



Synthesis, characterization and structure–property relationship studies of cobaloximes with dithienylglyoxime as the equatorial ligand

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ABSTRACT

The synthesis of cobaloximes, $X/RCo(dThgH)_2Py$ ($X = Cl$, $R = Me$, Et , $n-Pr$, $n-Bu$ and Bn) has been described. All the complexes have been characterized by elemental analyses and NMR spectral studies. The molecular structures of $ClCo(dThgH)_2Py$, $MeCo(dThgH)_2Py$, $EtCo(dThgH)_2Py$ and $BnCo(dThgH)_2Py$ complexes are determined by X-ray crystallography. The electron withdrawing nature of 2-thienyl ring affects the NMR as well as electrochemical behavior of these complexes. The electrochemical reduction from $Co(III)$ to $Co(II)$ and from $Co(II)$ to $Co(I)$ are much easier in $ClCo(dThgH)_2Py$ as compared to chlorocobaloximes with the other dioximes (gH , $dmgH$, $dpgH$, $dmestgH$). The molecular oxygen insertion in the $Co–C$ bond of benzyl complex (**6**) has been examined and a comparison of its reaction rate with other similar cobaloximes is discussed. The structural features of a dioxy complex $Bn(O_2)Co(dThgH)_2Py$ (**7**) have also been reported.

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1. Introduction

The spectral and structural properties of organocobaloximes² have been extensively studied and reviewed [1–5] over the past four decades ever since these have been proposed as structural and functional model of vitamin B₁₂ by G. N. Schrauzer [6–8]. These complexes have established an independent research field by itself due to their use as catalysts in chemical reactions [9,10] and as templates in organic syntheses [11–19]. However, the main interest remains in their role as models of vitamin B₁₂ coenzyme because the studies with cobaloximes have helped to understand the chemistry and biochemistry of B₁₂ coenzyme [20–22].

It is well known that cleavage of $Co–C$ bond is a necessary step in B₁₂-dependent enzymatic as well as cobaloxime-mediated reactions [1,3,11–19]. The weakening of $Co–C$ bond in organocobaloximes has been interpreted as a function of steric as well as electronic properties of R, L, and B ligands [1–3,23,24].

The recent works on organocobaloximes with different dioximes have shown that the effect of dioxime on the $Co–C$ bond (*cis* influence) far exceeds the *trans* influence of the axial base [25–32]. A slight variation in equatorial ligand results in significant change in $Co–C$ bond stability/reactivity as well as NMR chemical shifts. Hence, there has been considerable interest in the synthesis and structural characterization of organocobaloximes with modified equatorial dioxime and also study the structure–property relationship in these complexes.

Keeping the above in view, we have synthesized and characterized a series of $X/RCo(dThgH)_2Py$ ($X = Cl$, $R = Me$, Et , $n-Pr$, $n-Bu$ and Bn , **1–6**) with dithienylglyoxime (*dThgH*) as an equatorial ligand (Scheme 1). All these complexes are new and have been reported for the first time. The molecular structures of **1**, **2**, **3** and **6** have been determined by X-ray crystallography. In addition, we have also studied $Co–C$ bond reactivity in benzyl complex (**6**) with molecular oxygen under photolytic condition. The insertion of molecular oxygen in $Co–C$ bond of complex **6** has resulted in the dioxy complex, $Bn(O_2)Co(dThgH)_2Py$ (**7**). The structural features of oxygen inserted cobaloxime (**7**) are also reported.

2. Results and discussion

2.1. Synthesis of dithienylglyoxime and cobaloximes (**1–7**)

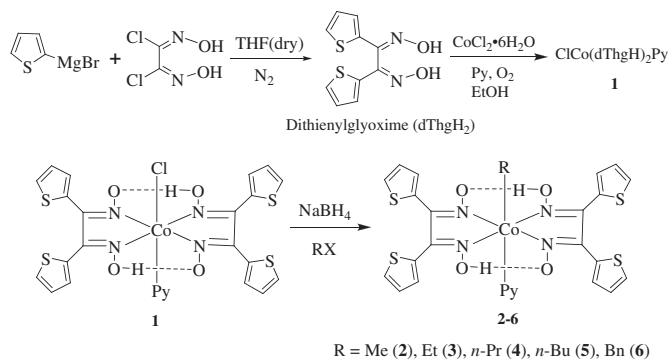
Dithienylglyoxime (*dThgH*₂) was synthesized from (2-thienyl)MgBr and dichloroglyoxime following the procedure developed for

