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Synthesis and Structural Studies of *trans*-[Bromo-Bis(Dimethylglyoximato] Cobalt(III) Complexes Containing Heterocyclic Nitrogen Donor Ligands

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Cobalt(III) complexes of the type $[Co(DH)_2LBr]$ where DH = dimethylglyoximato, anion L = (pyridine, piperidine, quinoline, isoquinoline, triazole, indole, benzimidazole, benzotriazole, carbazole) have been isolated and characterized on the basis of physico-chemical methods. The chemical analyses are in complete agreement with the above formula of the compounds. The IR spectra reveal the hydrogen bonding and bonding from nitrogen of the ligand to the cobalt. The NMR spectra indicate the stereochemistry of the compound. The UV spectra indicate the octahedral geometry of the complexes.

Key Words: Synthesis, Structure, Cobalt(III), Complexes.

INTRODUCTION

The cobaloxime and other related complexes have been found to possess a wide variety of biological[1] activities against bacteria, fungi and certain types of tumours. They closely stimulate the reaction of vitamin-B_{12} and are also important in vitamin-B_{12} model chemistry. The X-ray crystal structure of alkyl cobaloximes suggests that the cobalt atom in cobaloxime has slightly greater positive charge causing relatively stronger attachment of a base along the axial direction. Some works have been done on the transition metal[2–5] complexes containing dimethylglyoxime and different nitrogen donor ligands. From our point of view it was challenging to study the interaction between metal ions and heterocyclic nitrogen donor compounds that occur in living systems. It was also well known that heterocyclic compounds play a significant role in many biological systems, especially six members ring system being a component of several vitamins and drugs. It is known that some drugs act *via* chelation or *via* the inhabitation of metal enzymes, but little is known about the modification activity of most drugs when their legating potential is utilized. The interaction of Co(III) atom which plays a vital role in a number of quite different biological processes, is a subject of considerable interest. we have tried to synthesize and characterize the bromo-cobaloxime containing heterocyclic nitrogen donor ligands.

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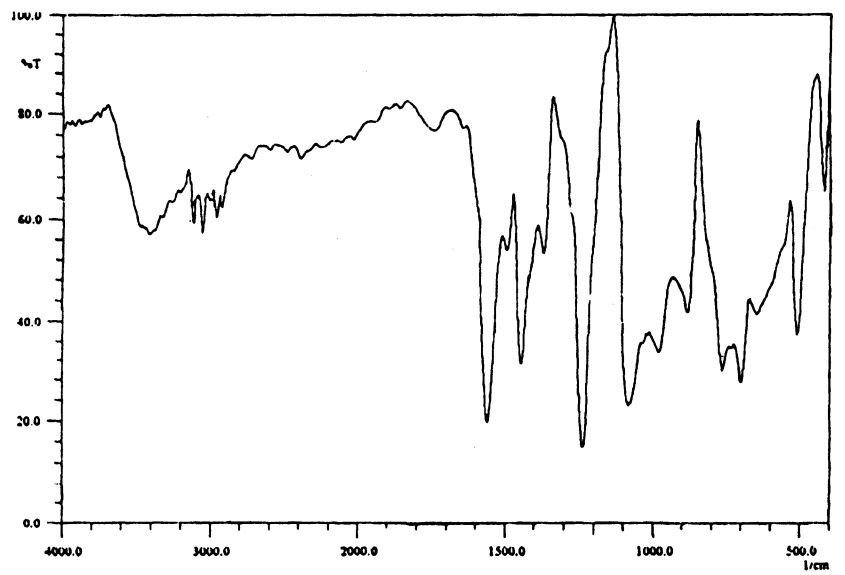
RESULTS AND DISCUSSION

Ten bromo-cobaloxime compounds which were synthesized are presented in Table-1 along with their analytical data, m.p. and conductance value. All conductance measurements were made in DMSO solution. The molar conductance values show that all the bromo-cobaloximes are non-ionic and neutral in nature. They never dissociate in the solution.

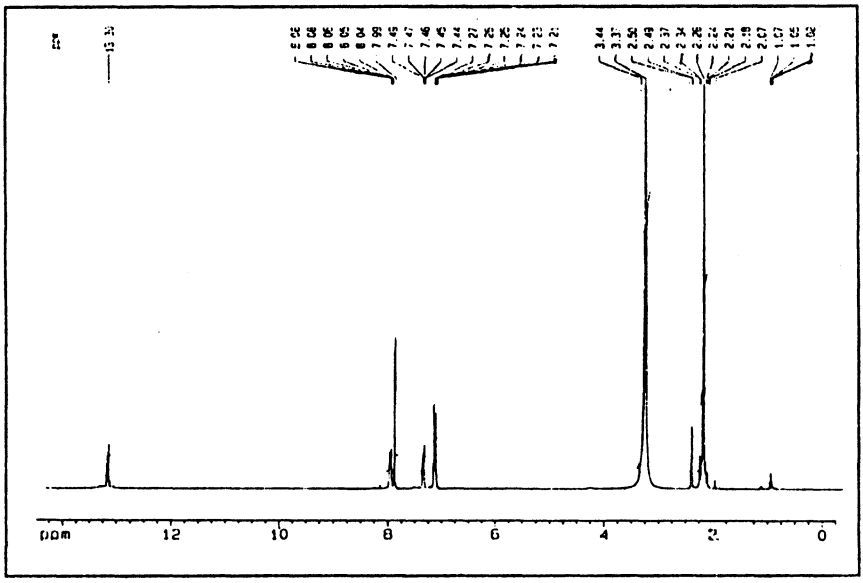
The electronic absorption spectra were taken in DMSO solution. We got the peak of weak to moderate intensity. A peak appeared at 18,000–20,000 cm^{-1}. It is due to spin allowed[6] $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The $^1A_{1g} \rightarrow {}^1T_{2g}$ band is masked by the intense charge-transfer bands. The charge transfer spectra of the *trans*-$[Co(DH)_2LBr]$ complexes show the band at about 40,000 cm^{-1}. It is due to the intra-ligand $\pi \rightarrow \pi^*$ transition of the coordinated DH. The bands occurring at 27,500 cm^{-1} are assigned to the indole $\rightarrow$ to Co(III). (LMCT) spectra . The bands at 33,000 cm^{-1} are due to the d_π Co(III) $\rightarrow \pi^*$(DH)(MLCT) transition[6]. The σDH Co(III) $\rightarrow$ (LMCT) is masked by the intense short wavelength bands of bromo-cobaloxime.



