INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES
(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com
Coden: IJCROO(USA) Volume 3, Issue 4 - 2016

Research Article

SOI: http://s-o-i.org/1.15/ijcrcps-2016-3-4-9

Macrocyclic Cobalt (III) Dioximes by Microwave Assisted Synthesis and Characterization of Coordination Complexes on Bromo Complexes

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Abstract

The ligand 3, 8-dimethyl-5, 6-benzo-4, 7-diazadeca-3, 7-diene-2, 9-dione dioxime [$(DOH)_2$bzo] has been synthesized by the condensation of an o-phenylene diamine with diacetyl monoxime in 1:5-mole ratio.These complexes have been alkylated using ethanol, acetone, DMSO and DMF in the presence of pyridine, imidazole, benzimidazole and pyridoxine (vitB_6) to obtain corresponding macrocyclicorganocobalt complexes. The parent cobalt complexes and their alkyl derivate have been characterized. The optical studies for this complex cobalt maximum absorption are conformed to these different complexes. The FTIR spectral studies confirmed the vibration modes of functional groups present in the title crystal. The^{1}HNMR proton is presented in confirmed by the position of aromatic rings cobalt bromodioxime complexes. The cyclic voltammetry spectral data of these complexes arehigh oxidation level of the cobalt atom of the complexes. This complexes used in the application of cobalt is essential Radioactive tracer and cancer-treatment agent used in radiotherapy.

Keywords: Macrocyclic Cobalt (III) bromodioxime complexes, Schiff base, Coordination template synthesis, UV spectroscopy, IR spectroscopy, ^{1}HNMR spectroscopy, cyclic voltammetry.

1. Introduction

Cobalt is an essential element in biology. This metal ion is among the significant toxic metals for environmental control, Simple and sufficiently Sensitive methods for the determination of the metal ion are necessary. For the determination of the trace element in aquatic systems, voltammetry techniques are very suitable owing to their low cost, sensitivity, and relative simplicity[1].Metal complexes have been extensively studied given theirs numerous applications. For example, many complexes play vital role as the catalyst in industrial synthesis.

Several complexes are known in biological systems as hemoglobin, cytochrome, vitamin $B_{12,}$etc. Cobalt (III) compounds containing direct Co–C bond thatoccupies an axial coordination position about a coronoid ring system[2,3].Naturally occurring macrocyclic ligand transition metal complexes such as complexes of the porphyrin or corrin ring systems and the metal phthalocyanine complexes have drawn considerable attention in the study of the coordination chemistry of biological interest[4].

Their stability depends on the nature and the geometry of the ligands. Macrocyclic ligand complexes are more stable than that with the simple ligands. Synthesis of such macrocyclic complexes is facilitated by the metal ion itself which is known as template synthesis. Cobalt applications alloys, such asSuper alloys, for parts in gas turbine aircraft engines[5]. Corrosion- and wear-resistant alloysHigh-speed steels.

Catalysts for the petroleum and chemical industries. Electroplating because of its appearance, hardness, and resistance to oxidation. Drying agents for paints, varnishes, and inks, Pigments(cobalt blue and cobalt green). Cobalt-60 has multiple uses as a gamma ray source:It is used in radiotherapy[6]. It is used in radiation treatment of foods for sterilization (cold pasteurization).It is usedforindustrial radiography to detect structural flaws in metal parts by simply exposing natural cobalt to neutrons in a reactor for a given time[7]. Cobalt-60 is a radioactive metal that is used in radiotherapy.

The 60Co source is about 2 cm in diameter and, as a result, produces a geometric penumbra, making the edge of the radiation[8]. Cobalt is a hard ferromagnetic silver-white element.It is frequently associated with nickel, and both are individual ingredients of Meteoric iron. Mammals require small amounts of cobaltsalts[9]. Cobalt-60, an artificially produced radioactive isotope of cobalt isessentialRadioactive tracer and cancer-treatment agent[10]. Cobalt has a relative permeability two-thirds that of iron[11].

Metallic cobalt commonly presents a mixture of two crystallographic structures hcp and fcc with a transition temperature of 722 K. Common oxidation states of +3,+2,+1[12].The tetra, macrocycles from 13 to16 members macrocyclic ring are found to be the main thrust area in the field of the coordination chemistry of transition and inner transition metals on coordination. 5 to 7 memberchelated rings are produced which are held coplanar with the metal ion,although twisting of the ligand is common in large ring macrocycles as in polyether[13].

The coplanar ion leads to extended conjugation of the unsaturated system, which in turns result in transmission of electronic effects of the Ligand throughout the molecular system[14]. The metal ion, in turn effectively increases the ligands field strength. The dynamic roles played by the metal ion in the living system can be attributed to this fact[15].

Compounds containing the group >C=N-OH called oximes can be derived from aldehyde and ketone by condensing them with hydroxylamine. The derived fromaldehyde are known as aldoximes, those from ketones as ketoximes. V. Meyer in 1982[16] first prepared them. They are either colorless liquid, which boils without decomposition or Crystalline solid with both fundamental and acidic in character. An originalproperty of the fact that oxime easily loses A.Wohi used water and form nitriles in the breaking down of sugar[17]. The coordination compound of dioximes has been widely investigated as analytical reagents, models for biological systems such as vitamin B_{12}[18].Compounds with columnar stacking thought to be their semiconducting properties and recently in viadioximereaction[19].

