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Cobaloximes with mixed dioximes having C and S side chains: Synthesis, structure and reactivity

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ABSTRACT

Ten mixed dioxime complexes RCo(L)(dmgH)Py [R = Cl, Me, Et, Bu, Benzyl] [L = dSPhgH (**1**–**5**) and dSEtgH (**6**–**10**)] have been synthesized and characterized by NMR. Formation of **1** and **6** is very fast and takes only 5 and 15 min in ethanol. Molecular oxygen insertion in **5** and **10** is monitored and forms mixture of products within 5 min. The crystal structure of **1**, **4**, **5**, **6**, **8** and **10** is reported. Benzyl ring is oriented over dmgH wing in both **5** and **10** and has a weak C–H…π interaction (3.33 Å and 3.22 Å) and this causes high upfield shift of the dmgH protons. Electrochemical study on **1**, **4**, **5**, **6**, **8** and **10** is also reported. Because of increased electron donation by SEt group, **6** is more difficult to reduce than **1**.

1. Introduction

Organocobaloximes[1] have been known for more than four decades [1–12] and have extensively been used to mimic the B_{12} coenzyme [13–18] and the studies have continued to compliment those on the more complex cobalamin and B_{12} based protein [19]. However, organocobaloximes with mixed dioximes have virtually been unknown until recently. The first mention of these complexes was made by Schrauzer and Windgassen in 1966 who proposed that the following ligand exchange reaction undoubtedly proceeded by stepwise displacement of the $dmgH_2$ ligand and the reaction did not involve an ionic intermediate like $CH_3{-}Co^{2+}$. However, they failed to isolate the intermediate mixed ligand complex, MeCo(dmgH)(chgH)B (B = Py or H_2O) [20].

$$\mathrm{MeCo(dmgH)_2H_2O + chgH_2 \xrightarrow[\text{toulene,Py}]{140^\circ C} MeCo(chgH)_2Py}$$

Subsequently, Johnson et al. in 1977 reported the kinetics and mechanistic details of the apparent alkyl transfer from alkylcobaloximes to cobaloxime (I), cobaloxime (II) and cobaloxime (III) reagents [21]. They proposed the formation of mixed ligand species, RCo(dmgH) (chgH)B in solution but did not isolate this intermediate. Only solution NMR values of the mixtures were reported.

The synthesis of RCo(L)(L′)Py complexes [L = dpgH and L′ = dmgH, gH, chgH; R = Cl, alkyl, benzyl] using different methods has recently been published from our group [22–26]. A mixture of three products, $RCo(L)_2Py$, $RCo(L')_2Py$, and RCo(L)(L′)Py was always formed and an equilibration between these products occurred in solution and was time dependent. Both the dioximes in all the reported complexes have carbon side chain. Since the nature of dioximes and solvent affect the equilibration process we have extended the study to mixed dioxime complexes having two dissimilar dioximes, one with C side chain(dmgH) and the other with S side chain (SPh or SEt). The study will allow us to make direct comparison with the previously reported mixed dioxime complexes in terms of synthesis, spectroscopy, structure and reactivity.

We herein report the synthesis and spectroscopic study of RCo(L)(dmgH)Py [R = Cl, Me, Et, Bu, Bn] [L = dSPhgH (**1**–**5**); dSEtgH (**6**–**10**)] complexes (Chart 1). The formation of **1** and **6** in different solvents has also been monitored with time. Molecular oxygen insertion in the benzyl complexes, **5** and **10** is carried out and carefully monitored. The X-ray structure of **1**, **4**, **5**, **6**, **8** and **10** is reported for the first time. Electrochemical study of some complexes is also reported.

2. Experimental section

2.1. Materials and physical measurements

Cobalt chloride hexahydrate (SD fine, India), glyoxime (Caution! it is highly flammable and explosive when dry) (Alfa Aesar,

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[1] 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 ligand (e.g. glyoxime (gH), dimethylglyoxime (dmgH), 1,2-cyclohexanedione dioxime (chgH), diphenylglyoxime (dpgH), dimesitylglyoxime (dmestgH), dithiophenylglyoxime (dSPhgH) and dithioethylglyoxime (dSEtgH).

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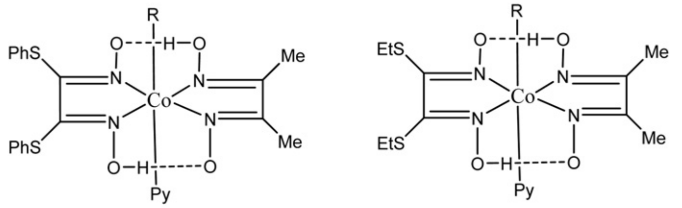

R=Cl, Me, Et, Bu, Bn(**1-5**) R=Cl, Me, Et, Bu, Bn(**6-10**)

Chart 1. Cobaloximes under consideration.

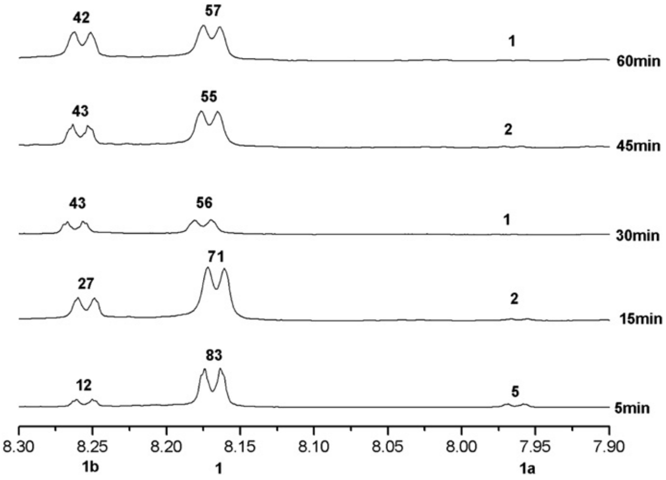

Fig. 1. Equilibration of **1**, **1a** and **1b** in ethanol.

