

Macrocyclic Cobalt (III) Dioximes By Microwave Assisted Synthesis And Characterization And 13&14-Membered Coordination 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 *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 (vitB6) to obtain corresponding macrocyclic organo cobalt complexes. The parent cobalt complexes and their alkyl derivatives have been characterized by elemental analyses, conductivity data, UV, IR, ¹HNMR spectral data and electrochemical behaviour of these complexes has been studied by cyclic voltammetry.

Keywords: Macrocyclic cobalt (III) complexes; Schiff base; Coordination template synthesis; Cyclic Voltammetry.

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I. Introduction:

The field of macro cyclic chemistry of metals is developed very rapidly because of its application and importance in the area of coordination chemistry. Studies on complexes of Schiff base macrocyclic ligand with different size and number of donor atoms for coordination with a variety cobalt (II) & (III) of porphyrin or corrin ring system and the metal phthalocyanine complexes have drawn considerable attention in the study of coordination chemistry of biological interest. 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. This is known as template synthesis. Cobalt -60 is a radioactive metal that is used in radiotherapy. It produces two gamma rays with energies of 1.17 Mev & 1.33Mev. Cobalt is a hard ferromagnetic silver-white element. The Curie temperature is of 1388k with 1.6-1.7BM per atom. Cobalt commonly present a mixture of two crystallographic structures hcp-fcc with a transition temperature is 722k. Common oxidation state of +3, +2, +1. Cobalt chloride is a well established chemical inducer of hypoxia-like responses such as erythropoiesis. Cobalt in small amount is essential to many living organisms including humans. Having 0.13 to 0.30 mg/kg of cobalt in soils markedly improve the health of grazing animals. cobalt is a central component of the vitamin B₁₂. Cobalt (II) has d⁷ configuration and forms coordination complexes with octahedral and tetrahedral geometries. The stable complexes with cobalt (III), the stability of trivalent cobalt greatly improved. Trivalent cobalt is also more stable in basic media than in acidic media the potential for the oxidation in acidic solutions containing no complexing anions is so high that free cobalt (III) is appreciable concentration rapidly oxidizes water. The tetraza, macrocycles from 13 to 16 member macrocyclic ring are found to be the main trust area in the field of the coordination chemistry of transition and inner transition metals on coordination, 5 to 7 member chelated rings are produced which are held coplanar with the metal ion, Compounds containing the group >C=N-OH called oximes, can be derived from aldehyde and ketone by condensing them with hydroxylamine. This derived from aldehyde are known as aldioximes, those from ketones as ketoximes. They were first prepared by V. Meyer in 1982. The study of the coordination chemistry of cobalt (III) dioximes has been extended to imine oximes, which are Schiff bases of carbonyl oximes and their simplest form they are also bidentate ligands. Cobalt (III) complexes, [C_o (L) X₂]⁺; (X= cl⁻, Br⁻ (L= (DOH)₂Bzo)]. The cobalt (III) complexes replaced by one chloride and one bromine in axial ligand as pyridine, imidazole, benzimidazole and vitamin B₆.

II. Experimental Methods:

REAGENT:

All chemicals were of analytical reagent grade and solutions were prepared with purified water of L.P grade. cobaltous chloride, cobaltous bromide was used as such for the synthesis of metal complexes. For synthesis of ligands(L) O-phenylene diamine and diacetyl monoxime. The metal complexes of Co [(DOH)₂bzo] Cl₂ and Co [(DOH)₂ bzo]Br₂ replaced by one chloride and one bromide in fixed axial ligand of pyridine,imidazole,benzimidazole and vitaminB₆.

SOLVENT:

Double distilled water was obtained by distilled over alkaline.KMnO₄ in all glass apparatus,it washed the complexes in diethyl ether and ethanol. The metal complexes prepared mainly used solvent is acetone for the all synthesis of cobalt complexes

SYNTHESIS OF LIGAND [(DOH)₂BZO]:

About 0.05 mole of o-phenylene diamine was added to 200ml of distilled water and the solution was exposed to microwave in an unmodified microwave oven for 30s.To this 0.1 mole of diacetyl monoxime was added and again exposed to microwave for about 30s. The solution was set aside for 10 or 24 hours to get straw yellow product (yield 98% and m.p.176°C it was, filtered, washed with cold water and recrystallised from hot water or ethanol.

