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Preparation and Characterization of Vitamin B_{12} Model Complexes

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Abstract

Cobaloxime complexes of the type $[CoCl(DMGH)_2(L)]$, where DMGH = dimethylglyoxime monoanion, L = tri-ethanolamine and 1,10-phenanthroline, were synthesized. The compounds were formulated on the basis of cobalt and chloride contents, IR and UV-visible spectral analyses and magnetic moment measurement. Cyclic voltammetric technique was also employed to investigate the interaction between Co(II) and the ligands under studied.

Keywords: Cobaloxime, Vitamin B_{12}, Dimethylglyoxime, Cyclic voltammetry

I. Introduction

Vitamin B_{12} is necessary for the rapid synthesis of DNA during cell division. This is especially important in tissues where cells are dividing rapidly, particularly the bone marrow tissues, responsible for red blood cell formation [1-3]. Deficiency of vitamin B_{12} causes anaemia. Prolonged vitamin B_{12} deficiency can result to nerve degeneration and irreversible neurological damage. Recently the chemistry of vitamin B_{12} and its model complexes have been attracted the biochemists, inorganic chemists and organometallic chemists [1]. During the past few decades the research works are primarily on the preparation of model complexes of vitamin B_{12} and investigation of their chemical behavior [4-15]. The conclusions reached from model complexes are then compared with vitamin B_{12} with a view to explore its reaction and functions. Despite the fact that many good chemical models are available in the literature, but to understand the mechanism of action of vitamin B_{12}, this line of work has met limited success.

The present research deals with the synthesis and characterization of two new cobaloxime derivatives of tri-ethanolamine and 1,10-phenanthroline. The study of such model compounds may assist us to understand the biological role and chemical mechanism of vitamin B_{12}.

II. Experimental

Materials

Dimethylglyoxime (LOBA Chemie Ltd., India), tri-ethanolamine (E. Mark, Germany), 1,10-phenanthroline (AJAX Chemical, Australia), N_2, 99.99% pure (BOC, Bangladesh) were used as purchased. Ethanol, methanol, n-hexane, acetone, hexamine, xylenol orange, nitrobenzene etc. used in analytical work were analar grade, E. Mark, Aldrich, or BDH product.

Equipments

A melting point apparatus, model SMP11 with a thermometer was used for the determination of melting point of the compounds. IR spectra of the complexes were recorded on a Shimadzu (Japan) Fourier Transform Infrared (FTIR) Spectrometer of model IR-470 in the region of 4000-400 cm^{-1} using KBr pellets. The UV-visible spectra were recorded using UV-visible recording spectrometer; model UV-160A, Shimadzu (Japan), in the wavelength range of 200-1100 nm using ethanol/or water as a solvent. Magnetic susceptibility measurement was done by the Sherwood Scientific Magnetic Susceptibility Balance, model Magway MSB MK1. Cyclic voltammetric measurement was performed using Computerized Electrochemical System, model HQ-2040 developed by Advanced Analytics, USA. The three electrodes electrochemical system consists of glassy carbon electrode (GCE) as the working electrode, Ag/AgCl (satd. KCl) as the reference electrode and platinum wire as the counter electrode were used.

Preparative Procedures

(i) Monochlorobis(dimethylglyoximato)triethanolamine cobalt(III) **A**

Dimethylgyoxime (1.12 g) was dissolved into 40 mL ethanol under hot condition on a water bath, and solid $CoCl_2.6H_2O$ (1.10 g) was added into it. When $CoCl_2.6H_2O$ was dissolved, tri-ethanolamine (0.8 mL) was added and the resultant green solution was cooled to room temperature. A stream of air was passed through the solution for about an hour while the color of the solution changed to brown. The resultant solution was allowed to stand at room temperature. A brown solid was formed which was separated by filtration, washed with ethanol, and dried in air. The solid product was then recrystallized from a warm solution of ethanol. A light red crystalline product was obtained, separated by decantation of mother liquor and dried in air.

IR bands, cm^{-1}: 3350(sb), 1640(m), 1480(m), 1450(m), 1400(vs), 1310(w), 1280(w), 1250(s), 1190(s), 1090(w), 1070(w), 1020(w), 1000(s), 915(s), 830(m), 750(w), 600(wb), 560(m), 520(m).

