

## Influence of coordinated ligands in a series of inorganic cobaloximes



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### ABSTRACT

The influence of the axial ligand on the Co–pyridine bond distance and on the extent of the pyridine dissociation was investigated in a series of cobaloximes featuring different inorganic ligands (X = Cl, N<sub>3</sub>, NO<sub>2</sub>) together with the corresponding metallorganic derivatives: ClCo(dmgh)<sub>2</sub>Py (**1**), N<sub>3</sub>Co(dmgh)<sub>2</sub>Py (**2**), NO<sub>2</sub>Co(dmgh)<sub>2</sub>Py (**3**), EtCo(dmgh)<sub>2</sub>Py (**4**), ClCo(dpgH)<sub>2</sub>Py (**5**) and EtCo(dpgH)<sub>2</sub>Py (**6**). The molecular structures of NO<sub>2</sub>Co(dmgh)<sub>2</sub>Py (**3**), EtCo(dmgh)<sub>2</sub>Py (**4**) and EtCo(dpgH)<sub>2</sub>Py (**6**) were determined by X-ray crystallography.

The analysis of the bond distances in the X–Co–Py fragment showed an increment of about 0.1 Å in the Co–Py bond distance when passing from the chloride derivatives **1** or **5** to the ethyl derivatives **4** or **6**. In the dmgh series, the Co–Py bond distance increases in the order **1** < **2** < **3** < **4**. The dissociation reactions in which the pyridine ligand is displaced by the solvent was also explored via NMR. At 303 K, the lowest equilibrium constant was observed for **1** ( $K_{\text{diss}} = 5.55 \times 10^{-5}$  M) while the highest one ( $K_{\text{diss}} = 1.37 \times 10^{-3}$  M) was determined for **4**. The corresponding standard free energy variations span over the range 3.97–5.90 kcal/mol.

The topological properties of the electronic density at bond critical points in the X–Co–Py fragment revealed that the bonds between the cobalt atom and the axial ligands are predominantly ionic with slight covalent contribution.

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## 1. Introduction

Cobaloximes are octahedral Co(III) complexes with a chemical composition of XCo(dmgh)<sub>2</sub>L where the equatorial dmgh ligands are monoanions of dimethylglyoxime (dmgh<sub>2</sub>), the axial base (L) is a nitrogen-coordinated molecule such as pyridine or imidazole and X is an organoligand. Over the past four decades cobaloximes have been extensively studied as structural and functional models for the coenzyme vitamin B<sub>12</sub> [1]. The simplicity of these complexes has 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 homolysis of the Co–C bond by the AdoCbl-based enzymes [2]. In the recent years the interest in these complexes has been renewed thanks to their ability to catalyze the hydrogen evolution from acidic non-aqueous solutions at moderate potentials [3]. Cobaloximes are among the few examples of electrocatalysts based on

first-row transition metals complexes that could constitute an effective alternative to the platinum-based catalysts for the economically viable hydrogen production [4]. A wealth of information about spectral and structural properties of a great number of cobaloximes has been collected. Trends in structural, NMR, thermodynamic, and kinetic properties as functions of steric and electronic effects of the coordinated ligands were observed and many different approaches to quantitatively rationalize these correlations have been reported [5]. The structural analysis of the existing X-ray data revealed for some alkylcobaloximes a peculiar phenomenon known as inverse trans influence (ITI) [6]. It consists in a cooperative stabilization or destabilization of metal–ligand bonds trans to one another resulting in a simultaneous shortening or elongation of both axial bond lengths in response to an axial ligand modification. The inverse trans influence is in contrast to the normal trans influence in which the M–L bond trans to a strongly bound ligand is effectively weakened, characterized by an elongation of that bond.

Most of the above information has, however, come from the study of cobaloxime featuring alkyl groups as axial ligands. Studies involving inorganic ligands with different steric and electronic

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properties are still few. In this work we considered a series of cobaloximes supported by two different glyoximate ligands, i.e. dimethylglyoximate (*dmgH*) and diphenylglyoximate (*dpgH*) featuring different weak field ligands ( $X = \text{Cl}^-$ ,  $\text{N}_3^-$ ,  $\text{NO}_2^-$ ) together with the corresponding ethyl derivatives. In particular we looked at the influence of the coordinated ligands on the Co–pyridine bond distance and on the extent of pyridine dissociation that occurs in methanol solution. We think that such studies could help to gain a coherent picture of these complexes rationalizing fundamental structural properties and providing practical guidance to their chemical modification and control.

