

SYNTHESIS AND CHARACTERIZATION OF CHLOROCOBALOXIMES CONTAINING PHOSPHOROUS DONOR LIGANDS AS POSSIBLE NON-ORGANOMETALLIC MODELS OF VITAMIN B₁₂

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Received: 08 December 2012

Accepted: 12 March 2013

ABSTRACT

Chlorocobaloximes of the type $trans-[Co(dmgH)_2(L)Cl]$, where $dmgH^-$ = Dimethylglyoxime monoanion, L = Triphenyl phosphine and Diphenyl(*p*-tolyl)phosphine, have been synthesized and characterized by elemental analysis, electronic spectral data, Infrared studies and magnetic measurements. In the electronic spectra of the complexes, the absorption bands which observed in the ultraviolet region are supposed to be due to charge transfer within the ligand and from ligand to metal ion. The IR spectra reveal the equatorial plane consists of four N atoms, two each from the dimethylglyoxime, while the two axial positions are occupied by chloride and phosphorus donor ligands to the cobalt atom. Magnetic measurements indicate that the complexes are diamagnetic and are therefore adopt six coordinate octahedral geometry.

Keywords: Chlorocobaloximes, Diamagnetic, Diphenyl(*p*-tolyl)phosphine, Octahedral, Triphenyl phosphine.

1. INTRODUCTION

Vitamin B₁₂ is the first vitamin found to contain a transitional metal, a cobalt atom at the center of the molecule. Vitamin B₁₂ is normally involved in the metabolism of every cell of the body, especially affecting the DNA synthesis and regulation. Deficiency of vitamin B₁₂ causes anemia as well as a range of symptoms such as fatigue, depression, and poor memory may be experienced. Since 1948, after isolation of vitamin B₁₂ and the establishment of its 'anti-pernicious anemia factor' its model complexes, has been prolonged. Cobaloximes have been used extensively as structural and functional mimics for vitamin B₁₂ (Brown, 2005). Cobaloximes contain a bisdimethylglyoximatocobalt(III) moiety, $Co(dmgH)^{+2}$ ($dmgH^-$ = monoanion of dimethylglyoxime). They are known to stimulate the reactions of vitamin B₁₂ and are important in vitamin B₁₂ model chemistry (Randaccio, 1989). Schrauzer's work on preparing model complexes of vitamin B₁₂ generated much interest; his work demonstrated that the cobalt atom, when surrounded by a planar array of nitrogen ligands, behaved similarly to cobalt in the macrocyclic corrin rings found in biological systems. Schrauzer's compounds thus serve as models for the biological coenzyme. During the past few decades their synthesis (Ramesh, 2008), structure (Revathi, 2009), chemical properties (Schrauzer, 1966) and spectroscopic (Dayalan, 2001) details have been studied widely. Most of the recent studies on cobaloximes have been focused on their structure-property relationships (Dutta, 2009).

The present research deals with the synthesis and characterization of two chlorocobaloxime derivatives of triphenyl phosphine and diphenyl(*p*-tolyl)phosphine. In this study organophosphorous ligands are of considerable interest, as they provide a potential binding site for metal ions and not much attention has been paid earlier in synthesis of chlorocobaloxime containing phosphorus donor ligands. The study of such model compounds may assists us to understand the correlation between biologically important vitamin B₁₂ and Phosphorus donor ligands (Gupta, 2004).

2. EXPERIMENTAL

2.1 Materials and Equipments

All chemicals and solvents were standard analytical grade obtained from E.Merck of Germany and BDH of

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England. Triphenyl phosphine and diphenyl(*p*-tolyl)phosphine were obtained from Sigma-Aldrich, England. Melting point was recorded in a Stuart; model SMP-11 of UK melting point apparatus with a capacity of recording the temperature up to 250°C. The solubility of the complexes was determined using various standard solvents like water, ethanol, dichloromethane, chloroform and hexane. Elemental analysis was carried out by using CHNS analyzer Elementar of Germany. The electronic spectrum of the prepared complexes was recorded in the region of 200-1100 nm on a Shimadzu UV-Visible spectrophotometer; model UV-160A of Japan. Infrared Spectra of all the complexes were recorded on a Shimadzu Infrared Spectrophotometer; model IR-470 of Japan in the region of 4000-400 cm^{-1} using KBr pellets. Magnetic moments of the complexes were determined using Sherwood Scientific Magnetic Susceptibility Balance; model Magway MSB MK1 of UK.

