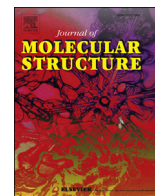




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The synthesis and investigation of different cobaloximines by spectroscopic methods

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ABSTRACT

In the present work, firstly a novel monoxime (**1**) and unsymmetric dioxime ligand (**LH₂**) (**2**) derived from 4-(4-hydroxyphenyl)-2-butanone as ketone was prepared under optimum conditions. Then, the cobaloxime complexes [(LH)₂ClCoB] (B = neutral base: **4-DAP** = 4-(dimethylamino)pyridine, **4-HP** = 4-hydroxypyridine, **4-CP** = 4-chloropyridine, **4-MP** = 4-methylpyridine, **4-EP** = 4-ethylpyridine, **4-TBP** = 4-*tert*-butylpyridine and **P** = pyridine) (**3–9**) with respect to varied axial groups were synthesized in a two-necked round-bottom reaction flask by direct contact of dioxime ligand (**2**), and different neutral base without special requirement of any additional chemical process. The prepared dioxime ligand (**2**) and its cobaloxime complexes (**3–9**) were characterized by means of NMR, FT-IR, UV–Vis and LC-MS spectroscopy, melting point and magnetic susceptibility measurements as well as elemental analysis. It is noteworthy that the coordination chemistry of this cobaloxime complexes is versatile, which is closely related to the nature of the unsymmetric dioxime ligand (**2**) derived from 4-(4-hydroxyphenyl)-2-butanone, as indicated by the results of the corresponding spectroscopic studies. Also, the spectroscopic results demonstrated that the proposed cobaloxime complexes are a six-coordinated species and octahedral geometry.

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1. Introduction

Because they were previously proposed as good models of Vitamin B₁₂ and related compounds in various metabolisms, over the past four decades, cobaloxime compounds have gained the attention in coordination chemistry, organometallic chemistry, bioinorganic chemistry and broad-scope potential applications. Because their ease of synthesis and characterization and the reactivity of Co–C bond of cobaloximes have provided an experimental test of this approach, the cobaloxime complexes have allowed the investigation of several properties such as the reactivity of Co–C bond and the influence of the axial base on the binding energy of the organo-ligand with the long-term goal to get insight into the yet unestablished mechanism for the hemolysis of the Co–C bond by the AdoCbl-based enzymes [1–3]. The weakening of the Co–C bond of cobaloxime complexes has been evaluated as an effect of

the steric as well as electronic properties of the various axial and equatorial ligands [4]. In addition; various symmetric or unsymmetric dioxime ligand containing cobaloxime compounds are bench stable and could be easily prepared in high yields [5].

Six-coordinated cobaloxime complexes formed from the different symmetric or unsymmetric dioxime ligands and various axial and equatorial ligands interactions have emerged in the past few years as one of the most efficient series of molecular catalysts for hydrogen evolution, and a significant number of studies have been performed to understand the mechanisms of their electro- and photocatalytic activities, due to the low overpotential required [6–10]. However, we recently reported a new generation of cobaloxime/organocobaloxime complexes incorporating different species tetradentate dioxime ligand, which was shown to be remarkable molecular catalysts for the fixation of CO₂ to cyclic carbonates [11–14]. Dreos et al. have reported that different organocobaloximes are good building blocks for the construction of supramolecular structure by the reaction with functionalized aromatic boric acid [15,16]. Kumar and Gupta have reported the synthesis and crystallographic studies of paddlewheel-based methyl cobaloxime assembly formed from methyl cobaloxime, isonicotinic

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acid and $\text{Zn}(\text{NO}_3)_2$ [17]. The N_4 ring in the cobaloxime model complexes is made up of two mono deprotonated different symmetric or unsymmetric dioxime ligands linked at two points by the intermolecular hydrogen bond $\nu(\text{O}-\text{H}\cdots\text{O})$. The result is essentially planar macrocyclic dioxime ligands. Generally, the most common cobaloxime or organocobaloxime compounds have been obtained by using the dimethylglyoxime ligand [18]. In contrast to these studies, in our previous published papers and in this study, the obtained novel dioxime ligands were synthesized from various ketones under optimum conditions.