Lancaster), iodomethane, ethyl, butyl and benzyl bromide (Aldrich chemical company) were purchased and used as received. Bis(thiophenyl)glyoxime and Bis(thioethyl)glyoxime were prepared from dichloroglyoxime following the reported procedure [10]. Silica gel (100–200 mesh) and distilled solvents were used in all reactions and chromatographic separations. A julabo UC-20 low temperature refrigerated circulator was used to maintain the desired temperature. Cyclic voltammetry measurements were carried out using a BAS Epsilon electrochemical work station with a platinum working electrode, Ag/AgCl reference electrode (3 M KCl) and a platinum-wire counter electrode. All the measurements were performed in 0.1 M $^nBu_4NPF_6$ in dichloromethane (dry) at a concentration of 1 mM of each complex.

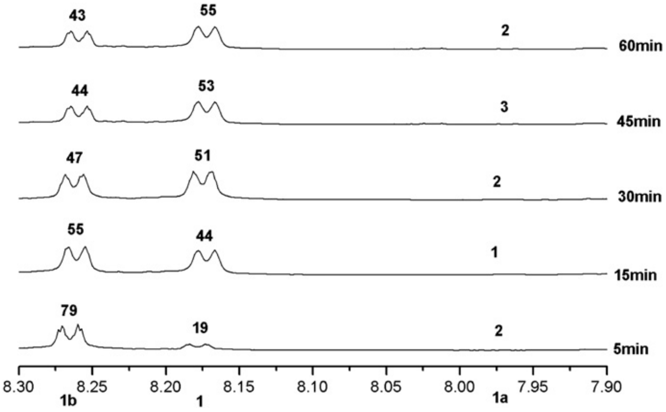

Fig. 2. Equilibration of **1**, **1a** and **1b** in acetone.

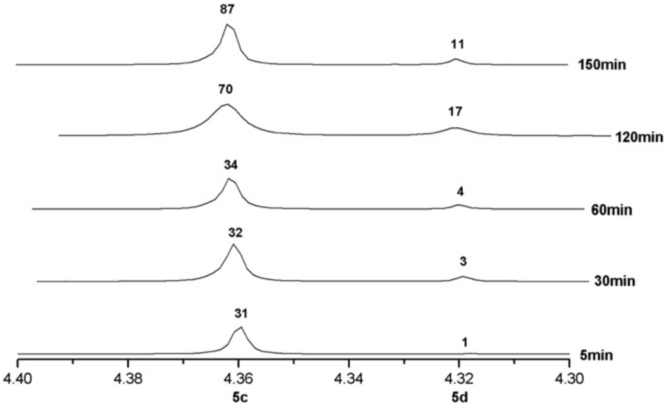

Fig. 3. Monitoring of oxygen insertion of **5** in dichloromethane at 0 °C under oxygen.

^{1}H and ^{13}C Spectra were recorded on a JEOL JNM LAMBDA 400 FT NMR Spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ solution with TMS as internal standard. NMR data are reported in ppm. Elemental analysis was carried out at IIT Kanpur.

The molar percentage of the species in Figs. 1 and 2 has been calculated from the integration of ^{1}H NMR signals of Py_α whereas in Figs. 3 and 4 it is calculated from the integration of ^{1}H NMR signals of CH_2 group bound to CoO_2. **1a**, **1b**, **6a**, **2a**–**5a**, **7a**–**10a**, **7b**–**10b**, **5c**, **5d**, **10c**, **10d** are characterized by ^{1}H NMR (Table S1).

2.2. X-ray crystal structure determination and refinements

A slow evaporation of solvent from the solution of complexes **1**, **4**, **5**, **6**, **8**, **10** (CH_2Cl_2/MeOH for **4**, **5**, **8** and **10** and CH_2Cl_2/MeOH/Hexane for **1** and **6**) in the refrigerator resulted in the formation of orange crystals. Single-crystal X-ray data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 100 K for **1**, **4**, **5**, **6** and **10**; at 273 K for **8**. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [27]. The data integration and reduction were processed with SAINT Software [28]. An empirical absorption correction was applied to the collected reflections with SADABS [29] using XPREP [30]. The structure was solved by direct methods

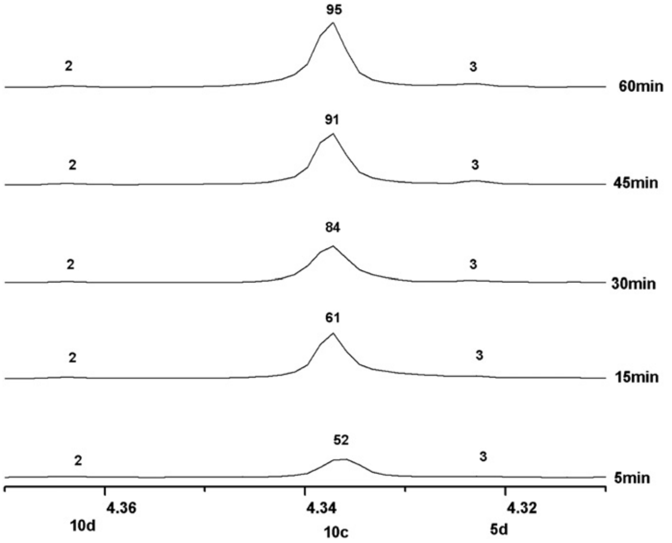

Fig. 4. Monitoring of oxygen insertion of **10** in dichloromethane at 0 °C under oxygen.