Among the three isomers, namely anti-, Amphi- and syn-, the first is more liable to form N, N –coordinated planar ComplexesStabilized by hydrogen bonding[20]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms make Vic-dioximes amphoteric ligands that form corrin-type, square planar, square pyramidal and the octahedral complexes with transition metal ions such as Ni(II), Cu (II),C_O(II) and Co(III) as central atoms[21]. Metal ions play a significant role inbio-inorganic chemistry and metal such as Fe,Co,Ni,Cu,Zn and Cd may exist in a trace amount in biological systems[22,23]. The cobalt (III) complexes are paramagnetic, and their magnetic susceptibility values are around 4.20-4.71 BM[24]. The values indicated are in good agreement with the literature. These results indicated an octahedral geometry for the cobalt (III) complexes. The cobalt (III) complexes were the most active and may be promising for the development of new antibiotics. The oxime complexes are slightly soluble in polar organic solvents such as EtOH, MeOH, DMSO,DMF,THF, and dioxin. The molar conductivities in DMF (~10^{-3}Msolution) are too small to account for any dissection of the dioxime ligand and oxime complexes in thesolvent[25]. Therefore, they can be regarded as non-electrolytes.

Subsequently, numerous others cobalt chelates were tested as possible vitamin B_{12} models, especially propylene and ethylene diamine Schiff bases of 2, 3-butanedione monoxime, and Schiff bases derived from salicylaldehyde and acetylacetone, particularly by Costa and coworkers[26].Among the models reported, Costa cobalt chelate of its ethylenediamine analog and related ligand are the only monoanionic macrocyclic dioxime ligand Mathur and Narang synthesized the ligand $(DOH)_2$bzo as a gravimetric reagent for the estimation of nickel (II) subsequently numerous cobalt (III) complexes. This ligand was prepared and characterized aspossible models for vitamin-B_{12}[27].

The discovery of the cations and anions form stable complexes with macrocyclic polyether’s and polyamides has paved the way to several broad and rich areas of chemical investigation[28]. Some macrocyclic complexes are having more than one areacyclic ring and having donor atoms such as nitrogen,sulfur,oxygen, phosphorus and nitrogen-oxygen combination[29], have been synthesized which led to much light on the theoretical aspects.

The ligands coordinate with cobalt through the four nitrogen donors,with the less of an oxime proton with the formation of the intramolecular hydrogen bond. Thus, the ligands in its complexes are monoanionic[30]. The known macrocyclic complexes of cobalt (III) include vitamin-B_{12}, the porphyrin and the phthalocyanine complexes and certain synthetic cyclic tetradentate secondary amine by Lindoy and Busch (1971). Cobaltic salt can often be prepared by electrolyzing a solution of cobaltous salt dissolved in a solution of the parent acid of the salt[31]. The unique position of cobalt in coordination chemistry, as regards to both number and variety of complexes and their appropriate case of synthesis arise[32].The ability of the aqua Co (II) ion and Co (II) complexes.The inertness of the Co (II) complexes in substitution. The slow rate of electron transfer between Co (II) and Co (III) complexes.

2. Experiment Method

2.1. Reagent:

All chemicals were of analytical reagent grade, and solutions were prepared with purified water of L.P. grade. Cobaltous bromide was used as such for the synthesis of metal complexes. For the synthesis of ligand (L) o-phenylenediamine and diacetyl monoxime. The metal complexes of $Co[(DOH)_2bzo]Br_2$ replaced by one bromine atom in fixed axial ligand of pyridine, imidazole, benzimidazole, and vitamineB_6.

2.2. Solvent:

Double distilled water was obtained by distilled over alkaline $KMnO_4$ inall-glass apparatus; it washed the complexes with diethyl ether and ethanol. The metal complexes prepared mainly used asolvent in acetone for all synthesis of cobalt complexes.

2.3. Synthesis of Ligand [$(DOH)_2$bzo]:

About 0.05 mole of o-phenylene diamine was added to 200ml of distilled water, and the solution was exposed to microwave in a first microwave oven for the 30s.To this 0.1 mole of diacetyl monoxime was added.

Moreover, again exposed to microwave for about the 30s. The solution was set aside. For 10 or 24 hours to get the yellow straw product (yield-98% and M.P.176^{0}C). It was, filtered, washed with cold water and recrystallized from hot water or ethanol[33].

2.4. Synthesis of [Co{$(DOH)_2$bzo}Br_2]:

About 0.01 moles of $CoBr_2.6H_2O$ was dissolved in 75ml of acetone with constant stirring for about 10 minutes. It was then mixed with 0.01 moles of $(DOH)_2$bzo and stirred well. A parrot greencolorcore complex was formed. It was then allowed to stir for onehour[34]. The product was filteredmoreover, washed with diethyl ether.

2.5. Synthesis of [Co{$(DOH)_2$bzo}(Py)Br]:

About 0.005 moles of dibromo complex was added to 75 ml of ethanol and allowed to stir for five minutes. The solution under stirring condition was mixed with 0.005 moles of pyridine and refluxed for about 3hrs at 40^{0}C.The green colored solution turned dark brown[35]. The complex was washedwith ethanol and diethyl ether.

2.6. Synthesis of [Co{$(DOH)_2$bzo}(Im)Br]:

About 0.005 moles of dibromo complex was added to 75ml of ethanol and allowed to stir for five minutes. The solution under stirring condition was mixed with 0.005 moles of imidazole and refluxed for about 3hrs at 40^{0}C. The green colored solution turned pale yellow[36]. The complex was washed with ethanol and diethyl ether.

