



## Hydrogen bonding interaction of CpCo(Dithiolene) complex with monocyclic 2-pyridonyl substituent and unexpected formation of dithiolene-fused tricyclic pyridone derivative

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### ABSTRACT

One-pot reaction of [CpCo(CO)<sub>2</sub>], elemental sulfur with some heterocycle-substituted alkynes (R–C≡C–HET) produced [CpCo(dithiolene)] complexes with <sup>2</sup>PyOBn (**2**), with both <sup>2</sup>PyOBn and 2-hydroxy-2-propyl groups (C(OH)Me<sub>2</sub>) (**5**), both <sup>2</sup>Py and C(OH)Me<sub>2</sub> (**8**), both <sup>4</sup>Py and C(OH)Me<sub>2</sub> (**11**), and with <sup>4</sup>Py substituent (**13**). A deprotection of benzyl group (Bn) from **2** with trimethylsilyl iodide formed [CpCo(dithiolene)] with 2-pyridonyl substituent (**3**). Heating reaction of **8** without any base resulted in the C(OH)Me<sub>2</sub> group elimination to form the 2-pyridylethylenedithiolate complex (**9**), but **11** underwent only dehydration at the C(OH)Me<sub>2</sub> under heating. While the preparation of **5**, the benzyl free complex (**6**) was obtained as a main product. **6** has a dithiolene-fused tricyclic pyridone skeleton. The structures of **3**, **5**, **6**, **8**, and **11** were determined by X-ray diffraction studies. Intramolecular OH⋯N(<sup>2</sup>Py) hydrogen bondings are found in **5** and **8**, and an intermolecular OH⋯N(<sup>4</sup>Py) one is found in **11** at solid state. In the 2-pyridonyl complex **3**, intermolecular NH⋯O and CH(dithiolene)⋯O hydrogen bondings are observed. **8** showed an intermolecular Cp⋯Cp face-to-face interaction. The tricyclic complex **6** exhibited lower energy electronic absorption (λ<sub>max</sub> = 668 nm) compared with the others (λ<sub>max</sub> = 562–614 nm), due to an extended π-conjugation of aromatic cobaltadithiolene ring.

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### 1. Introduction

Metal dithiolene complexes have been extensively investigated due to their combination of functional properties, specific geometries, and intermolecular interactions that confer them an enormous interest in the field of magnetism [1], conductivities [2], and optical properties [3]. On the other hand, metal dithiolene complex biochemically functions as a coenzyme as well [4]. Some model compounds relating to biochemically functional materials have been studied by using oxo-molybdenum and oxo-tungsten bisdithiolene complexes as oxo-transfer sources [5]. Garner and Joule et al. reported some [CpCo(dithiolene)] (Cp = η<sup>5</sup>-cyclopentadienyl) complexes having heterocycles such as 2-quinoxaliny [6], pteridin-6-yl [7], pyrano[2,3-b]quinoxaline [8], and pyrano[2,3-g]pteridine [9] which can be also model compounds for a proton-transfer (Chart 1). Among them, [CpCo(dithiolene)] with 2-quinoxaliny group shows 2e<sup>-</sup>/2H<sup>+</sup> reduction system in the presence of a

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proton source [6]. In addition, the oxo-molybdenum bisdithiolene complex [Mo(O)(qdt)<sub>2</sub>] (qdt = quinoxaline-2,3-dithiolate) undergoes thermally driven valence tautomerism by an intramolecular charge transfer (M/L-CT) [10]. Nishihara et al. reported proton and photo responsive [CpCo(dithiolene)], [M(dithiolene)<sub>2</sub>] and [(P<sup>∧</sup>P)M(dithiolene)] (M = Ni, Pd, Pt; P<sup>∧</sup>P = diphosphine) complexes with azobenzene unit due to those *cis-trans* isomerizations [11].

On the other hand, 2-pyridone derivatives have been attracted due to their promising features as an important core structure for the development of biologically active molecules [12]. Pharmaceuticals with the 2-pyridone structure have been investigated for antitumor [13], antifungal [14], antibacterial [15], antiviral [16], and antithrombotic agents [17]. In general, 2-pyridone derivatives could be one of strong hydrogen bonding motifs by the NH⋯O interaction. Dimeric hydrogen bonding interaction (Chart 2, A) has been well known [18]. Wuest reported dipyriddyonyl acetylenes which show dimeric (Chart 2, B) and polymeric hydrogen bonding networks (Chart 2, C) [19]. Theoretical studies for dipyriddyonyl acetylenes have been investigated [20].

In this work, we prepared [CpCo(dithiolene)] complex having 2-pyridonyl substituent which can be also an important metal complex as a biochemically functional material and to be a hydrogen bonding network. Furthermore, 2-pyridonyl group may be

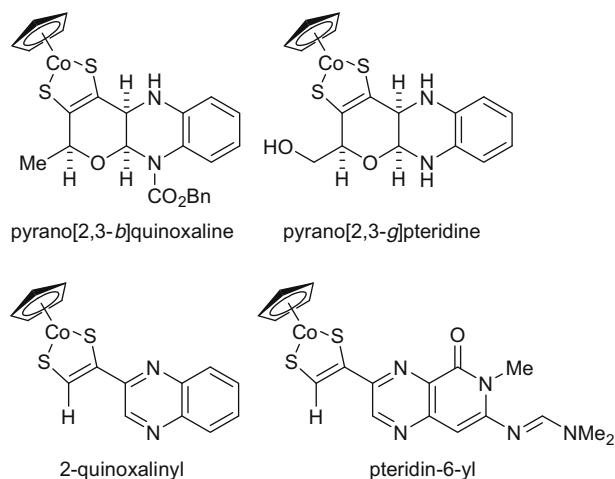


Chart 1. CpCo(dithiolene) complexes with heterocycles.