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(ii) Monochlorobis(dimethylglyoximato)(1,10-phenanthroline)cobalt(III) **B**

Dimethylglyoxime (1.10 g) was dissolved into 40 mL ethanol under hot condition on a water bath, and solid $CoCl_2.6H_2O$ (1.12 g) was added into it. When it was dissolved, 1,10-phenanthroline (0.85 g) was added, and the resulting green solution was cooled to room temperature. The color of solution was changed to brown while a stream of air was passed through the liquid for about an hour. The solution was then allowed to stand, a brown powdery solid was formed under room temperature, which was separated by filtration, washed with ethanol, and dried in air. The product was then recrystallized from a warm solution of ethanol. A reddish brown needle like crystal was collected from the solution and dried in air.

IR bands, cm^{-1}: 3400(vsb), 3000(w), 2900(w), 1820(wb), 1760(wb), 1640(w), 1620(w), 1560(s), 1500(w), 1480(w), 1420(s), 1360(wb), 1280(s), 1230(vs), 1080(s), 970(s), 910(m), 830(s), 720(s), 500(s), 420(m).

III. Results and Discussion

The compounds **A** and **B** are prepared respectively in 20% and 24% yield which are stable both in air and light. Solubility data show that the compound **A** is soluble in methanol, ethanol and insoluble in water, while **B** is soluble in hot water but insoluble in common organic solvents. The melting points are 177-179 and 128-130°C for compound **A** and **B** respectively. Cobalt(III) and chloride contents of the complexes under study are determined by complexometric and Volhard's methods respectively and the results are summarized in Table 1. Their estimated percentages are agreed well with the theoretically calculated values of the proposed formulae, $[CoCl(C_4H_7N_2O_2)_2(C_2H_4OH)_3N]$ and $[CoCl((C_4H_7N_2O_2)_2(C_{12}H_8N_2)]$ respectively.

Table. 1. Amount of cobalt(III) and chloride contents into the compounds A and B.

Complexes	Cobalt(III) content, %		Chloride content, %	
	Found	Calcd.	Found	Calcd.
A	11.87	12.36	9.24	7.45
B	10.80	11.27	7.39	6.80

IR Spectral Analysis: The strong but broad band appearing at 3350 cm^{-1} for $[CoCl(C_4H_7N_2O_2)_2(C_2H_4OH)_3N]$ and 3400 cm^{-1} for $[CoCl(C_4H_7N_2O_2)_2(C_{12}H_8N_2)]$ is possibly due to stretching vibration of O-H group of dimethylglyoximate anion or of water of hydration. But absence of HOH bending mode in the region 1630-1600 cm^{-1}, that usually observed in the hydrated compounds, exclude the possibility of the presence of hydrated water in the complexes. Comparison of the position of free O-H stretching, observed only in water vapor at 3750 cm^{-1}, with the corresponding positions in the complexes indicate that the O-H of DMGH is involved in -O-H ··· O type hydrogen bonding. In fact, involvement of hydrogen bonding weakened the O-H bond and thus the O-H stretching frequency is lowered. The stronger the hydrogen bond the weaker is the O-H bond and lower are the O-H stretching frequencies if other conditions are equal. It is reported that the displacement of the associated O-H stretching frequency compare to that of the free hydroxyl group frequency ($\Delta\nu$) provides a delicate measure of the strength of the O-H ··· O bond. In the present study, $\Delta\nu$ values are 390 cm^{-1} for $[CoCl(C_4H_7N_2O_2)_2(C_2H_4OH)_3N]$, and 300 cm^{-1} for $[CoCl(C_4H_7N_2O_2)_2(C_{12}H_8N_2)]$. The large $\Delta\nu$ values demonstrate that the complexes possess significantly strong O-H···O bonds but not as strong as those observed in square planner complexes, like $[Ni(DMGH)_2]$ ($\Delta\nu$ = 1150 cm^{-1}), $[Pt(DMGH)_2]$ ($\Delta\nu$ = 1132 cm^{-1}), $[Pd(DMGH)_2]$ ($\Delta\nu$ = 1110 cm^{-1}).