SYNTHESIS OF CHOLO COBALT (III) DIOXIMES:

1. [Co {(DOH)₂BZO}Cl₂]:

About 0.01 moles of CoCl₂.6H₂O was dissolved in 75ml of acetone with constant stirring for about 10 minutes. It was then mixed with 0.01 moles of (DOH)₂BZO and stirred well. A green colour core complex was formed. It was then allowed to stir for one hour. The product was filtered and washed with ether.

2. [Co {(DOH)₂Bzo}(Im) Cl]:

About 0.005 mole of dichloro complex was added to 75ml of ethanol and allowed to stir for five minutes. The solution under stirring condition was mixed with 0.005moles of Imidazole and refluxed for about 3 hrs at 40 °C. The green colored solution turned yellow. The complex thus obtained was washed with ethanol and diethyl ether.

3. [Co {(DOH)₂Bzo}(Bim)Cl

About 0.005 mole of dichloro 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 benzimidazole and refluxed for about 3hrs at 40°C. The green colored solution turned pale brown. The complex thus obtained was washed with ethanol and diethyl ether.

4. [Co {(DOH)₂Bzo}(Py)Cl]

About 0.005 mole of dichloro 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 pyridine and refluxed for about 3hrs at 40°C. The green coloured solution turned dark brown. The complex thus obtained was washed with ethanol and diethyl ether.

5. [Co{(DOH)₂Bzo}(Pyn)Cl]

Extraction of pyridoxine hydrochloride

Pyridoxine hydrochloride of required equimolar quantity use as such for 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 6 hour in excess absolute alcohol. Then the resulting mixture was filtered and the filtered was used as such for preparing the desired complexes.

About 0.005 mole of dichloro complex was added to 75ml of ethanol and allowed to stir for five minutes. The solution under stirring condition with added 0.005 mole of Pyridoxine with condenser and the solution was stirred for about 3hour at 40°c. The green coloured solution turned brown. That solution was filtered using sintered crucible and the complex was washed with ethanol and with diethyl ether.

III. Synthesis Of Bromo Cobalt (III) Dioximes:

1. [Co{(DOH)₂Bzo}Br₂]

About 0.01 moles of CoBr₂.6H₂O was dissolved in 75ml of acetone with constant stirring for about 10 minutes. It was then mixed with 0.01 moles of (DOH)₂Bzo and stirred well. A parrot green colour core complex was formed. It was then allowed to stir for one hour. The product was filtered and washed with diethyl ether

2. [Co{(DOH)₂Bzo}(Im)Br]

About 0.005 mole 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°C. The green colored solution turned pale yellow. The complex was washed with ethanol and diethyl ether.

3. [Co{(DOH)₂Bzo}(Bim)Br]

About 0.005 mole 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 benzimidazole and refluxed for about 3hrs at 40°C. The green colored solution turned brown. The complex was washed with ethanol and diethyl ether

4. [Co{(DOH)Bzo}(Py)Br]

About 0.005 mole 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°C. The green colored solution turned dark brown. The complex was washed with ethanol and diethyl ether.

5. [Co{(DOH)Bzo}(Pyn)Br]

About 0.005 mole of dichloro 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 condenser and the solution was stirred for about 3hrs at 40°C. The green coloured solution turned brown. The complex was washed with ethanol and diethyl ether

PHYSICAL MEASUREMENTS

An Electronic Spectra study spectrum was conducted on a complex was obtained from LAMBDA-125 spectra photometer using 1cm matched quartz cells. Alcoholic solution of the complexes of suitable concentrations was used. UV-Visible spectrometer in the wavelength 200-600 nm.

IR spectra of the complexes were obtained using PERKIN ELMER spectrum-1 in KBr disc by making pellets of the complexes. The spectra were recorded wavenumber range of 4000-400cm⁻¹.