2.7. Synthesis of [Co{$(DOH)_2$bzo}(Bim)Br]:

About 0.005 moles of dibromo complex was added to 75ml of ethanol and allowed to stir for five minutes. The solution under stirring condition was mixed with 0.005 moles of Benz imidazole and refluxed for about 3hrs at 40^{0}C. The green colored solution turned brown[37]. The complex was washedwith ethanol and diethyl ether.

2.8. Synthesis of [Co{$(DOH)_2$bzo}(Pyn)Br]:

Extraction of pyridoxine hydrochloride:

Pyridoxine hydrochloride of required equimolar quantity use as such for the preparation of complexes hence pyridoxine hydrochloride was treated with a base to get free pyridoxine. Here the use of sodium bicarbonate was over sodium hydroxide was preferred to avoid interference by the hydroxyl ions in the synthesis of complexes.Pyridoxine hydrochloride was stirred with solution bicarbonate for 6hours in absolute excessalcohol. Then the resulting mixture was filtered, and the filtered was used as such for preparing the desired complexes.

About 0.005moles of dibromo complex was added to 75ml of ethanol and allowed to stir for five minutes. The solution under stirring condition was mixed with 0.005 moles of Pyridoxine with a condenser, and the solution was stirred for about 3hrs at 40^{0}C. The green colored solution turned brown[38]. The complex was washed with ethanol and diethyl ether.

3. Characterizations:

The UV-visible spectrum of the complexes was obtained from LAMBDA-125 spectral photometer using 1cm matched quartz cells using an alcoholic solution of the complexes of suitable concentration were used. IR spectra of the complexes were obtained using PERKIN ELMER spectrum-1 in KBr disc by making pellets of the complexes. The ^{1}H magnetic resonance spectra of the complexes were recorded in DMSO-d6 on a JOEL-400 MH_Z NMR spectrophotometer. Cyclic voltammogram of the complexes was obtained using general purpose electrochemical system (GPES) version 4.9 by using suitable concentration ofthe complexes.

4. Results and Discussion

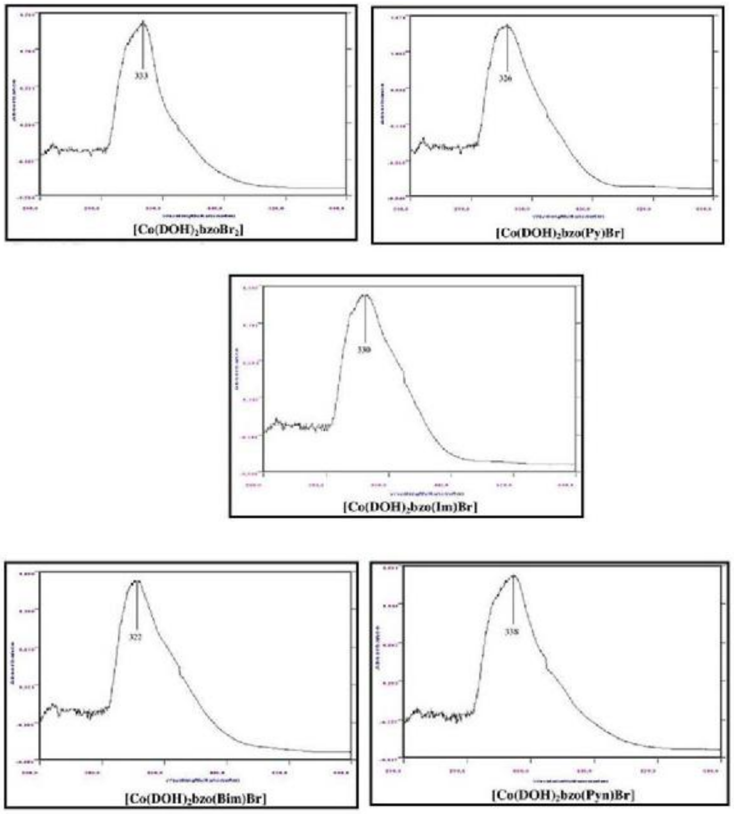
4.1. Optical studies:

4.1.1. UV spectrum of Ligand[$(DOH)_2$bzo]:

The recrystallized ligand melts at 276°c as reported in the literature. The UV spectra of the complexes showed that the position of the intense highabsorption and in the range 312-352nm may be attributed to π-π*transition of the complexes[39] shown in the fig.1. The absorption band remains unaltered even in their complexes. The moderately intense bands around 260-340nm which may be ascribed to π-π* of the [$(DOH)_2$bzo] which also remain unaltered even in their complexes. The LMCT peak was reported to be disappearing. Upon reduction of the cobalt (III) complexes by indicating the LMCT nature[40]**.**The cobaltbromodioxime complexesare obtained absorption shown in the table1.