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² Organocobaloximes have the general formula $RCo(L)_2B$, where R is an organic group σ -bonded to cobalt. B is an axial base trans to the organic group and L is a monoanionic dioxime e.g. glyoxime (*gH*), dimethylglyoxime (*dmgH*), 1,2-cyclohexanedione dioxime (*chgH*), diphenylglyoxime (*dpgH*), dimesitylglyoxime (*dmestgH*), bis(thiophenyl)glyoxime (*dSPHgH*) and bis(phenylselanyl)glyoxime (*dSePhgH*).



Scheme 1. Synthesis of dithienylglyoxime (dThgH₂) and cobaloximes (**1–6**).

dmgstgH₂ [33]. The synthetic route is shown in Scheme 1. The 2-thienyl group displaced the chloride of dichloroglyoxime and gave the desired dithienylglyoxime product. The synthesis of ClCo(dThgH₂)₂Py (**1**) was accomplished by refluxing a stoichiometric mixture of CoCl₂·6H₂O, dThgH₂ and pyridine in ethanol/THF solvent mixture followed by the aerial oxidation. We found that the synthesis of **1** in ethanol/THF solvent mixture (1:1) gave better yield (70%) than in ethanol only (30%). The complexes **2–6** were prepared by oxidative alkylation of cobaloxime(I) anion generated *in situ* by NaBH₄ reduction of ClCo(dThgH₂)₂Py in CH₃OH. The reaction of molecular oxygen with benzyl cobaloxime (**6**) in CH₂Cl₂ at 0 °C under visible light proceeds smoothly and the dioxy cobaloxime (**7**) is formed in good yield within 1 h.

2.2. NMR spectral studies (¹H and ¹³C)

¹H and ¹³C NMR data for all complexes (**1–7**) and dThgH₂ are summarized in experimental section. The solubility of free ligand dThgH₂ is poor in CDCl₃ and hence a few drops of DMSO-*d*₆ are necessary to record the NMR. The ¹H NMR spectra of the complexes are easily assigned on the basis of the chemical shifts, their relative intensities and also assignments are consistent with the previously described complexes [25,26,29].

The Co–C bond stability in organocobaloximes depends on both the *cis* and *trans* influences. The *cis* influence study has gained importance only recently [25–32,34–36]. Usually, to study the *cis* influence, either the axial ligands R/X or base B is varied, keeping the same dioxime, or the dioxime is varied, keeping the axial ligands constant and changes are monitored spectroscopically. The NMR studies of cobaloximes with different dioximes have shown that the chemical shifts of Py_α, C=N and the α-carbon bound to cobalt are most affected.

The extent of electron density on the metallabicyclic for different dioximes (keeping R/X and Py constant) can be understood by comparing the coordination shift, Δδ(¹³C_{C=N}) values [37]. In general, δ¹³C_{C=N} in free dioxime is shifted upfield on coordination to cobalt. We find that the δ¹³C_{C=N} signals in dThgH complexes (**1–6**) appeared significantly downfield as compared to the values in cobaloximes with other dioximes. The order based on the upfield shift value is gH > dmgH > dpgh > chgH > dmgstgH > dThgH (Table S1). This suggests the charge density on C=N is much lower in dThgH complexes than the other dioxime complexes. The electrochemical study also shows up this effect (see later). The charge density on C=N should also affect the chemical shifts for O–H···O proton signals. The lower the charge density on C=N, weaker the hydrogen bond and hence a more downfield shift of O–H···O resonance would be expected. Indeed a considerable downfield shift of O–H···O signals is observed in **1–6** as compared to the

complexes with other dioximes and follows the order dThgH > dmestgH > dpgh > dmgH (Table S2).