relatively easy to introduce to a molecule compared with pteridine and quinoxaline analogues (Chart 1). Interestingly, we unexpectedly found two different pyridone-containing dithiolene complexes. One is an expected pyridone-substituted dithiolene complex to show a hydrogen bonding interaction, but the other one is the dithiolene-fused *tricyclic pyridone* complex formed by an unexpected intramolecular cyclization. Generally, multicyclic pyridone derivatives are also biologically useful as antibacterial agents [21]. Furthermore, this paper also reports on [CpCo(dithiolene)] complex having 2-pyridyl (<sup>2</sup>Py) or 4-pyridyl (<sup>4</sup>Py) substituent for purpose of a comparison.

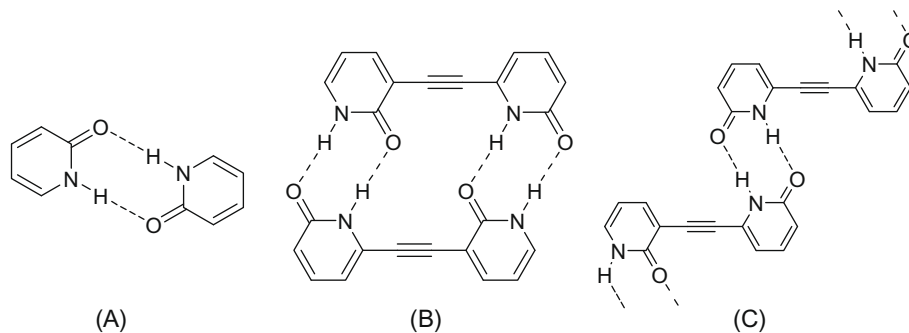
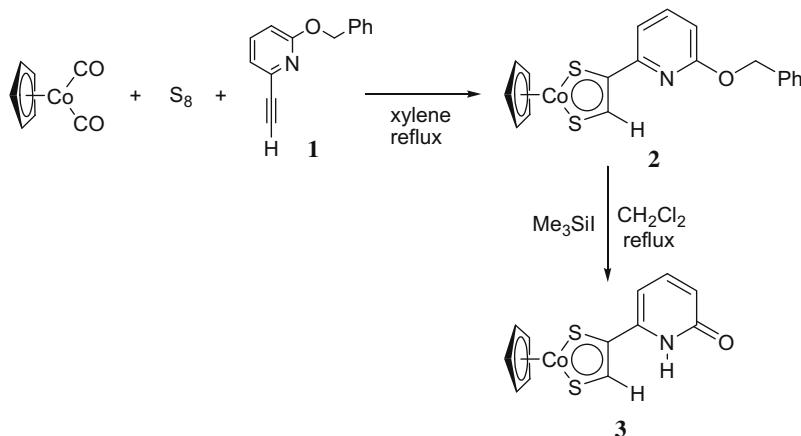


Chart 2. Dimeric and polymeric hydrogen bonding in 2-pyridone derivatives.



Scheme 1.

## 2. Results and discussion

### 2.1. Syntheses of CpCo(dithiolene) complexes using one-pot reaction

Garner and Joule et al. reported the synthesis of dithiolene's precursor (1,3-dithiol-2-one derivative) related to molybdopterin from diisopropyl xanthogen disulfide and alkynes [22]. On the other hand, many [CpCo(dithiolene)] complexes can be prepared by one-pot reactions of CpCo<sup>I</sup> species, elemental sulfur and alkynes, which have been well developed in our research group [23,24]. [CpCo(CO)<sub>2</sub>], elemental sulfur and 2-(benzyloxy)-6-ethynylpyridine (**1**) reacted in refluxing xylene for 17 h to form the [CpCo(dithiolene)] complex with <sup>2</sup>PyOBn substituent (**2**) in 26% yield (Scheme 1). A deprotection of the benzyl group was performed by using a conventional way [25]. The treatment of complex **2** with excess trimethylsilyl iodide in refluxing CH<sub>2</sub>Cl<sub>2</sub> resulted in the dithiolene complex with 2-pyridonyl substituent (**3**) in 56% yield (Scheme 1). Both products **2** and **3** were identified with spectroscopic data and elemental analyses. The <sup>1</sup>H NMR of **2** and **3** showed dithiolene protons at 9.59 and 9.12 ppm, respectively. In general, a ring current effect due to an aromatic dithiolene leads to a quite lower magnetic shift [26]. In **3**, a broad singlet signal for the NH group was found at 9.60 ppm. This is evidence for an existence of pyridonyl substituent on the cobaltadithiolene ring.

The reaction of [CpCo(CO)<sub>2</sub>], elemental sulfur with 4-(6-(benzyloxy)pyridin-2-yl)-2-methylbut-3-yn-2-ol (**4**) in refluxing xylene gave the complex (**5**) with both <sup>2</sup>PyOBn and 2-hydroxy-2-propyl substituents (–C(OH)Me<sub>2</sub>) on the cobaltadithiolene ring in 18% yield, and formed the tricyclic complex (**6**) in 29% yield as well (Scheme 2). **6** has a 2-pyridonyl substituent but the N atom binds

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