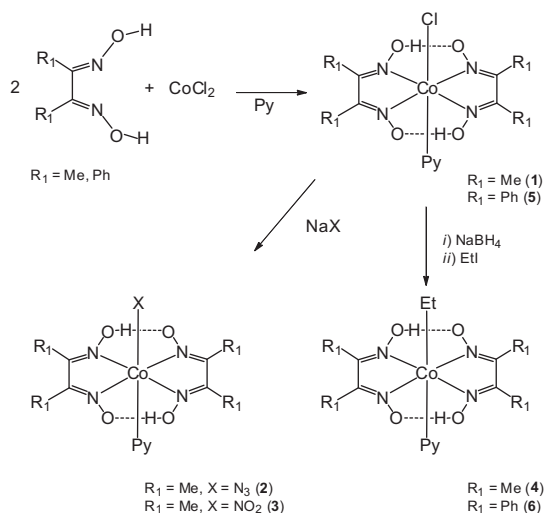
## 2. Results and discussion

### 2.1. Synthesis

We synthesized the following complexes  $\text{ClCo}(\text{dmgH})_2\text{Py}$  (**1**),  $\text{N}_3\text{Co}(\text{dmgH})_2\text{Py}$  (**2**),  $\text{NO}_2\text{Co}(\text{dmgH})_2\text{Py}$  (**3**),  $\text{EtCo}(\text{dmgH})_2\text{Py}$  (**4**),  $\text{ClCo}(\text{dpgH})_2\text{Py}$  (**5**) and  $\text{EtCo}(\text{dpgH})_2\text{Py}$  (**6**). The chloride complexes **1** and **5** were prepared by aerial oxidation of the stoichiometric mixture of  $\text{CoCl}_2$  and dioxime according to the reported procedures [7]. The azide and nitrite complexes **2** and **3** were prepared by substitution of chloride anion in **1** by the proper anion [8]. Finally the ethyl derivatives **4** and **6** were obtained converting the preformed chlorocobaloxime to transient Co(I) species that, in basic conditions, have sufficient anionic character to react with electrophilic ethyl iodide (Scheme 1) [7].

### 2.2. X-ray crystallographic studies of **3**, **4** and **6**

Recrystallization of **1–6** easily gave crystals suitable for X-ray crystallographic analysis. The X-ray structures of **3** and **6** had not been previously reported, the X-ray structure of **4** was redetermined with higher resolution than that previously reported [9]. The ORTEP [10] drawings of compounds **3**, **4** and **6** are shown in Figs. 1–3. A selection of bond distances and angles is given in Table 1. In all compounds the Co(III) centers adopt a distorted octahedron coordination geometry with four nitrogens of two dimethylglyoximate (*dmgH*) ligands in structure **3** and **4**, and two diphenylglyoximate (*dpgH*) ligands in structure **6**, in the equatorial plane. The axial sites are occupied by a nitrogen bonded pyridine and an ethyl group in **4** and **6**, and by a nitrite,  $\text{NO}_2^-$ , anion in **3**. In all compounds the CoI atoms are situated on the mean plane defined by the chelate nitrogen atoms, N1, N2, N3 and N4, being



Scheme 1. Synthetic route for complexes **1–6**.

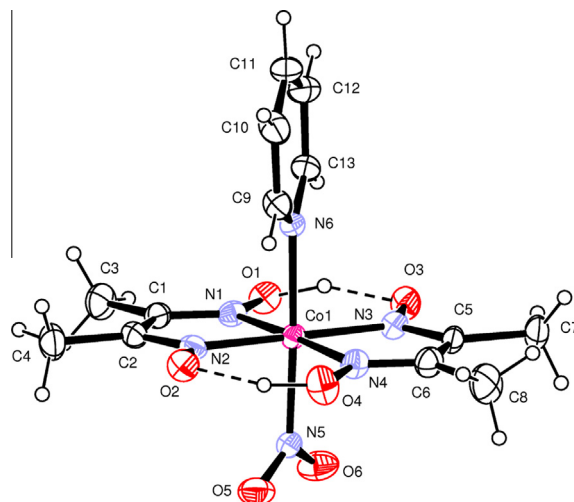


Fig. 1. ORTEP view of  $\text{NO}_2\text{Co}(\text{dmgH})_2\text{Py}$  (**3**) with the thermal ellipsoids at 30% probability.

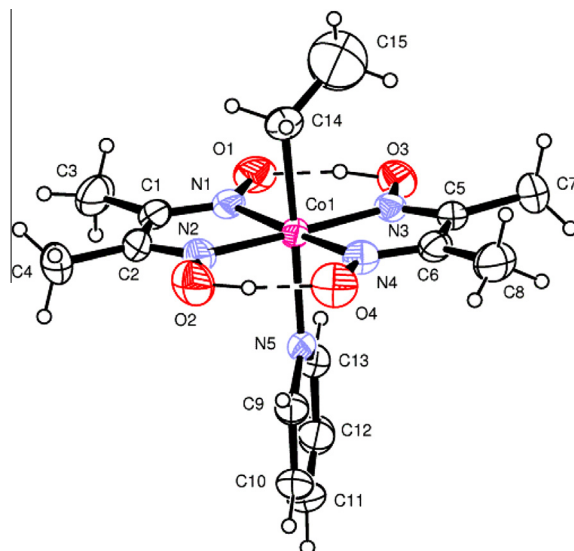


Fig. 2. ORTEP view of  $\text{EtCo}(\text{dmgH})_2\text{Py}$  (**4**) with the thermal ellipsoids at 30% probability.

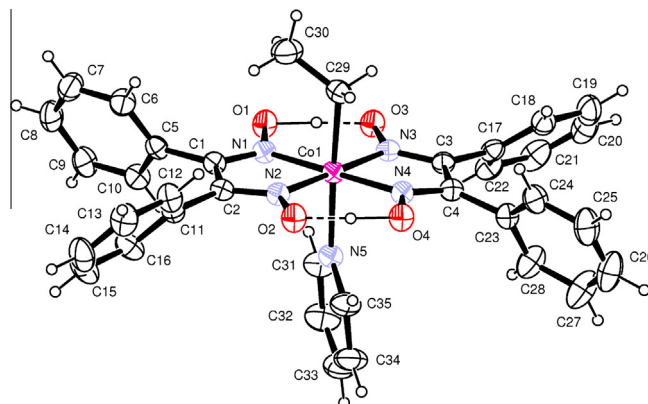


Fig. 3. ORTEP view of  $\text{EtCo}(\text{dpgH})_2\text{Py}$  (**6**) with the thermal ellipsoids at 30% probability.

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