgH)_2(py)]$, suggesting an influence of the pytpy axial ligand on the chloride lost equilibrium [8]. On the other hand, the Co(II)/Co(I) reduction wave appears, between the experimental error, at the same potential.

2.5. X-ray Crystallography

Slow diffusion of ethylic ether in a dichloromethane solution of the compound yielded appropriate crystals for X-ray diffraction studies. The refined structure is shown in Figure 5. Cobalt is octahedrally coordinated to a diphenylglyoximate ligand (dpg) and a diphenylglyoxime ligand ($dpgH_2$) in the equatorial plane. The axial sites are occupied by a chloride anion and a nitrogen of the pyridine residue of the 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine ligand. Representative bond distances and bond angles of the coordination sphere are listed in Table 2.

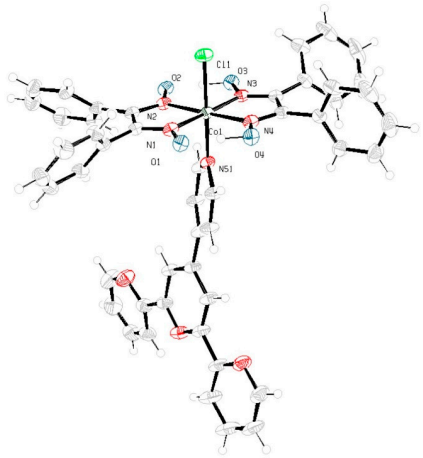

Figure 5. Oak Ridge Thermal Ellipsoid Plot (ORTEP) of $[CoCl(dpgH)_2(pytpy)]$ (50% probability displacement ellipsoids).

Table 2. Selected bond lengths and bond angles for [CoCl(dpgH)$_2$(pytpy)].

Bond Length (Å)		Bond Angles (°)	
Co1-N1	1.8930	N1-Co1-N2	81.880
Co1-N2	1.8866	N2-Co1-N3	98.672
Co1-N3	1.8995	N3-O3-H1	101.476
Co1-N4	1.8945	N1-C1-C2	112.681
Co1-N5	1.9640	N2-C2-C1	112.563
Co1-Cl1	2.2236	N3-C3-C4	111.986
N1-C1	1.3030	N4-C4-C3	112.946
N2-C2	1.3050	Cl1-Co1-N1	89.776
N3-C3	1.2980	N1-Co1-N5	89.770
N4-C4	1.2945	N3-O3-H1	101.476
N1-O1	1.3332	N4-O4-H2	102.600
N2-O2	1.3370	O1-N1-C1	121.800
N3-O3	1.3463	O2-N2-C2	121.870
N4-O4	1.3453		

The crystallographic data of this complex is summarized in Table 3.

Table 3. Experimental details of the crystal structure determination.

Property	
Empirical formula	$C_{49}H_{38}Cl_3CoN_8O_4$
Temperature	173(2) K
Crystal system	Triclinic
Space group	P-1
a	12.4698(6) Å
b	14.1285(8) Å
c	15.5801(8) Å
α	109.681(4)°
β	112.975(4)°
γ	96.414(4)°
Volume	2284.0(2) Å^3
Z	2
Density (calculated)	1.408 Mg/m^3
Absorption coefficient	0.606 mm^{-1}
F(000)	996
Crystal size	0.370 × 0.350 × 0.340 mm^3
Theta range for data collection	3.191° to 26.452°
Index ranges	$-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$
Reflections collected	41,194
Independent reflections	9334 [R(int) = 0.0560]
Completeness to theta = 25.000°	99.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9334/0/604
Goodness-of-fit on F^2	0.987
Final R indices [I > 2sigma(I)]	R1 = 0.0564, wR2 = 0.1502
R indices (all data)	R1 = 0.0630, wR2 = 0.1552
Extinction coefficient	n/a

3. Materials and Methods

3.1. Apparatus and Reagents

All reagents were from commercial sources and were used without further purification. Anti-diphenylglyoxime (97%), 4-pyridinecarboxaldehyde (97%), 2-acetylpyridine (99%), and cobalt(II)

chloride hexahydrate (97%) were purchased from Aldrich, sodium hydroxide (98%), methanol was purchased from Merck.