The ¹H magnetic resonance spectra of the complexes were recorded in DMSO-d₆ on a JOEL-400 MHz NMR spectro photometer at room temperature.

Cyclic voltammogram of the complexes were obtained using general purpose electrochemical system (GPES) Version 4.9 by using suitable concentration of the complexes.

RESULT AND DISCUSSION:

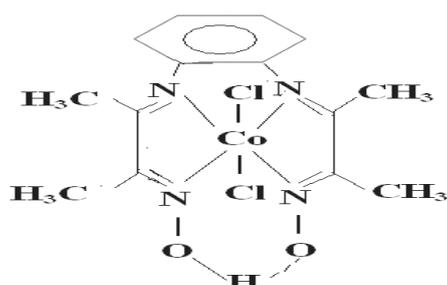
Characterisation of Ligand[(DOH)₂bzo]

The recrystallised pure ligand melts at 276°C as reported in the literature. The UV spectra of the complexes showed that the position of the high intense absorption and in the range 312-352nm may be attributed to π-π* transition of the complexes. 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)₂bzo 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.

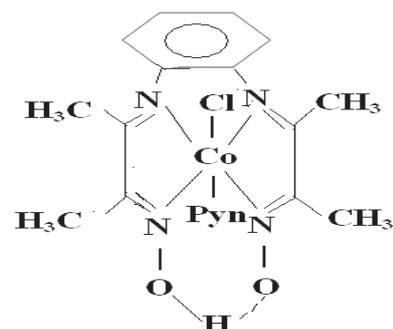
The ¹H NMR spectra of cobaloximes clearly showed that on coordination, the δ due to the CH₃ group of [(DOH)₂bzo] at 2.382ppm undergoes a downfield shift by 0.43 to 2.33ppm. In the all complexes δ appears as a singlet indicating the equivalence of four methyl groups present in the structure. The δ due to OH proton in dioxime appeared at 11.33. This aromatic benzene ring 3, 6 positions is 7.80ppm in an up field Shift and 4, 5 positions is 7.65ppm in an up field shift.

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 699cm⁻¹ is attributed to CH₃(oxime) while a similar band at 1384cm⁻¹ is assigned to -C=N- is 1640cm⁻¹. the N-O stretching vibration is 1215cm⁻¹ is sharp band. The hydrogen bonded N-OH is assigned to 3430cm⁻¹.

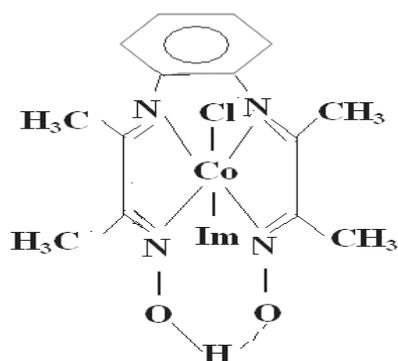
Characterisation of chloro cobalt(III) dioxime complexes:



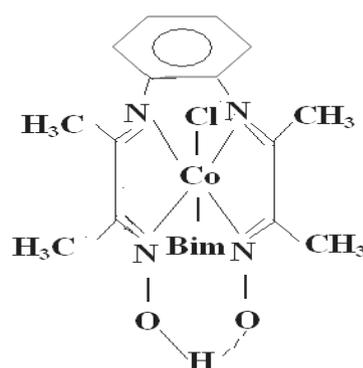
[Co {(DOH)₂bzo} Cl₂]
Parent compound



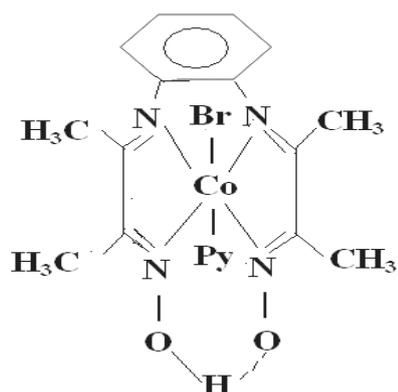
[Co {(DOH)₂bzo} (Pyn) Cl]