A free tri-ethanolamine molecule shows two peaks at 1140 cm^{-1} and 1030 cm^{-1} resulting from the ν(C-N), and ν(C-O) vibrations respectively. However, the bonded tri-ethanolamine molecule in the complex $[CoCl(C_4H_7N_2O_2)_2(C_2H_4OH)_3N]$ shows these peaks at 1090 cm^{-1} and 1000 cm^{-1}. A free 1,10-phenanthroline molecule shows bands at 1640 cm^{-1}, 1570 cm^{-1} and 1240 cm^{-1} resulting from the ν(C=N), ν(C=C) and ν(C-N) vibrations respectively. However, in the complex $[CoCl(C_4H_7N_2O_2)_2(C_{12}H_8N_2)]$ these peaks appear at 1640 cm^{-1} for ν(C=N), 1560 cm^{-1} for ν(C=C) and 1230 cm^{-1} for ν(C-N).

Moreover, the non-involvement in bonding of the -OH group with metal is indicated by the non-removal of the ν(N-O) band of the DMGH anion in the complexes. This band appears at 1250 cm^{-1} in $DMGH_2$, at 1250 cm^{-1} in $[CoCl(DMGH)_2(C_2H_4OH)_3N]$ and at 1280 cm^{-1} in $[CoCl(DMGH)_2(C_{12}H_8N_2)]$. Peaks at 520 and 500 cm^{-1} in the spectra of the complexes may be accounted for Co-N stretching motions. The Co-Cl stretching vibration of cobaloxime complexes appears at about 420 cm^{-1} [16].

UV-Vis Spectral Analysis: The UV-visible spectra of compound **A** in ethanol and **B** in water were recorded. A strong band at 217 nm for **A**, while four strong bands at 210, 220, 245 and 262 nm for **B** are observed. Each compound shows high intensity absorption bands in the ultraviolet region. These bands result from either $\pi\rightarrow\pi^*$ and/ or $n\rightarrow\pi^*$ electronic transition that occurs within the ligand. Both the spectral pattern and the λ_{max} of the complexes compare to those of ligands (236 nm for dimethylglyoxime, 207 nm for tri-ethanolamine, and 226 and 262 nm for 1,10-phenanthroline) are different. This suggests that the ligands are bonded to Co(III) through their respective donor sites.

Magnetic Measurement: The magnetic susceptibilities of compounds **A** and **B** were measured. They are about -5.55×10^{-7} and $-2.88\times10^{-7}cm^3g^{-1}$ respectively. The negative values suggest that the studied complexes are diamagnetic with only paired electrons. According to the 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. DMGH anion is a strong field ligand and in general, complexes with the ligands having strong field possess the configuration with minimum number of unpaired electrons, called low spin or spin paired configuration, $t_{2g}^6 e_g^0$.

Cyclic Voltammetric Study

Cyclic voltammetric response of Co(II) in 0.5 M KCl solution at GCE

The redox behavior of 2 mM Co(II) in 0.5 M KCl solution within the potential window of -1200 to +200 mV at different scan rate was studied. The blank voltammogram shows no peak indicating the absence of any adsorbed electroactive species on the electrode surface. The recorded voltammogram of 2 mM Co(II) in 0.5 M KCl solution with scan rate of 100 mVs^{-1} is depicted in Fig. 1.

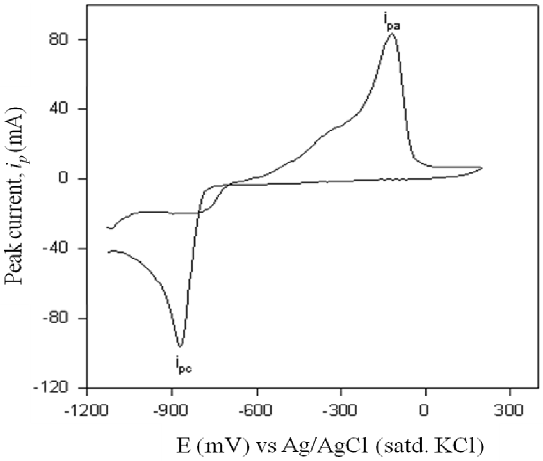


Fig. 1. Cyclic voltammogram of 2 mM Co(II) in 0.5 M KCl solution at a scan rate of 100 mVs^{-1}.