The absorption spectra were obtained using a Jasco 530 UV–Visible spectrophotometer (Tokyo, Japan). Electrochemical measurements were performed using a Princeton Applied Research PG 580 potentiostat and a classical three-electrode setup consistent on a vitreous carbon flat disk working electrode (3 mm diameter), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. NMR spectra were recorded on a Brucker AVANCE 400 MHz spectrometer (Bremen, Germany) using DMSO-d6 with tetramethylsilane (TMS) as internal reference. High-resolution mass spectrometer Exactive™ Plus Orbitrap, ThermoFisher Scientific (Bremen, Germany). Scan parameters: Resolution: 140,000, automatic gain control target: 1e6, Max. inject time: 200. HESI source: Sheath gas flow: 12, Aux gas flow rate: 2, Sweep gas flow rate: 0, Capillary temp.: 300 °C, S-lens RF level: 100, Heater temp: 100 °C.

The complex $Co(dpgH_2)(dpgH)Cl_2$ was synthesized as reported in the literature [13].

3.2. 4′-(4′-Pyridyl)-2,2′:6′,2″-Terpyridine (Pytpy)

4-pyridinecarboxaldehyde (0.88; 8.20 mmol) was dissolved in 10.0 mL of methanol, then a mixture of 2-acetylpyridine (2.0 g; 16.4 mmol) and 1.0 mL of 10% sodium methoxide solution was added. The solution was stirred for three hours at 0 °C and then ammonium acetate (1.50 g; 20.0 mmol) was added along with 20.0 mL of methanol, the mixture was brought to reflux conditions for 3 h. The white solid is filtered and washed with two portions of cold methanol and then recrystallized by slow evaporation of a methanol/chloroform mixture (10/3). Yield 1.2 g (47%). UV/Vis ($CHCl_3$, nm): 247, 279, 319. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.2 Hz, 2H), 8.75 (s, 2H), 8.72 (d, *J* = 4.2 *J* = 7.8, 1.6 Hz, 2H), 7.80–7.76 (m, 2H), 7.36 (dd, *J* = 6.9, 5.3 Hz, 2H).

3.3. Synthesis of [CoCl(dpgH)$_2$(Pytpy)]

$Co(dpgH_2)(dpgH)Cl_2$ (0.40 g, 0.65 mmol) and pytpy (0.20 g, 0.65 mmol) were mixed in 15.0 mL of methanol. The mixture was brought to reflux conditions for six hours. The solid formed is filtered and washed with portions of methanol and finally crystallized by slow diffusion between dichloromethane and ether. Yield 0.32 g (55%). ^{1}H-RMN (400 MHz, DMSO-d_6) δ 8.77 (s, 2H), 8.75 (d, *J* = 4.8 Hz, 2H), 8.67 (d, *J* = 7.9 Hz, 2H), 8.50 (d, *J* = 6.1 Hz, 2H), 8.25 (d, *J* = 6.1 Hz, 2H), 8.05 (td, *J* = 7.8, 1.8 Hz, 2H), 7.55 (dd, *J* = 7.4, 5.0 Hz, 2H), 7.34 (d, *J* = 6.9 Hz, 12H), 7.23–7.17 (m, 8H). MS *m*/*z*: Calculated: 883.20; Found: 883.1935.

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1535750. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

4. Conclusions

The new cobaloxime [CoCl(dpgH)$_2$(pytpy)] was successfully prepared and fully characterized; the spectroscopic and electrochemical properties are similar to previously reported cobaloximes, maintaining its ability to achieve the Co(I) oxidation state at relatively positive potentials. The terpyridine moiety of the axial ligand contains three nitrogen atoms which are available for coordination to other metal centers, making the capacity to form binuclear complexes easier.

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Author Contributions: Alvaro Delgadillo and Ivan Brito conceived and designed the experiments; Priscilla Astudillo performed the synthesis of the compounds; Sebastian Pizarro performed the electrochemical experiments; Francisco Gajardo prepared samples for RMN and UV–Vis spectroscopy, Ivan Brito performed X-ray diffraction experiments and solve the structure.

Conflicts of Interest: The authors declare no conflict of interest.

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