Table 1: Electronic spectra of the cobaltbromodioxime complexes:

S.No	Complexes	π-π*λmax,nm	π-π* $(DOH)_2$bzo λmax,nm	LMCT
1.	[$Co(DOH)_2bzoBr_2$]	333	285	425
2.	[$Co(DOH)_2bzo(Py)Br$]	326	290	430
3.	[$Co[(DOH)_2bzo](Im)Br$]	330	300	435
4.	[$Co(DOH)_2bzo(Bim)Br$]	322	340	440
5.	[$Co(DOH)_2bzo(Pyn)Br$]	338	345	445



[$Co(DOH)_2bzoBr_2$]

[$Co(DOH)_2bzo(Py)Br$]

[$Co(DOH)_2bzo(Im)Br$]

[$Co(DOH)_2bzo(Bim)Br$]

[$Co(DOH)_2bzo(Pyn)Br$]

Fig.1: Electronic spectrum of Cobalt bromodioxime Complexes.

4.2. FTIR Spectral studies:

4.2.1. IR spectrum of Ligand [$(DOH)_2$bzo]:

The IR spectrum of ligand shows to the absorption of frequencies to the functional group of phenyl the sharp band of medium intensity occurred at 699$cm^{-1}$is attributed to CH_3 (oxime) while a similar band at 1384 $cm^{-1}$is assigned to C=N is 1640 cm^{-1}.The N-O stretching vibration is 1215cm^{-1} isan excellent band. The hydrogen bonded N-OH is assigned to 3430cm^{-141} as shown in the fig.2.

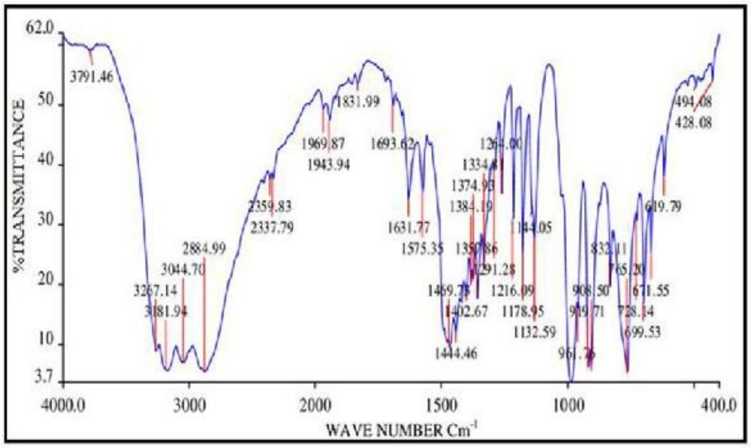


Fig.2:IR spectrum of Ligand [$(DOH)_2$bzo]

4.2.2. IR Spectrum of [Co[$(DOH)_2$bzo]Br_2]:

The IR spectrum of cobalt complex shows to the absorption of frequencies to thefunctional group is assigned to –C=N- is 1636cm^{-1}. The Co-N stretching vibration is 510cm^{-1} isasharp band. The hydrogen bonded -OH is assigned to 3444cm^{-1}**.**The aromatic C-H stretching vibration is 2995 cm^{-1}.The C-H out of plane bending is 740cm^{-1}.The CH_3 stretching vibration is 2362cm^{-1}[42] as shown in the fig.3.

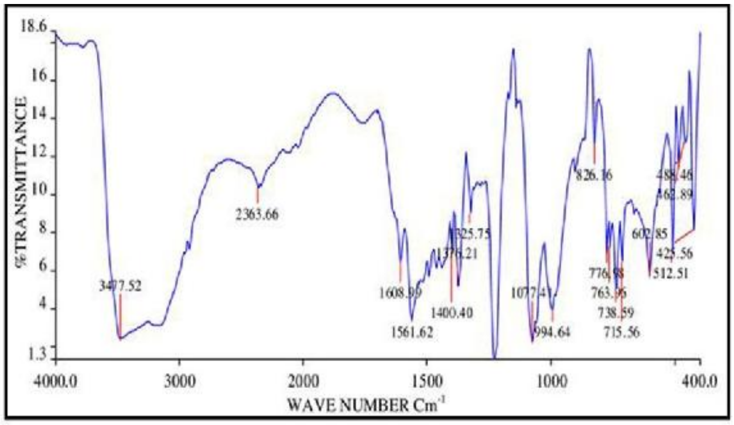


Fig.3:IR Spectrum of [Co[$(DOH)_2$bzo]Br_2]

4.2.3. IR Spectrum of [Co[$(DOH)_2$bzo)](Py)Br]:

The IR spectrum of cobalt complex shows to the absorption of frequencies to the functional group is assigned to –C=N- is 1635cm^{-1}. The Co-N stretching vibration is 515cm^{-1} isa sharp band. The hydrogen bonded -OH is assigned to 3323cm^{-1}**.**The aromatic C-H stretching vibration is 3112 cm^{-1}.The C-H out of plane bending is 767cm^{-1}. The CH_3 stretching vibration is 2956cm^{-1}. The C-N stretching vibration is 1368cm^{-1}.The N-H stretching vibration is 3417cm^{-1}[43] as shown in the fig.4.