[Co {(DOH)₂bzo} (Im)Cl]



[Co {(DOH)₂bzo} (Bim) Cl]



[Co {(DOH)₂bzo} (Py) Br]

Electronic spectra of the chloro cobalt (III) dioxime complexes

. No	Complexes	$\pi-\pi^*$ λ max	$\pi-\pi^*$ [(DOH) ₂ bzo] λ max	LMCT
1	[Co{(DOH) ₂ bzo}Cl ₂]	332	260	400
2	[Co(DOH) ₂ bzo(Py)Cl]	323	265	410
3	[Co(DOH) ₂ bzo(Im)Cl]	352	270	415
4	[Co(DOH) ₂ bzo(Bim)Cl]	312	275	420
5	[Co(DOH) ₂ bzo(Pyn)Cl]	325	280	425

IV. IR Spectrum Of The Chloro Cobalt (III) Dioxime Complexes

1. [Co (DOH)₂bzo]Cl₂

The IR spectrum of complex the absorption of frequencies to the functional group of phenyl the sharp band of medium intensity occurred at 740cm⁻¹ is attributed to CH₃(oxime) while a similar band at 1379cm⁻¹ is assigned to –C=N- is 1627cm⁻¹. The Co-N stretching vibration is 514cm⁻¹ is sharp band. The hydrogen bonded OH is assigned to 3392cm⁻¹

2. [Co (DOH)₂bzo](Im)Cl

The IR spectrum of complex to the absorption of frequencies to the functional group of phenyl the sharp band of medium intensity occurred at 743cm⁻¹ is attributed to CH₃(oxime) while a similar band at 1369cm⁻¹ is assigned to –C=N- is 1670cm⁻¹. The Co-N stretching vibration is 512cm⁻¹ is sharp band. The bonded OH is assigned to 3282cm⁻¹. The C-H stretching vibration is 2917cm⁻¹ is sharp band. The bonded C-N is assigned to 1331cm⁻¹.The hydrogen bonded N-H is assigned to 3425cm⁻¹.

3. [Co (DOH)₂bzo](Bim)Cl

The IR spectrum of complex shows to the absorption of frequencies to the functional group of phenyl the sharp band of medium intensity occurred at 742cm⁻¹ is attributed to CH₃(oxime) while a similar band at 1375cm⁻¹ is assigned to –C=N- is 1619cm⁻¹. The Co-N stretching vibration is 514cm⁻¹ is sharp band. The bonded OH is assigned to 3399cm⁻¹. The C-H stretching vibration is 3059cm⁻¹ is sharp band. The bonded C-N is assigned to 1307cm⁻¹.The hydrogen bonded N-H is assigned to 3410cm⁻¹.

4. [Co (DOH)₂bzo](Py)Cl

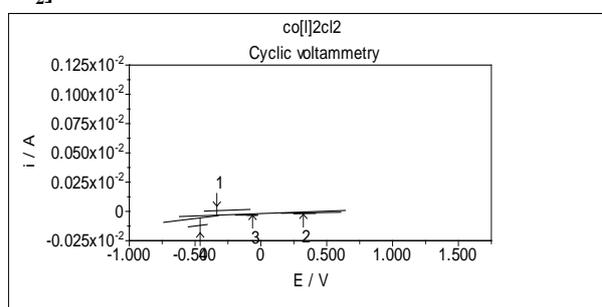
The IR spectrum of complex shows to the absorption of frequencies to the functional group of phenyl the sharp band of medium intensity occurred at 742cm⁻¹ is attributed to CH₃(oxime) while a similar band at 1375cm⁻¹ is assigned to –C=N- is 1607cm⁻¹. The Co-N stretching vibration is 513cm⁻¹ is sharp band. The bonded OH is assigned to 3437cm⁻¹. The C-H stretching vibration is 2917cm⁻¹ is sharp band. The bonded C-N is assigned to 1295cm⁻¹.The hydrogen bonded N-H is assigned to 3475cm⁻¹.