In this paper, we describe a new the monoxime (**1**) from 4-(4-hydroxyphenyl)-2-butanone as ketone and then dioxime ligand (**2**) have been synthesized under suitable conditions. Then, the structurally different cobaloxime (**3–9**) complexes were obtained by use of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in presence of different axial neutral bases in EtOH solvent. We used various characterization techniques such as; ^1H and ^{13}C NMR, FT-IR, UV-Vis and LC-MS spectroscopy, melting point measurements, magnetic susceptibility measurements and elemental analysis for understanding of the spectroscopic properties of these compounds.

2. Experimental section

2.1. General considerations

All starting materials and other chemical compounds were purchased from a commercial company and used without further purification. Nuclear magnetic resonance (NMR) spectra were acquired at 298 K on a Bruker 300 MHz Ultrashield TM 300 spectrometer (^1H : 300 MHz; ^{13}C : 75.0 MHz) in DMSO- d_6 as solvent and values are reported relative to the internal standard Me_4Si . Chemical shifts were reported in delta (δ) units in ppm downfield from TMS and J values are given in Hertz. Fourier transform infrared (FT-IR) spectra were performed using a Perkin-Elmer Two UATR-FT spectrophotometer in the range of $4000\text{--}400\text{ cm}^{-1}$ at room temperature with equipped ATR accessory. UV-Vis absorption spectra were measured on a Perkin-Elmer model Lambda 25 spectrometer in the scan range of $200\text{--}1100\text{ nm}$ using quartz cuvettes at room temperature and studied in $\text{C}_2\text{H}_5\text{OH}$ and DMF. Elemental analyses were conducted with a LECO CHNS 932 model analyzer and the results were compared with the theoretical values. To understand whether the target molecules occur, LC-MS spectra were obtained on an Agilent LC-MS Spectrometer (LC-MS/MS). To determine the melting point of the novel ligand and its cobaloxime complexes, an Electrothermal 9100 melting point apparatus was used and values were obtained without any correction. Magnetic Susceptibilities were performed on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [19].

2.2. Synthesis of the monoxime (1) and dioxime ligand (LH₂) (2)

In this study, the monoxime (**1**) and dioxime ligand (**LH₂**) (**2**) were prepared from 4-(4-hydroxyphenyl)-2-butanone under optimum conditions, following the similar procedure with some modifications [20]. The corresponding syntheses are briefly given in Scheme 1.

Monoxime (1): Color: brown, yield (%): 84, m. p: 65°C , Elemental Analysis ($\text{C}_{10}\text{H}_{11}\text{NO}_3$, F. W: 193.2 g/mol): Calculated: C, 62.17; H, 5.74; N, 7.25. Found: C, 62.14; H, 5.71; N, 7.22. LC-MS (Scan ES^+): m/z (%) 193.2 [$\text{M}]^+$. FT-IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3368 $\nu(\text{O}-\text{H})$, 3020 $\nu(\text{Ar}-\text{CH})$, 2949–2861 $\nu(\text{Aliph}-\text{CH})$, 1696 $\nu(\text{C}=\text{O})$, 1617 $\nu(\text{C}=\text{N})$, 1594–1511 $\nu(\text{C}=\text{C})$, 1228 $\nu(\text{N}-\text{O})$. ^1H NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 9.62 (s, 1H, $\text{C}=\text{N}-\text{OH}$), 8.46 (s, 1H, $\text{HC}=\text{N}$), 6.96