There is an anodic peak (i_{pa}) and a cathodic peak (i_{pc}) in the voltammogram. In the forward scan the anodic peak is at about -170.0 mV while in the reverse scan the cathodic peak is at about -839.0 mV. The anodic peak corresponds to the oxidation of Co(II) to Co(III) species and the cathodic peak arises due to the reduction of Co(III) to Co(II).

The voltammograms of 2 mM Co(II) in 0.5 M KCl solution at various scan rates are also recorded. The variation of peak current and peak potential with scan rate are gathered in Table 2. The peak current for both anodic and cathodic peaks varies linearly with square root of scan rate indicating that the redox process is diffusion controlled. It is also observed that the peak current ratio, i_{pa}/i_{pc} for Co(II) in 0.5 M KCl solution at different scan rates is almost unity but the peak potential separation, ΔE_p is very large. This suggests that the electrochemical process is quasi-reversible in the studied medium.

Cyclic voltammetric response of Co(II) in presence of dimethylglyoxime and triethanolamine in 0.5 M KCl solution at GCE

Fig. 2 reveals that the cyclic voltammogram of Co(II) (dotted line), and Co(II) in presence of dimethylglyoxime and triethanolamine (solid line) in 0.5 M KCl with scan rate of 100 mVs^{-1}. The anodic peak potential -170.0 mV for Co(II) ion alone is shifted significantly towards more negative values (-450 mV) when ligands are added to it as shown in Fig. 2. Such a change of the peak potential is an indicative of the participation of cobalt in complex formation with dimethylglyoxime and triethanolamine which makes the reduction of Co(III) to Co(II) ion difficult. The cathodic peak potential is also shifted a little towards negative values. The shapes of voltammogram for Co(II) alone, and Co(II) in presence of ligands are very similar with the exception that in the later both anodic and cathodic peak currents decreases remarkably. This is because of the formation of complex under the experimental condition.

Table. 2. The data obtained from the voltammograms recorded for 2 mM Co(II) at GCE.

Scan rate, v mVs^{-1}	Peak current, µA		Peak potential, mV		Peak potential separation, mV	Peak current ratio
	i_{pa} (+)	i_{pc} (-)	E_{pa} (-)	E_{pc} (-)	$\Delta E_p = E_{pa} - E_{pc}$	i_{pa}/i_{pc}
25	65.42	76.28	242.88	884.60	641.72	0.86
50	83.75	95.56	115.92	872.20	756.28	0.88
100	84.87	100.05	126.97	883.23	756.26	0.85
150	105.99	123.66	121.45	905.31	783.86	0.86
200	118.84	125.26	126.86	921.88	795.02	0.95

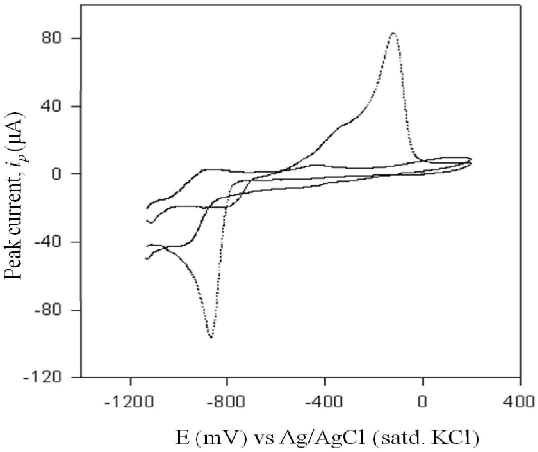


Fig. 2. Cyclic voltammograms of Co(II) (dotted line), and Co(II) along with dimethylglyoxime and triethanolamine (solid line) in 0.5 M KCl solution at a scan rate of 100 mVs^{-1}.