5. [Co (DOH)₂bzo](Pyn)Cl

The IR spectrum of complex shows to the absorption of frequencies to the functional group of phenyl the sharp band of medium intensity occurred at 680cm⁻¹ is attributed to CH₃(oxime) while a similar band at 1378cm⁻¹ is assigned to –C=N- is 1637cm⁻¹. The Co-N stretching vibration is 513cm⁻¹ is sharp band. The bonded OH is assigned to 3437cm⁻¹. The C-H stretching vibration is 2917cm⁻¹ is sharp band. The bonded C-N is assigned to 1295cm⁻¹.

CYCLIC VOLTAMMETRY

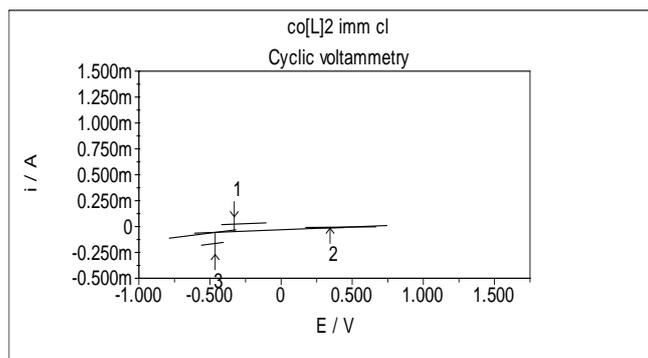
1. [Co (DOH)₂bzo] Cl₂



The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl system in potential range -0.8 to 1.5V contained a reduction and oxidation wave. In the [Co [(DOH)₂Bzo] Cl₂], the cathodic peaks arising at -0.334 and 0.322V s⁻¹ corresponding to Co²⁺ and Co⁺ state respectively. The anodic peak arising at -0.063 Vs⁻¹ and -0.461 Vs⁻¹ with respect to Co²⁺ and Co³⁺ state. The ΔE value of position 1 and 4 was found to be 0.0635V.

2. [Co (DOH)₂bzo](Im)Cl

The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl system in the potential range -0.8 to 1.5V contained a reduction and oxidation wave. In the [Co [(DOH)₂Bzo] (Im) Cl] complex, the cathodic peaks arising at -0.330 and 0.352Vs⁻¹ corresponding to Co²⁺ and Co⁺ state respectively. The anodic Peak arising at -0.04 Vs⁻¹ and -0.46 Vs⁻¹ with respect to Co²⁺ and Co³⁺ state. The ΔE value of position 1 and 3 was found to be 0.067Vs⁻¹.



3. [Co (DOH)₂bzo](Bim)Cl]

The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl system in the potential range -0.8 to 1.5V contained a reduction and oxidation wave. In the [Co [(DOH)₂Bzo] (Bim) Cl] complex, the cathodic peaks arising at -0.332 and 0.352Vs⁻¹ corresponding to Co²⁺ and Co⁺ state respectively. The anodic peak arising at -0.042 and -0.464Vs⁻¹ with respect to Co²⁺ and Co³⁺ state. The ΔE value of position 1 and 4 was found to be 0.066Vs⁻¹

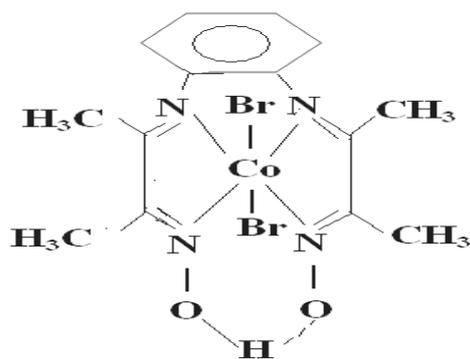
4. [Co (DOH)₂bzo](Py)Cl]

The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl system in the potential range -0.8 to 1.5V contained a reduction and oxidation wave. In the [Co[(DOH)₂Bzo(Py)Cl] complex, the cathodic peaks arising at -0.293 and 0.264V corresponding to Co²⁺ and Co⁺ state respectively. The anodic peak arising at -0.010 and -0.454 V with respect to Co²⁺ and Co³⁺ state. The ΔE value of position 1 and 3 was found to be 0.0065Vs⁻¹