2.2 Preparation of the chlorocobaloximes $[\text{Co}(\text{dmgH})_2(\text{L})\text{Cl}]$

Dimethylglyoxime (1.39 g) was added into 50 mL of warm ethanol in a beaker. The mixture was heated in a water bath and stirred to dissolve, the solid $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.42 g) was added slowly and stirred. When it was dissolved, Ligand (Ligand=1.57 g triphenyl phosphine for complex **A** and 1.66 g diphenyl(*p*-tolyl)phosphine for complex **B**) was added to dissolve and the resulting green solution was cooled to room temperature. A stream of air was passed through the liquid for about an hour while the color of the solution changed to brown. The solution was then allowed to stand an hour at room temperature. The brown solid was separated out, collected by filtration, washed with little aliquots of water then ethanol and finally diethyl ether and dried in air. The solid product was then re-crystallized from a warm solution of dichloromethane: ethanol (1:1). A brown to dark brown crystalline product was obtained separated by decantation of mother liquor and dried in air. The yield found 26.87% and 26.40% for the complex **A** and **B** respectively. The color of the crystals gradually changes from brown to dirty brown on exposure to light and air [Silverstein R. M.; 1984].

3. RESULTS AND DISCUSSION

Complexes reported in this work are presented in Table 1 along with their elemental analytical data and melting point. The chlorocobaloximes are sparingly soluble in dichloromethane, warm ethanol and but insoluble in water, chloroform and hexane. Cobalt and chlorine were determined by complexometric and volhard's methods. Elemental analytical data are agreed with the theoretically calculated values of the proposed formulae of complex **A**, $\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{18}\text{H}_{15})\text{P}$ and complex **B**, $\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{19}\text{H}_{17})\text{P}$.

Table 1: Elemental data and melting properties of the chlorocobaloximes

Complex	Formula	M_r	Found, Cal (%)					M.P. °C
			Co	Cl	C	H	N	
A	$\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{18}\text{H}_{15})\text{P}$	586.90	9.74	5.91	51.15	5.10	9.51	198-200
			10.04	6.04	53.21	4.98	9.55	
B	$\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{19}\text{H}_{17})\text{P}$	600.93	9.34	5.27	53.51	5.51	8.81	198-200
			9.81	5.90	53.97	5.20	9.32	

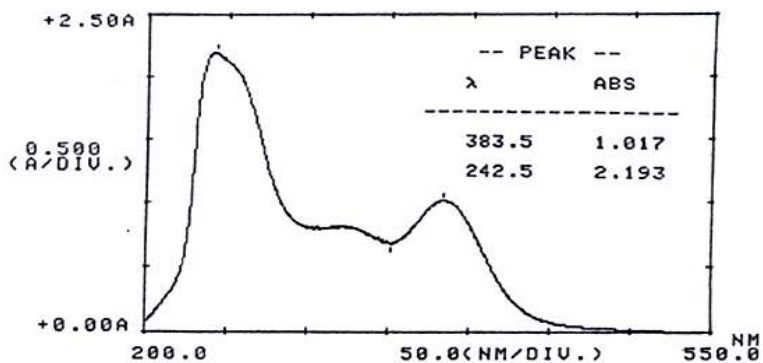


Figure 1: Electronic spectra of $\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{19}\text{H}_{17})\text{P}$

3.1 Electronic spectra

The electronic spectra of the complexes in ethanol show intense absorption around 247 and 242.5 nm for complex **A** and **B** (Figure 1) respectively. These bands may be attributed to $\pi \rightarrow \pi^*$ transition of the dmgh group. A shoulder around 322 and 383.5 nm for complex **A** and **B** respectively may be due to the ligand to metal charge transfer (LMCT). This LMCT peak was found to disappear upon reduction of the cobalt (III) by Fe (II) or Cr (II).