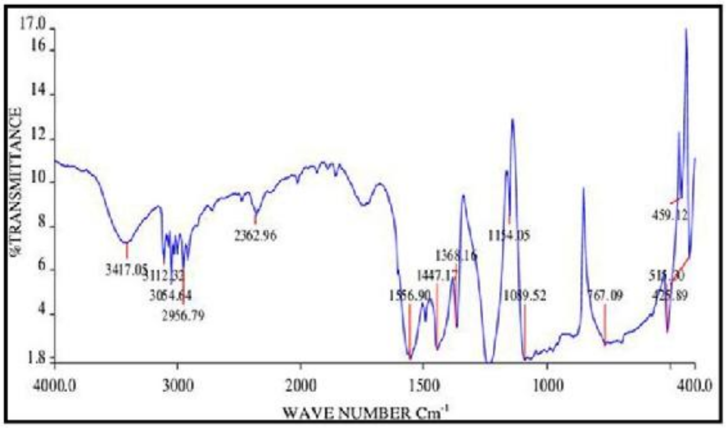


Fig.4:IR Spectrum of [Co[$(DOH)_2$bzo](Py)Br]

4.2.4. IR Spectrum of [Co[(DOH)$_2$bzo](Im)Br]:

The IR spectrum of cobalt complex shows to the absorption of frequencies to the functional group is assigned to –C=N- is 1670cm^{-1}. The Co-N stretching vibration is 511cm^{-1} isa sharp band. The hydrogen bonded -OH is assigned to 3300cm^{-1}**.**The aromatic C-H stretching vibration is 3143 cm^{-1}.The C-H out of plane bending is 742cm^{-1}. The CH$_3$ stretching vibration is 2913cm^{-1}. The C-N stretching vibration is 1332cm^{-1}.The N-H stretching vibration is 3430cm^{-144} as shown in the fig.5.

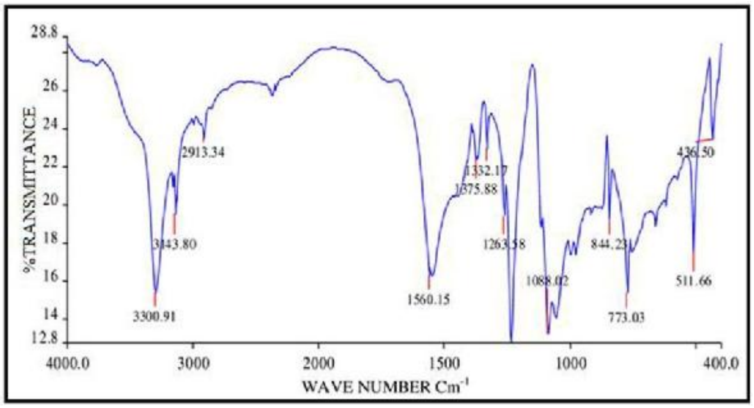


Fig.5: IR Spectrum of [Co[(DOH)$_2$bzo](Im)Br]

4.2.5. IR Spectrum of [Co[(DOH)$_2$bzo](Bim)Br]:

The IR spectrum of cobalt complex shows to the absorption of frequencies to the functional group is assigned to –C=N- is 1620cm^{-1}. The Co-N stretching vibration is 514cm^{-1} isa sharp band. The hydrogen bonded -OH is assigned to 3401cm^{-1}**.**The aromatic C-H stretching vibration is 3143 cm^{-1}.The C-H out of plane bending is 742cm^{-1}. The CH$_3$ stretching vibration is 2919cm^{-1}. The C-N stretching vibration is 1306cm^{-1}.The N-H stretching vibration is 3569cm^{-145} as shown in the fig.6.

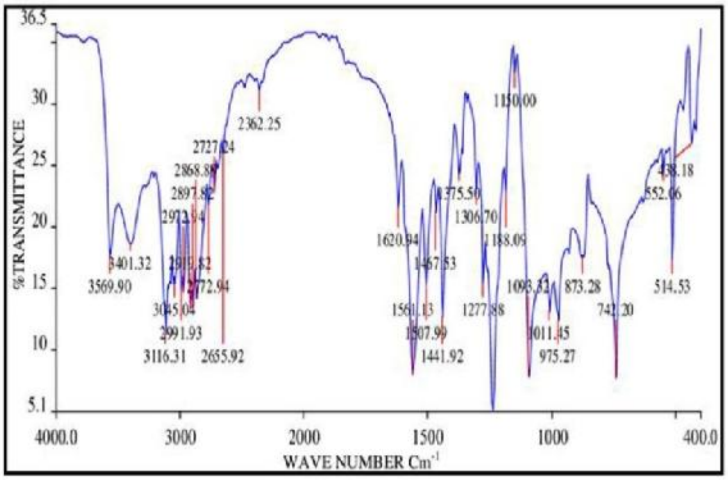


Fig.6:IR Spectrum of[Co[(DOH)$_2$bzo](Bim)Br]

4.2.6. IR Spectrum of [Co[(DOH)$_2$bzo](Pyn)Br]:

The IR spectrum of cobalt complex shows to the absorption of frequencies to the functional group is assigned to –C=N- is 1629cm^{-1}. The Co-N stretching vibration is 509cm^{-1} isa sharp band. The hydrogen bonded -OH is assigned to 3369cm^{-1}**.**The aromatic C-H stretching vibration is 3143 cm^{-1}.The C-H out of plane bending is 720cm^{-1}. The CH$_3$ stretching vibration is 2946cm^{-1}. The C-N stretching vibration is 1325cm^{-1}.The N-H stretching vibration is 3440cm^{-146} as shown in the fig.7.