Cyclic voltammetric response of Co(II) in presence of dimethylglyoxime and 1,10-phenanthroline in 0.5 M KCl solution at GCE

The cyclic voltammogram of Co(II) (dotted line), and Co(II) in presence of dimethylglyoxime and 1,10-phenanthroline (solid line) in 0.5 M KCl solution with scan rate of 100 mVs^{-1} are recorded and shown in Fig. 3.

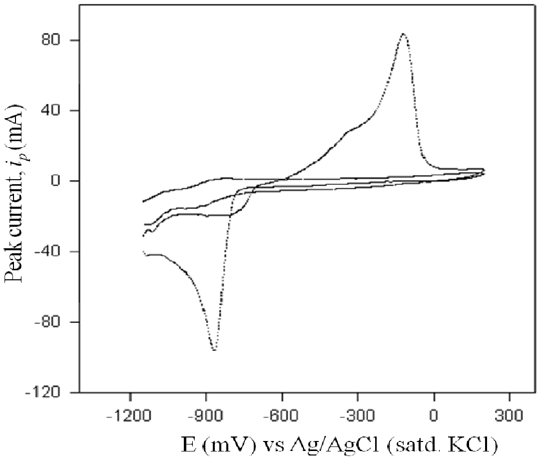


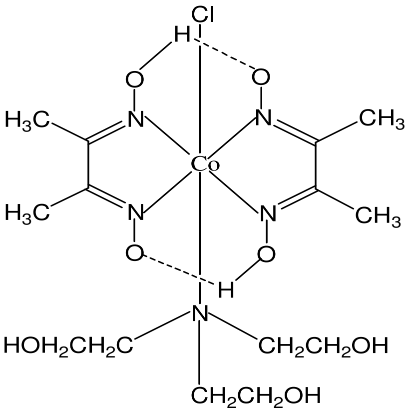
Fig. 3. Cyclic voltammograms of Co(II) (dotted line), and Co(II) along with dimethylglyoxime and 1,10-phenanthroline (solid line) in 0.5 M KCl solution at a scan rate of 100 mVs^{-1}.

In the forward scan the anodic peak potential for solely Co(II) ion is observed at about -170.0 mV while that for Co(II) in presence of ligands is at about -850.0 mV. The shifting of the peak towards the negative potential indicates the participation of cobalt in complex formation reaction with dimethylglyoxime and 1,10-phenanthroline. The cathodic peak potential also shifted a little towards the negative values.

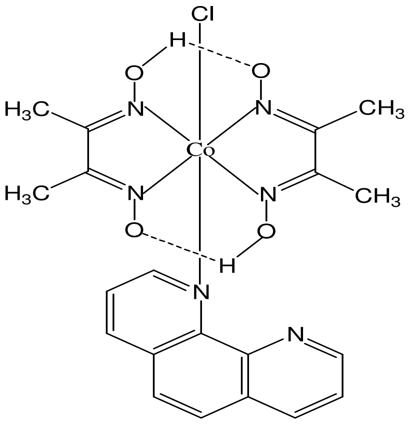
The voltammogram of Co(II), and Co(II) with dimethylglyoxime and 1,10-phenanthroline are very similar with the exception that the anodic and cathodic peak currents decrease significantly. This is due to the formation of complex under the experimental condition.

IV. Conclusions

Vitamin B_{12} model complexes of type [CoCl(DMGH)$_2$(L)], where DMGH = dimethylglyoxime monoanion, L = triethanolamine or 1,10-phenanthroline, were prepared. To characterize them, various physico-chemical parameters such as cobalt(III) and chloride contents, spectral analyses, magnetic susceptibility measurement and electrochemical study were employed. Based on the results obtained, the complexes are formulated as [CoCl(DMGH)$_2$(C$_2$H$_4$OH)$_3$N] and [CoCl(DMGH)$_2$(C$_{12}$H$_8$N$_2$)]. The geometry of the complexes are possibly octahedral around the central Co(III) ion with the following structural arrangement of the ligands:



[CoCl(DMGH)$_2$(C$_2$H$_4$OH)$_3$N] **A**



[CoCl(DMGH)$_2$(C$_{12}$H$_8$N$_2$)] **B**

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