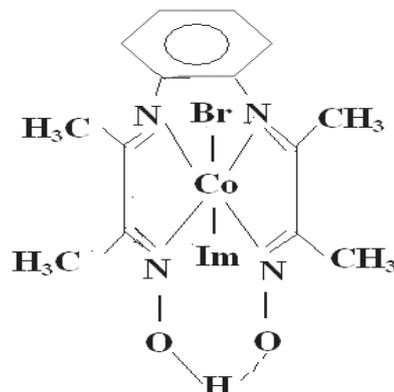
5. [Co (DOH)₂bzo](Pyn)Cl]

The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl system in the potential range -0.8 to 1.5V contained a reduction and oxidation wave. In the [Co [(DOH)₂Bzo] (Pyn) Cl] complex, the cathodic peaks arising at -0.293 and 0.264Vs⁻¹ corresponding to Co²⁺ and Co⁺ state respectively. The anodic peak arising at -0.010 and -0.454Vs⁻¹ with respect to Co²⁺ and Co³⁺ state. The ΔE value of position 1 and 4 was found to be 0.081Vs⁻¹

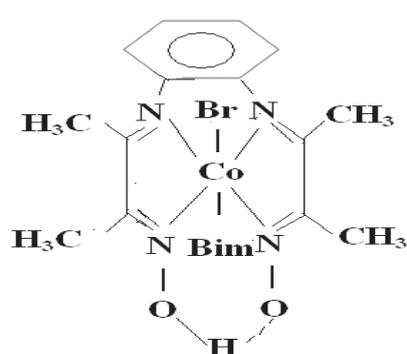
Characterisation of bromo cobalt(III)dioxime complexes



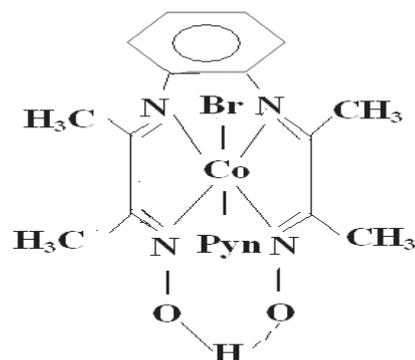
[Co [(DOH)₂ bzo]Br₂
Parent Compound



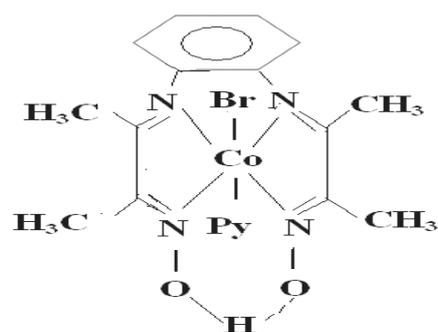
[Co [(DOH)₂ bzo] (Im) Br]



[Co (DOH)₂ bzo] (Bim) Br]



[Co (DOH)₂ bzo] (Pyn) Br]



[Co (DOH)₂ bzo] (Py) Br]

Electronic spectra of the brom cobalt(III) dioxime complexes

No	Complexes	$\pi-\pi^*\lambda$ max	$\pi-\pi^*[(\text{DOH})_2\text{bzo}]\lambda$ max	LMCT
1	[Co(DOH) ₂ bzoBr ₂]	333	285	425
2	[Co(DOH) ₂ bzo(Py)Br]	326	290	430
3	[Co[(DOH) ₂ bzo](Im)Br]	330	300	435
4	[Co(DOH) ₂ bzo(Bim)Br]	322	340	440
5	[Co(DOH) ₂ bzo(Pyn)Br]	338	345	445

IR Spectrum of the bromocobalt (III) dioxime complexes

1. [Co (DOH)₂bzoBr₂]

The IR spectrum of complexes the absorption of frequencies to the functional group of C-H out of plane bending intensity occurred at 740cm⁻¹ is attributed to CH₃ while a similar band at 2362cm⁻¹ assigned to -C=N- is 1636cm⁻¹. The Co-N stretching vibration is 512cm⁻¹ is sharp band. The bonded OH is assigned to 3444cm⁻¹. The aromatic C-H vibration is 2995m⁻¹ is sharp band.