(d, 2H, $J = 8.4\text{ Hz}$, $\text{Ar}-\text{CH}$), 6.64 (d, 2H, $J = 8.1\text{ Hz}$, $\text{Ar}-\text{CH}$), 5.56 (s, 1H, $\text{Ar}-\text{OH}$), 2.64 (t, 2H, $J = 5.7\text{ Hz}$, CH_2-CH_2) and 2.06 (s, 2H, CH_2-CH_2). ^{13}C NMR (DMSO- d_6 , TMS, 75 MHz, δ ppm): 208.34 ($\text{C}=\text{O}$), 155.40 ($\text{C}=\text{NOH}$), 175.15, 130.98, 128.97 and 115.04 ($\text{Ar}-\text{CH}$), 44.53 (CH_2-CH_2) and 29.70 (CH_2-CH_2). UV-Vis ($\lambda_{\text{max}}/(\text{nm})$, * = shoulder peak): 224, 278 and 324* (in $\text{C}_2\text{H}_5\text{OH}$); 238, 282 and 328* (in DMF).

Dioxime ligand (LH₂) (2): Color: dark brown, yield (%): 80, m. p: 62°C , Elemental Analysis ($\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3$, F. W: 208.2 g/mol): Calculated: C, 57.68; H, 5.81; N, 13.45. Found: C, 57.65; H, 5.78; N, 13.41%. LC-MS (Scan ES^+): m/z (%) 208.2 [$\text{M}]^+$. FT-IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3378 and 3271 $\nu(\text{O}-\text{H})$, 3021 $\nu(\text{Ar}-\text{CH})$, 2961–2852 $\nu(\text{Aliph}-\text{CH})$, 1635 $\nu(\text{C}=\text{N})$, 1550–1509 $\nu(\text{C}=\text{C})$, 1233 $\nu(\text{N}-\text{O})$. ^1H NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 10.32 (s, 2H, $\text{C}=\text{N}-\text{OH}$), 8.56 (s, 1H, $\text{HC}=\text{N}$), 6.95 (d, 2H, $J = 8.4\text{ Hz}$, $\text{Ar}-\text{CH}$), 6.67 (d, 2H, $J = 8.7\text{ Hz}$, $\text{Ar}-\text{CH}$), 5.02 (s, 1H, $\text{Ar}-\text{OH}$), 2.65 (t, 2H, $J = 5.6\text{ Hz}$, CH_2-CH_2) and 2.32 (t, 2H, $J = 5.6\text{ Hz}$, CH_2-CH_2). ^{13}C NMR (DMSO- d_6 , TMS, 75 MHz, δ ppm): 155.62 and 154.61 ($\text{C}=\text{NOH}$), 173.49, 131.08, 128.95 and 115.05 ($\text{Ar}-\text{CH}$), 31.24 (CH_2-CH_2) and 22.70 (CH_2-CH_2). UV-Vis ($\lambda_{\text{max}}/(\text{nm})$, * = shoulder peak): 226, 281 and 318* (in $\text{C}_2\text{H}_5\text{OH}$); 252, 281 and 325* (in DMF).