3.2 IR spectra

The oxime part (C=N) takes part in the chelate ring formation in cobalt complexes. The C=N stretching vibration of the oximes in its complexes was observed at 1620-1640 cm^{-1} and the intramolecular hydrogen bonded O-H appearing around 3570 cm^{-1} and 3590 cm^{-1} for complex **A** and **B** respectively and suggested *trans* conformation [Laavanya, 1998, Gillard, 1963]. Comparison of the position of free O-H stretching, observed only in water vapor at 3750 cm^{-1} . Both the complexes show the sharp bands at 2300 cm^{-1} , which may be attributed to another hydrogen-bonded O-H frequency of bisdimethylglyoximate moiety, according to Hadži [Bline R. & Hadzi D; 1958], the hydrogen atoms in the hydrogen bridges may not occupy a central position between the oxygen atoms, which would result in the appearance of another O-H band in 2300-2400 cm^{-1} . A moderate intense band at around 1215-1225 cm^{-1} for both the complexes, may be assigned to the =N-O- stretching of the oxime into the complexes. The characteristic band at 505 cm^{-1} for the complexes is assignable to Co-N stretching frequency between Co (III) and nitrogen atoms of dimethyl glyoximate ligands. Aromatic C=C ring stretch in ligands and their complexes observed in the range of 1500-1400 cm^{-1} and 1550-1420 cm^{-1} respectively. =C-H stretches occurred for the ligands and the complexes at values greater than 3000 (3010-3380) cm^{-1} as well as out of plane bending occurred in 690 and 740 cm^{-1} . A characteristic band was observed at 805 cm^{-1} in complex **B** (Figure 2) which may be for C-H bending for the para substitute methyl group in the ligand diphenyl(*p*-tolyl)phosphine (Figure 3). The ring carbon and phosphorous bond C-P band observed at 1080 cm^{-1} in the ligands which observed as a short band in the complexes may be due to Co-P bond formation. The Co-Cl stretching vibration has been reported to appear around at 200-300 cm^{-1} . Due to limitation of our IR instrument this particular band could not be observed.

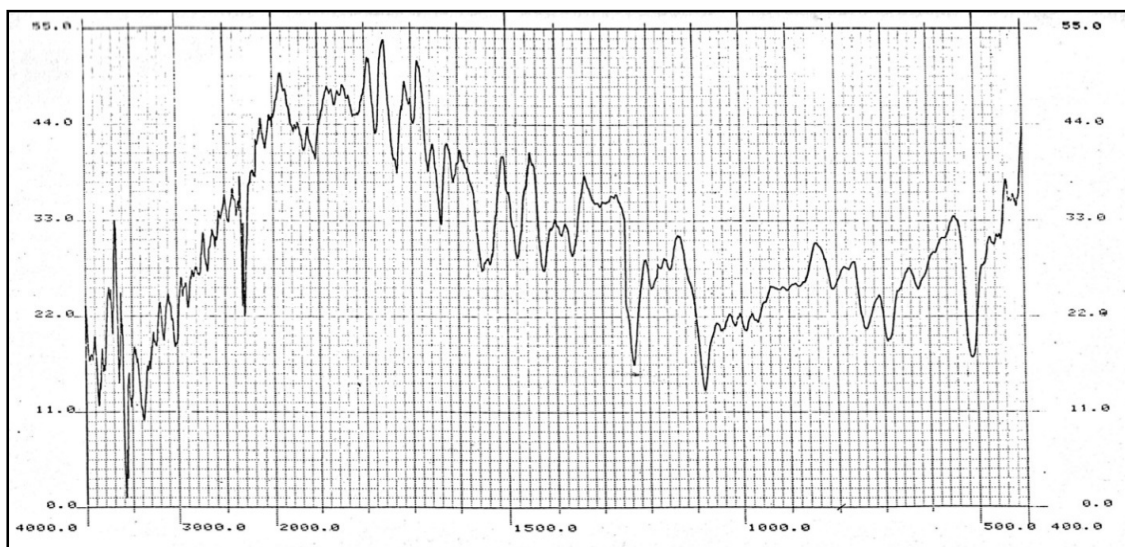


Figure 2: Infrared spectra of $\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{19}\text{H}_{17})\text{P}$