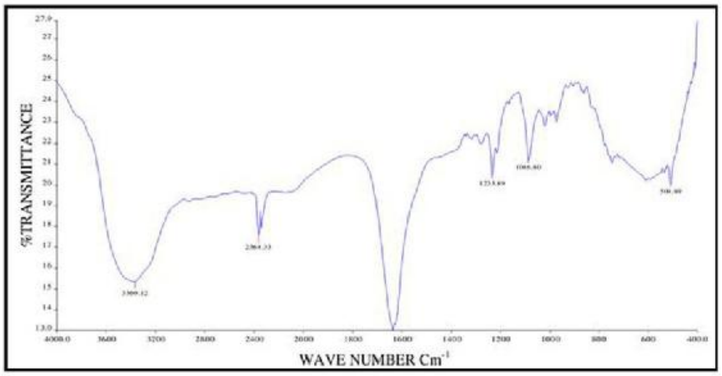


Fig.7:IR Spectrum of [Co[$(DOH)_2$bzo](Pyn)Br]

4.3.^{1}H NMR Studies:

4.3.1.^{1}HNMR of [$(DOH)_2$bzo)]:

The ^{1}H NMR spectra of cobaltoximes clearly showed that on coordination, the δ due to the CH3 group appears Quartet at 7.766 and 7.786ppm. In all complexes, δ appear as an indicating the equivalence of four methyl groups present in the structure. The δ due to OH proton in dioxime appears singlet at 1.916 and 2.555ppm. This aromatic benzene ring 3, 6 positions is 7.638ppm in an up field Shift and 4; 5positions is 7.758ppm in multipletshift[47] as shown in the fig.8.

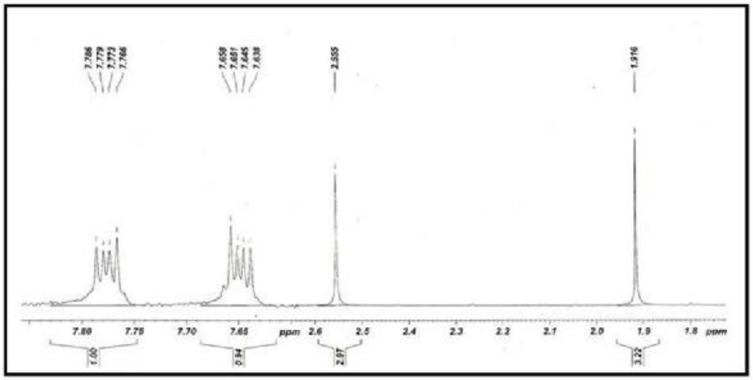


Fig.8:^{1}HNMR Spectrum of [$(DOH)_2$bzo]

4.3.2.^{1}HNMR of [Co$(DOH)_2$bzo) Br_2]:

The ^{1}H NMR spectra of cobaltoximes clearly showed that on coordination, the δ due to the CH3 group appears Quartet at 7.902 and 8.037ppm. In allcomplexes, δ appear as an indicating the equivalence of four methyl groups present in the structure. The δ due to 2 molecule OH proton in dioxime appears singlet at 2.412 and 2.474ppm. This aromatic benzene rings 2.779ppm in multiplet shift. Cobalt atom appears in a singlet at 2.553ppm[48] as shown in the fig.9.

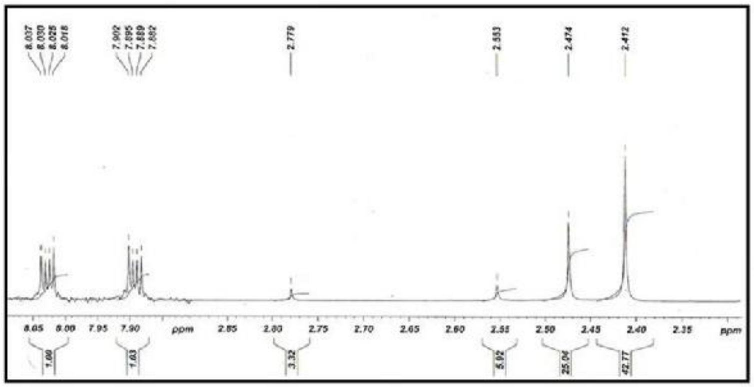


Fig.9:^{1}HNMR Spectrum of[Co[$(DOH)_2$bzo]Br_2]

4.3.3.^{1}HNMR of [Co[(DOH)$_2$bzo](Im)Br]:

The ^{1}H NMR spectra of cobaltoximes clearly showed that on coordination, the δ due to the CH3 group appears Quartet at 7.90 and 8.05ppm. In allcomplexes, δ appear as an indicating the equivalence of four methyl groups present in the structure. The δ due to 2 molecule OH proton in dioxime appears singlet at 2.541 and 2.553ppm. This aromatic benzene rings 3, 6 positions at 2.396ppm and 4, 5 positions at 2.492ppm appears on multiplet shift. Cobalt atom appears in a singlet at 2.603ppm.The heterocyclic ring of imidazole on axial ligand hydrogen atom at 2.514ppm appears on asinglet[49] as shown in the fig.10.