The chemical shift of Py_α protons is affected not only by the *trans* effect of the R/X group but also by the ring current in the metallabicyclic. The Py_α shows a downfield shift of 0.07–0.14 ppm in **2–6** and an upfield shift of 0.14 ppm in **1** as compared to the unligated pyridine (Table S3). This is due to the *trans* effect that works differently in inorganic and organic cobaloximes as shown recently [38]. The *cis* influence of the dioxime ligand on pyridine is observed by comparing the coordination shift of pyridine protons (Δδ¹H), keeping the same R/X but changing the equatorial ligand. A comparison of the Δδ¹H(Py_α) values in **1–6** with the values in other cobaloximes, RCo(dioxime)₂Py, gives the order dmestgH > dpgh > dThgH > gH ≈ dmgH ≈ chgH (Table S3).

Since the chemical shift of the axial Co–C_α protons (CoCH₃ protons in **2** and CoCH₂ protons in **3–6**) depends on the *cis* influence of the dioxime moiety and the ring current in the dioxime moiety, the Co–C_α protons in complexes **2–6** appear downfield from the corresponding dmgH complexes and this downfield shift is comparable with the dpgh and dmestgH complexes (Table S4).

The chemical shift values of CH₂, Py_α and the dioxime (C=N) are further affected in the dioxy complex **7**. The signal for CH₂O₂ is shifted downfield by 0.97 ppm in ¹H NMR and 43.67 ppm in ¹³C NMR as compared to precursor complex **6**. The Py_α protons are shifted upfield (0.19 ppm) whereas ¹³C(Py_α) and ¹³C_{C=N} signals are appeared downfield by 0.88 and 2.0 ppm, respectively as compared to **6**.

2.3. Electrochemical studies (cyclic voltammetry)

The electrochemical behavior of **1**, **3** and **6** has been studied to understand the effect of dioxime (dThgH) on the redox potentials of the cobalt center. The cyclic voltammograms are shown in Figs. 1 and 2, and the CV data are given in Table 1. Three types of redox couple; Co(III)/Co(II), Co(II)/Co(I) and Co(IV)/Co(III) in the cyclic voltammogram are expected in any cobaloxime but complexes that describe entire redox processes are very few [39–42].

The cyclic voltammogram of **1** (Fig. 1) shows one irreversible peak at –0.239 V and one quasi-reversible peak (E_{1/2} = –0.643 V) in the reductive half corresponding to Co(III)/Co(II) and Co(II)/Co(I), respectively. In the oxidation half only one quasi-reversible wave corresponding to Co(IV)/Co(III) (E_{1/2} = 1.368 V) is observed. The

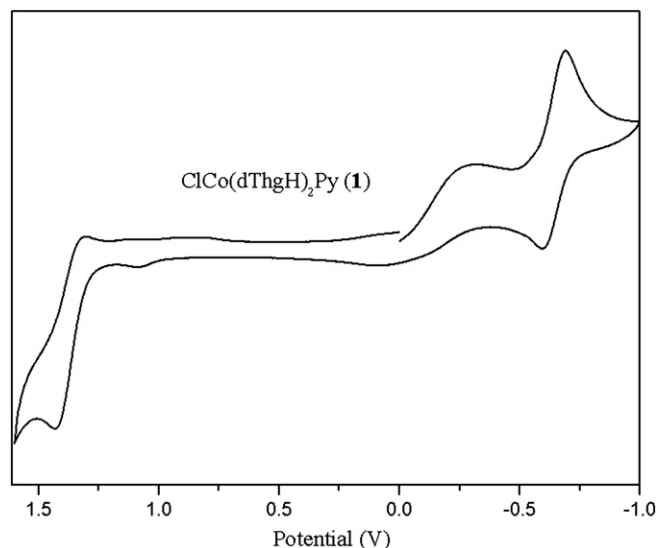


Fig. 1. Cyclic voltammogram of **1** in CH₂Cl₂ with 0.1 M nBu₄NPF₆ as supporting electrolyte at 0.1 V/s at 25 °C.

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