2.3. Synthesis of the cobaloxime complexes [(LH)₂ClCoB] (3–9)

To a suitable round-bottomed flask containing 50 mL ethanol (99.5%), dioxime ligand (**LH₂**) (**2**) (1.0 g, 4.8 mmol) was added as one portion and the solution was stirred in open air for 40 min for all cobaloxime complexes (**3–9**). While the solution stirring, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.60 g, 2.4 mmol) was added as a solid and the solutions turned green immediately. Then the resulting solutions were refluxed for 5 h. Upon cooling to room temperature, 4-(dimethylamino)pyridine (**4-DAP**) (0.33 g, 2.4 mmol) for [(LH)₂ClCo(4-DAP)] (**3**) complex, 4-hydroxypyridine (**4-HP**) (0.25 g, 2.4 mmol) for [(LH)₂ClCo(4-HP)] (**4**) complex, 4-chloropyridine (**4-CP**) (0.36 g, 2.4 mmol) for [(LH)₂ClCo(4-CP)] (**5**) complex, 4-methylpyridine (**4-MP**) (0.23 g, 2.4 mmol) for [(LH)₂ClCo(4-MP)] (**6**) complex, 4-ethylpyridine (**4-EP**) (0.27 g, 2.4 mmol) for [(LH)₂ClCo(4-EP)] (**7**) complex, 4-*tert*-butylpyridine (**4-TBP**) (0.35 g, 2.4 mmol) for [(LH)₂ClCo(4-TBP)] (**8**) complex, and pyridine (**4-P**) (0.19 g, 2.4 mmol) for [(LH)₂ClCo(4-P)] (**9**) complex were added to mixtures as a neutral base in the presence of air. The initial green solution turned brown or dark brown upon a neutral base and 5.0 mL of water addition. The air was passed through the mixtures for about 5 h. Then, the solvent of the filtrate was removed using rotary evaporation and the desired complexes were isolated by filtration as solids by crystallization from $\text{CHCl}_3/\text{EtOH}$ (1:3). After that, the obtained products were washed with diethyl ether and hexane to afford pure compounds.

[(LH)₂ClCo(4-DAP)] (3): Color: brown, yield: % 68, m. p: $>300^\circ\text{C}$, Elemental Analysis ($\text{C}_{27}\text{H}_{32}\text{N}_6\text{O}_6\text{ClCo}$, F. W: 631.0 g/mol): Calculated: C, 51.40; H, 5.11; N, 13.32. Found: C, 51.37; H, 5.14; N, 13.29%. μ_{eff} = Dia, LC-MS (Scan ES^+): m/z (%) 631.1 [$\text{M}]^+$. FT-IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3547 $\nu(\text{O}-\text{H})$, 3014 $\nu(\text{Ar}-\text{CH})$, 2960–2861 $\nu(\text{Aliph}-\text{CH})$, 1722 $\nu(\text{O}-\text{H}\cdots\text{O})$, 1613 $\nu(\text{C}=\text{N})$, 1564–1443 $\nu(\text{C}=\text{C})$, 1231 $\nu(\text{N}-\text{O})$ and 532 $\nu(\text{Co}-\text{N})$. ^1H NMR (DMSO- d_6 , TMS, 300 MHz, δ ppm): 18.68 (s, 2H, $\text{O}-\text{H}\cdots\text{O}$), 9.36 (s, 2H, $\text{HC}=\text{N}$), 7.70 (s, 4H, $\text{Ar}-\text{CH}$), 6.90 (s, 4H, $\text{Ar}-\text{CH}$), 6.69 (s, 4H, $\text{Ar}-\text{CH}$), 4.52 (s, 2H, $\text{Ar}-\text{OH}$), 1.75 (s, 4H, CH_2-CH_2), 1.29 (s, 4H, CH_2-CH_2) and 0.87 (s, 6H, $\text{N}-(\text{CH}_3)_2$). UV-Vis ($\lambda_{\text{max}}/(\text{nm})$, * = shoulder peak): 228, 260, 280 and 551* (in $\text{C}_2\text{H}_5\text{OH}$); 234, 248, 269 and 597* (in DMF).

[(LH)₂ClCo(4-HP)] (4): Color: brown, yield: % 66, m. p: $>300^\circ\text{C}$, Elemental Analysis ($\text{C}_{25}\text{H}_{27}\text{N}_5\text{O}_7\text{ClCo}$, F. W: 603.9 g/mol): Calculated: C, 49.72; H, 4.51; N, 11.60. Found: C, 49.70; H, 4.48; N, 11.57%. μ_{eff} = Dia, LC-MS (Scan ES^+): m/z (%) 603.8 [$\text{M}]^+$. FT-IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3553 $\nu(\text{O}-\text{H})$, 3086 $\nu(\text{Ar}-\text{CH})$, 2969–2874 $\nu(\text{Aliph}-\text{CH})$, 1724

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