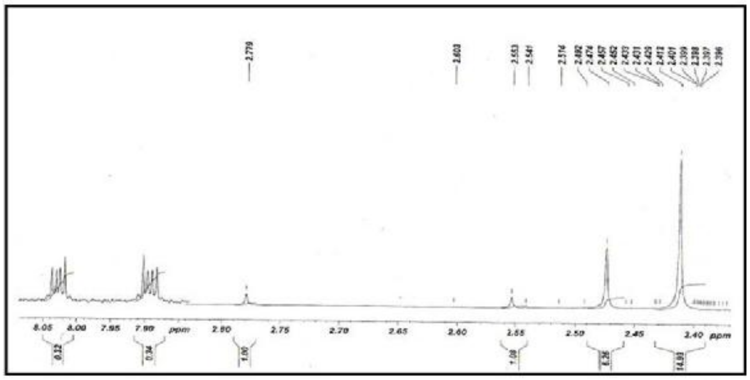


Fig.10:^{1}HNMR Spectrum of [Co[(DOH)$_2$bzo](Im)Br]

4.3.4.^{1}HNMR of [Co[(DOH)$_2$bzo](Bim)Br]:

The ^{1}H NMR spectra of cobaltoximes clearly showed that on coordination, the δ due to the CH_3 group appears Quartet at 7.88 and 8.15ppm. In all complexes,δ appear as an indicating the equivalence of four methyl groups present in the structure. The δ due to 2 molecule OH proton in dioxime appears singlet at 2.531 and 2.543ppm. This aromatic benzene rings 3, 6 positions at 2.386ppm and 4, 5 positions at 2.482ppm appears on multiplet shift. Cobalt atom appears in a singlet at 2.613ppm.The heterocyclic ring of Benzimidazole on axial ligand hydrogen atom at 2.534ppm appears on a singlet. The axial ligand of Benzimidazole on benzene ring appears multiplet on 2.401ppm[50] as shown in the fig.11.

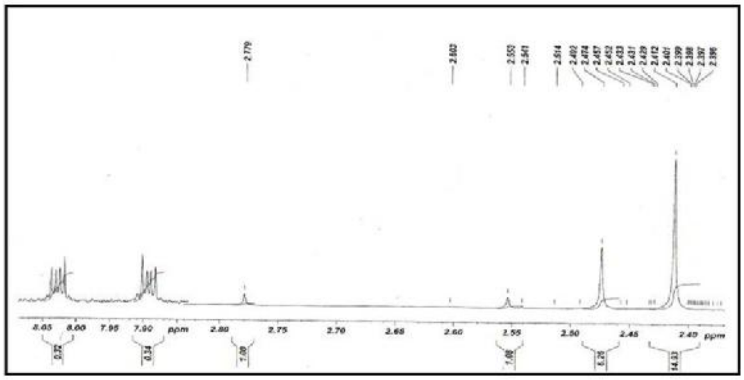


Fig.11:^{1}HNMR Spectrum of [Co[(DOH)$_2$bzo](Bim)Br]

4.4 Cyclic voltammetry:

4.4.1.Cyclic Voltammogram [Co[(DOH)$_2$bzo] Br$_2$]:

The cyclic voltammogram of a glassy carbon electrode with Ag/AgClthe system in the potential range -0.8 to 1.5V contained a reduction and Oxidation wave. In the [Co[(DOH)$_2$bzo]Br$_2$] complex, the cathodic peaks arising at -0.491 and 0.681Vs-1 corresponding to Co^{2+} and Co^+ state respectively. The anodic peak arising at –0.256 Vs^{-1} and -0.332 Vs^{-1} with respect to Co^{2+} and Co^{3+} state. The ΔE value of position 2 and 3 was foundto be 0.079Vs^{-1}[51] as shown in the fig.12.

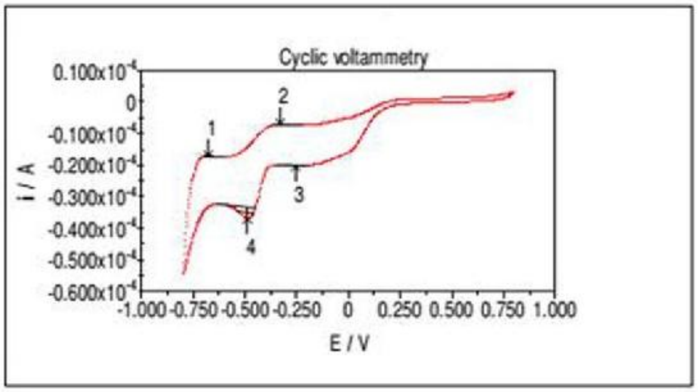


Fig.12: Cyclic Voltammogram of [Co[(DOH)$_2$bzo] Br$_2$]

4.4.2. Cyclic Voltammogram of [Co[(DOH)$_2$bzo](Im)Br]:

The cyclic voltammogram of a glassy carbon electrode with Ag/AgCl the system in the potential range -0.8 to 1.5Vs-1 contained a reduction and oxidation wave. In the [Co[(DOH)2bzo](Im)Br] complex, the cathodic peaks arising at -0.347 and 0.291Vs-1 corresponding to Co^{2+} and Co^{+} state respectively. The anodic peak arising at–0.466 Vs^{-1}on Co^{2+} and Co^{3+} state. The ΔE value of position 1 and 3 was found to be 0.0595Vs^{-152}as shown in the fig.13.