2. [Co [(DOH)₂bzo(Im)Br]

The IR spectrum of complexes the absorption of frequencies to the functional group of C-H out of plane bending intensity occurred at 742cm⁻¹ attributed to CH₃ while a similar band at 2913cm⁻¹ assigned to -C=N- is 1670cm⁻¹. Co-N stretching vibration is 511cm⁻¹ is sharp band. The bonded OH is assigned to 3300cm⁻¹. the aromatic C-H vibration is 3143cm⁻¹ is sharp band. The aromatic C-N vibration is 1332cm⁻¹ is sharp band. The aromatic N-H vibration is 3430cm⁻¹ is sharp band.

3. [Co (DOH)₂Bzo(Bim)Br]

The IR spectrum of complexes the absorption of frequencies to the functional group of C-H out of plane bending intensity occurred at 742cm⁻¹ attributed to CH₃ while a similar band at 2919cm⁻¹ assigned to -C=N- is 1620cm⁻¹. Co-N stretching vibration is 514cm⁻¹ is sharp band. The bonded OH is assigned to 3401cm⁻¹. the aromatic C-H vibration is 3116cm⁻¹ is sharp band. The aromatic C-N vibration is 1306cm⁻¹ is sharp band. The aromatic N-H vibration is 3569cm⁻¹ is sharp band.

4. [Co (DOH)₂Bzo) (Py) Br]

The IR spectrum of complexes the absorption of frequencies to the functional group of C-H out of plane bending intensity occurred at 767cm⁻¹ attributed to CH₃ while a similar band at 2956cm⁻¹ assigned to -C=N- is 1635cm⁻¹. Co-N stretching vibration is 515cm⁻¹ is sharp band. The bonded OH is assigned to 3323cm⁻¹. the aromatic C-H vibration is 3112cm⁻¹ is sharp band. The aromatic C- N vibration is 1368cm⁻¹ is sharp band. The aromatic N-H vibration is 3417cm⁻¹ is sharp band

5.[Co(DOH)₂Bzo(Pyn)Br]

The IR spectrum of complexes the absorption of frequencies to the functional group of C-H out of plane bending intensity occurred at 720cm⁻¹ attributed to CH₃ while a similar band at 2946cm⁻¹ assigned to -C=N- is 1629cm⁻¹. Co-N stretching vibration is 509cm⁻¹ is sharp band. The bonded OH is assigned to 3369cm⁻¹. the aromatic C-H vibration is 3143cm⁻¹ is sharp band. The aromatic C- N vibration is 1325cm⁻¹ is sharp band. The aromatic N-H vibration is 3440cm⁻¹ is sharp band.

¹H NMR spectrum bromocobalt (III) dioxime complexes

1. [Co (DOH)₂Bzo) Br₂]

The ¹H NMR spectra of cobaloximes clearly show that on coordination, the δ due to the CH₃ group of [DOH)₂Bzo] at 2.382ppm undergoes a downfield shift by 0.43 to 2.33ppm. In the all complexes δ appeared as a singlet indicating the equivalence of four methyl groups present in the structure. The δ due to OH proton in dioxime appeared at 11.33. This aromatic benzene ring 3, 6 positions is 7.80ppm in an up field Shift and 4, 5 positions is 7.65ppm in an up field shift.