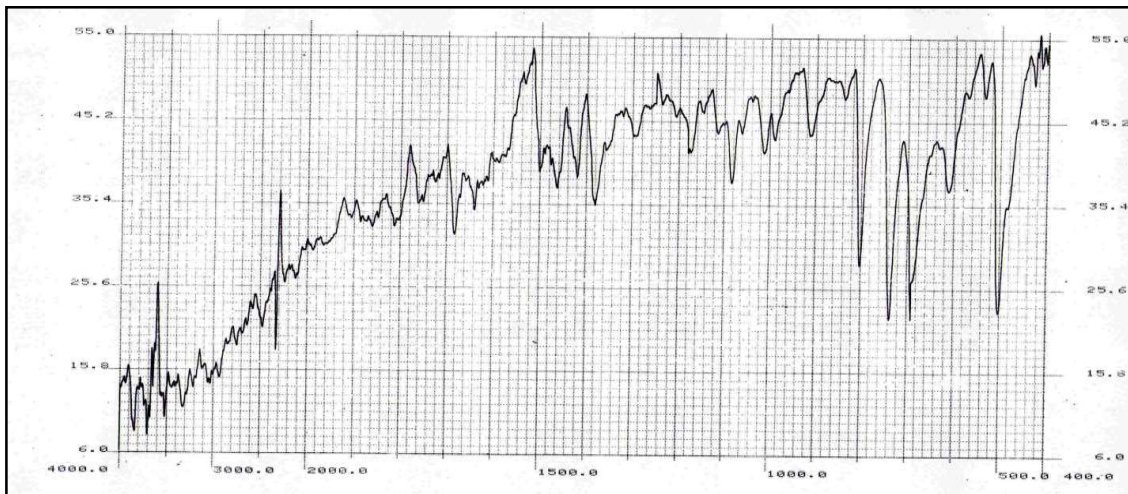


Figure 3: Infrared spectra of diphenyl(p-tolyl)phosphine

3.3 Magnetic measurements

In the study of the magnetic susceptibility of the synthesized complexes, similar magnetic behavior was observed. The gram susceptibility (χ_g) of the complexes which were negative suggesting that the complexes were six coordination Co^{3+} complexes and they were diamagnetic and with only paired electrons, shown in Table 2. According to crystal field theory the cobalt complexes show this behavior only when they belong to low spin octahedral stereochemical arrangement of the ligand around the central cobalt (III) ion. This kind of configuration with minimum number of unpaired electrons is called low spin or spin paired configuration, $t_{2g}^6 e_g^0$. The expression used for the calculation of gram susceptibility (χ_g) of the complexes under these investigations was, $\chi_g = C_{\text{Bal}} \times l \times (R - R_0) / 10^9 \times m$. Where, l = the sample length, m = the sample mass, R = the reading for the tube plus sample, R_0 = the empty tube reading; C_{Bal} = the balance calibration constant.

Table 2: The magnetic susceptibility of the chlorocobaloximes

Complex	Formula	C_{Bal}	l	$R - R_0$	m	χ_g
			cm		g	C.G.S. unit
A	$\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{18}\text{H}_{15})\text{P}$	1.0283	2	-17	0.0930	-3.760×10^{-7}
B	$\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{19}\text{H}_{17})\text{P}$	1.0312	1.9	-5	0.1210	-8.096×10^{-8}

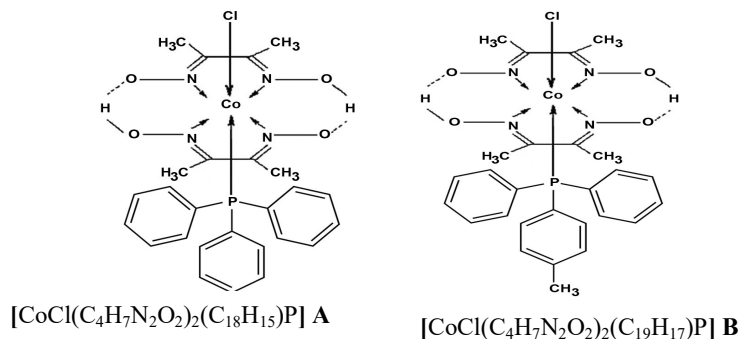


Figure 4: Possible structure of the complexes

4. CONCLUSION

Two chlorocobaloximes containing phosphorous donor ligands as possible non-organometallic models of vitamin B₁₂ complexes were prepared. On the basis of their various physic-chemical parameters the complexes are formulated as $\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{18}\text{H}_{15})\text{P}$ and $\text{CoCl}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2(\text{C}_{19}\text{H}_{17})\text{P}$. The probable geometry of the complexes are almost certainly octahedral around the central Co(III) ion with the arrangement of the ligands are given in Figure 4.

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