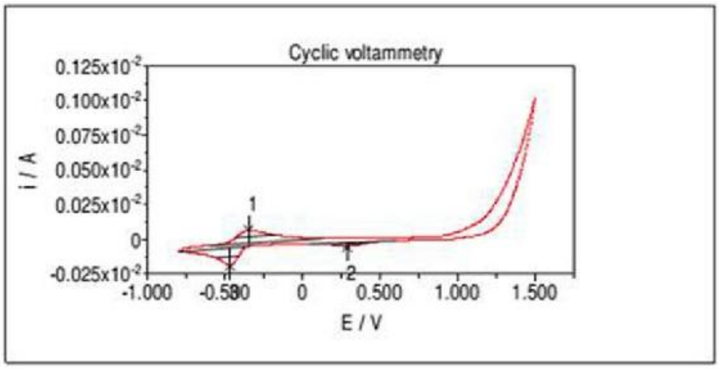


Fig.13: Cyclic Voltammogram of [Co[(DOH)$_2$bzo](Im)Br]

4.4.3. Cyclic Voltammogram of [Co[(DOH)$_2$bzo](Bim)Br]:

The cyclic voltammogram of a glassy carbon electrode with Ag/AgCl the system in the potential range -0.8 to 1.5Vs-1 contained a reduction and oxidation wave. In the [Co [(DOH)$_2$bzo](Bim)Br] complex, the cathodic peaks arising at -0.359 and 0.266Vs^{-1} corresponding to Co^{2+} and Co^{+} state respectively. The anodic peak arising at –0.461 Vs^{-1}on Co^{2+} and Co^{3+} state. The ΔE value of position 1 and 3 was found to be 0.051Vs^{-153} as shown in the fig.14.

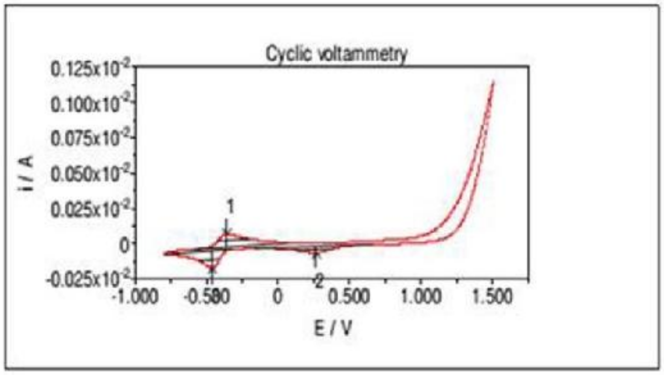
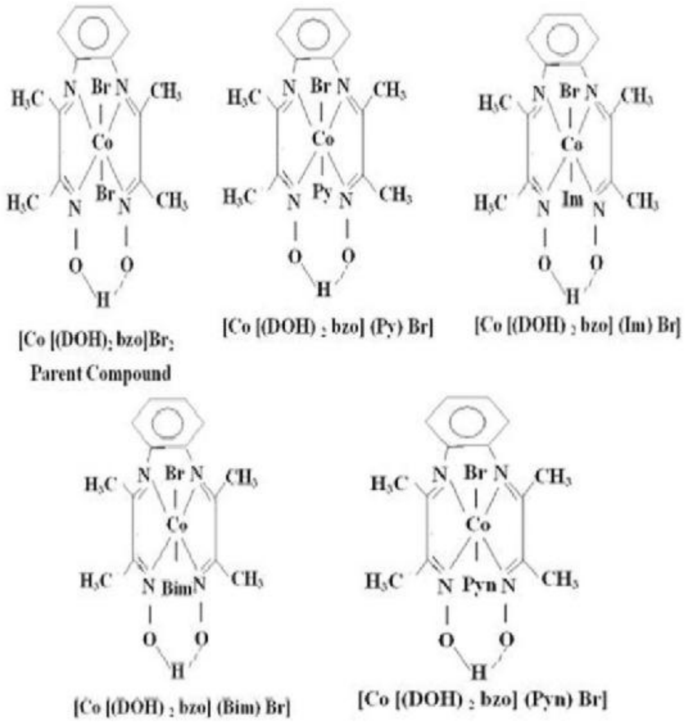


Fig.14: Cyclic Voltammogram of [Co[(DOH)$_2$bzo](Bim)Br]

4.5. Cobalt (III) bromo dioxime ligand complexes structure:



$[Co[(DOH)_2bzo]Br_2$ Parent Compound

$[Co[(DOH)_2bzo](Py)Br]$

$[Co[(DOH)_2bzo](Im)Br]$

$[Co[(DOH)_2bzo](Bim)Br]$

$[Co[(DOH)_2bzo](Pyn)Br]$

Fig.15: Structure of Cobalt (III)bromodioxime complexes.

5. Conclusions

In conclusion, it could be stated that the macrocyclic dioxime Viz $[(DOH)_2bzo]$ behaves like dimethylglyoxime. So that the cobalt (III) macrocyclicdioxime prepared shows similarity to cobaltoximes. It is used as a model compound for vitamin-B_{12}. The catalytic activity was found to be mainly depending on heterocyclic axial ligand viz., pyridine,imidazole, benzimidazole, and pyridoxine. They may be attributed to greater tendency for the complexes to undergo protonation becoming more positive in the case. The above facts reveal that the macrocyclic ligands and their complexes discussed in the research work would be serving as a bridge between synthetic inorganic chemistry and biomedical sciences.

Acknowledgments

The authors wish to thank SAIF IIT Madras for providing a ^{1}HNMR spectrum analysis. We would like to acknowledge the support of Loyola College, Chennai. I think my guide on Dr. A. Dayalan, H.O.D of chemistry Loyola College and Chennai.

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How to cite this article:

S. Senthamil Selvi, A. Dayalan. (2016). Macrocyclic Cobalt (III) Dioximes by Microwave Assisted Synthesis and Characterization of Coordination Complexes on Bromo Complexes. Int. J. Curr. Res. Chem. Pharm. Sci. 3(4): 88-98.