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Macrocyclic Cobalt (III) Dioximes By Microwave Assisted Synthesis And Characterization UV and IR Spectra Of Coordination Complexes On Chloro 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, actone, 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 derivates have been characterized by elemental analyses, conductivity data, UV, IR, spectral data.

Keywords: Macrocyclic cobalt (III) complexes; Schiff base; Coordination template synthesis;UV spectroscopy and IR spectroscopy.

Introduction:

The field of macro cyclic chemistry of metals is developed very rapidly because of its application and importance in the area of coordination chemistry¹. 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 porpyrin or corrin ring system and the metal phthalocyanine complexes have drawn considerable attention in the study of coordination chemistry of biological interest². Their stability depends on the nature and the geometry of the ligands. Macrocyclic ligand complexes are more stable then 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 radiotherapy³. 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 is small amount is essential to many living organisms including humans⁴. 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 then 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 to16 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 oximes⁵, can be derived from aldehyde and ketone by condensing them with hydroxylamine. This derived from aldehyde are known as aldoximes, 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, $[C_o (L) X_2]^+$; $(X = cl^-, Br^-(L = (DOH)_{2bzo})]^6$. The cobalt (III) complexes replaced by one chloride and one bromine in axial ligand as pyridine, imidazole, benzimidazole and vitamin B₆.

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 vitaminB₆⁷.

Solvent:

Double distilled water was obtained by distilled over alkaline. $KMnO_4$ 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 complexes⁸

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 ethanol⁹.

Synthesis of cholo cobalt (III) Dioximes:

1. [CO {(**DOH**)₂**BZO**}CL₂]:

About 0.01 moles of $CoCl_2.6H_2o$ was dissolved in 75ml of acetone with constant stirring for about 10 minutes. It was then mixed with 0.01 moles of $(DOH)_2BZO$ 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 ether¹⁰.

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 $^{\circ}$ C. The green colored solution turned yellow. The complex thus obtained was washed with ethanol and diethyl ether¹¹.

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 ether¹².

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 ether¹³.

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 ether¹⁴.

Physical Measurements

An ElectronicSpectra 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 nm¹⁵.

IR spectra of the complexes were obtained using PERKIN ELMER spectrum-1 in KBr disc by making pellets of the complexes. The spectrawere recorded wavenumber range of 4000-400cm-1¹⁶.

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 - * 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 - * 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 nature¹⁷.

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 $CH_3(\text{oxime})$ 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-1¹⁸.

Characterisation of chloro cobalt(III) dioxime complexes:





[Co [(DOH) 2 bzo] (Im)Cl]





[Co [(DOH) 2 bzo] (Py) Br]

 $\begin{array}{c|c} \mathbf{H}_{3}\mathbf{C} & \mathbf{N} & \mathbf{CIN} & \mathbf{CII}_{3} \\ & & & & \\ & & & \\ \mathbf{H}_{3}\mathbf{C} & \mathbf{N} & \mathbf{Pyn}_{\mathbf{N}} & \mathbf{CH}_{3} \\ & & & & \\ & & & \\ & & & \\ & & & \\ \mathbf{H} & & \\ & & \\ \mathbf{Co} & (\mathbf{DOH})_{2} \text{ bzo} (\mathbf{Pyn}) \text{ CI} \end{array}$

Electronic spectra of the chloro cobalt (III) dioximecomplexes

. No	Complexes	_ *	- *	LMCT
	Ĩ	max	[(DOH) ₂ bzo]	
			max	
1	$[Co{(DOH)_2bzo}Cl_2]$	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

Electronic spectra of the chloro cobalt (III) dioxime complexes Figure: 1. [Co $(DOH)_2bzo)Cl_2$]



2. [Co (DOH)₂bzo)(Im)Cl]



3. [Co (DOH)₂bzo)(Bim)Cl]



4. [Co (DOH)₂bzo)(Py)Cl]



5. [Co (DOH)₂bzo)(Pyn)Cl]



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 $CH_3(\text{oxime})$ 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-1¹⁹.

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 $CH_3(\text{oxime})$ 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-1.²⁰

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 $CH_3(\text{oxime})$ 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-1²¹.



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 $CH_3(\text{oxime})$ 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-1²².



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 $CH_3(\text{oxime})$ 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-1²³.



Conclusions

In conclusion it could be stated that the macrocyclic dioxime Viz $[(DOH)_2bzo]$ behaves like dimethylglyoxime²⁴. 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 case²⁵.

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