2. [Co (DOH)₂Bzo) (Im) Br]

The ¹H NMR spectra of cobaloximes clearly showed that on coordination, the δ due to the CH₃ group of [DOH)₂Bzo] at 2.382ppm undergoes a downfield shift by 0.43 to 2.33ppm. In the all complexes δ appeared as a singlet indicating the equivalence of four methyl groups present in the structure. The δ due to OH proton in dioxime appeared at 11.33. This aromatic benzene ring 3, 6 positions is 7.80ppm in an up field Shift and 4, 5 positions is 7.65ppm in an up field shift. The imidazole down field multiplicity and quartet were obtained

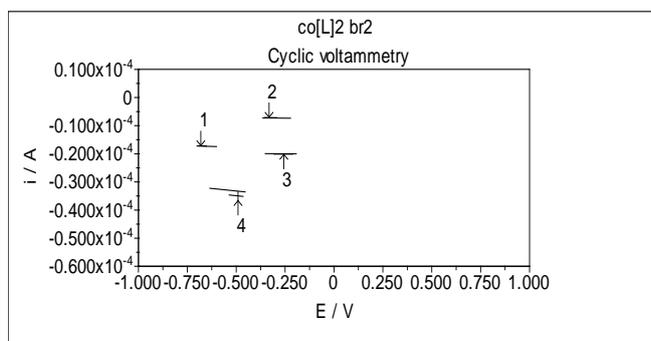
3. [Co (DOH)₂Bzo) (Bim)Br]

The ¹H NMR spectra of cobaloximes clearly showed that on coordination, the δ due to the CH₃ group of [DOH)₂Bzo] at 2.382ppm undergoes a downfield shift by 0.43 to 2.33ppm. In the all complexes δ appeared as a singlet indicating the equivalence of four methyl groups present in the structure. The δ due to OH proton in dioxime appeared at 11.33. This aromatic benzene ring 3, 6 positions is 7.80ppm in an up field Shift and 4, 5 positions is 7.65ppm in an up field shift. The Benzimidazole down field multiplicity and quartet were obtained.

Cyclic Voltammetry

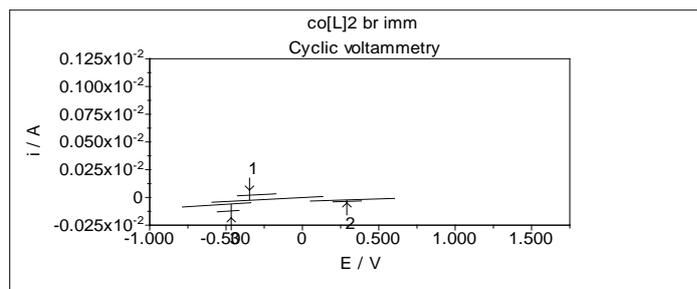
1. [Co [(DOH)₂Bzo] Br₂]

The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl system in the potential range -0.8 to 1.5V contained a reduction and oxidation wave. In the [Co [(DOH)₂Bzo]Br₂] complex, the cathodic peaks arising at -0.491 and 0.681Vs⁻¹ corresponding to Co²⁺ and Co⁺ state respectively. The anodic peak arising at -0.256 Vs⁻¹ and -0.332 Vs⁻¹ with respect to Co²⁺ and Co³⁺ state. The ΔE value of position 2 and 3 was found to be 0.079Vs⁻¹



2. [Co [(DOH)₂Bzo](Im) Br]

The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl 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 Co²⁺ and Co⁺ state respectively. The anodic peak arising at -0.466 Vs⁻¹ with respect to Co²⁺ and Co³⁺ state. The ΔE value of position 1 and 3 was found to be 0.0595Vs⁻¹



3. [Co [(DOH)₂Bzo](Bim) Br]

The cyclic voltammogram on a glassy carbon electrode with Ag/AgCl system in the potential range -0.8 to 1.5Vs^{-1} contained a reduction and oxidation wave. In the [Co [(DOH)₂Bzo](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 -0.461Vs^{-1} with respect to Co^{2+} and Co^{3+} state. The ΔE value of position 1 and 3 was found to be 0.051V .

CONCLUSIONS

In conclusion it could be stated that the macrocyclic dioxime Viz [(DOH)₂bzo] behaves like dimethylglyoxime. So that the cobalt (III) macro cyclic dioxime prepared shows similarity to cobaloximes. It is used as a model compound for vitamin-B₁₂ the catalytic activity was found to be mainly depending on heterocyclic axial ligand viz., pyridine, imdazole, benzimidazole, and pyridoxine. This may be attributed to greater tendency for the complexes to undergo protonation becoming more positive in the case.

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