IR spectra of $[Co(DH)_2PyBr]$

IR Spectra: The IR spectra of dimethylglyoxime and complexes were taken and presented in Table-2. It was found that there was no band at 1240 cm^{-1}. But in all the complexes the peak was observed between 1245–1235 cm^{-1}. It is due to ν(N—O) of ionized (N—OH) group of dimethylglyoxime[7]. The additional band[8] for [ν(N—O)] appears at 1095–1085 cm^{-1}. So it is clear that all bondings between nitrogen to oxygen in these complexes are not equivalent. The normal stretching vibration ν(C=N) of free DH_2 generally appears at 1620 cm^{-1}. In the present case this band in all the complexes shifted from 1605 to 1560 cm^{-1} confirms that the nitrogen from oxime part is bonded to cobalt in all the

complexes. The weak band appearing at 3420–3400 cm^{-1} belongs to the intramolecular hydrogen bridge and suggests a *trans*-configuration . The characteristic band[9] ν(Co—N) (N of DH—) appears at 520–515 cm^{-1}. The ν(Co—N) band appears at 430–418 cm^{-1}. Due to limitation of our IR instrument the peak for metal to bromide cannot be ascertained. But it is reported that the peak for such bonding generally appears at 320–300 cm^{-1}.



Proton NMR Spectra of $[Co(DH)_2bmzBr]$ in DMSO-d_6 solution
bmz= benzimidazole

^{1}H NMR spectra: In dimethylglyoxime the signal due to proton[10] in methyl group generally appears at 1.98 ppm. In the bromo-cobaloxime complex this signal shifts downfield to around 0.4 ppm and appears at 2.33–2.41 ppm. In every compound this signal appears as singlet indicating the equivalence of four methyl groups and presence of *trans*-structure. The signal for proton in heterocyclic nitrogen donor ligand generally shifts downfield on coordination. For benzimidazole signals for H-1 and H-2 appear at 7 ppm and 6.42 ppm respectively. These two signals shift downfield and appear at 7.26 ppm and 7.21 ppm on coordination. The proton H-4 and H-7 in free benzimidazole appear at 7.53 ppm. In complex this signal is shifted downfield and appears at 7.99 ppm. The signal for H-5 and H-6 in benzimidazole appears at 7.39 ppm. This signal shift downfield and appears at 7.49 ppm on coordination. For benzotriazole H-1 signal appears at 7 ppm. This signal shift downfield and appears at 7.38 ppm on coordination. The signal for H-5 and H-6 appears at 7.39 ppm in benzotriazole. This signal shift downfield and appears at 7.54 ppm. The H-4 and H-7 protons appear at 7.53 ppm in benzotriazole. This signal shift downfield on coordination

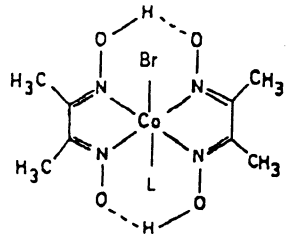
and appears at 7.73 ppm. Chemical shift for OH proton in dimethylglyoxime appears at 11.33 ppm; this signal shift downfield and appears at 13.30 ppm in all the complexes.

TABLE-1
ANALYTICAL DATA AND OTHER PHYSICAL PROPERTIES OF $[Co(DH)_2LBr]$ COMPLEXES

Complexes	m.f. (m.w.)	% Found /(Calculated)					Conductance (Ω)	m.p. (°C)
		Co	Br	C	H	N		
$[Co(DH)_2pyBr]$	$CoC_{13}H_{19}N_5O_4Br$ (448)	13.20 (13.16)	17.86 (17.85)	34.79 (34.82)	4.26 (4.24)	15.56 (15.62)	8.31	>240
$[Co(DH)_2piBr]$	$CoC_{13}H_{23}N_5O_4Br$ (454)	12.95 (12.99)	17.61 (17.62)	34.41 (34.36)	5.12 (5.06)	15.42 (15.41)	8.45	> 240
$[Co(DH)_2pipBr]$	$CoC_{12}H_{24}N_6O_4Br$ (455)	12.93 (12.96)	17.57 (17.58)	31.62 (31.64)	5.26 (5.27)	18.42 (18.46)	11.45	> 240
$[Co(DH)_2quiBr]$	$CoC_{17}H_{21}N_5O_4Br$ (498)	11.82 (11.84)	16.12 (16.06)	40.92 (40.96)	4.22 (4.21)	14.12 (14.05)	9.43	> 240
$[Co(DH)_2isoquiBr]$	$CoC_{17}H_{21}N_5O_4Br$ (498)	11.82 (11.84)	16.12 (16.06)	40.92 (40.96)	4.22 (4.21)	14.05 (14.06)	11.32	> 240
$[Co(DH)_2triaBr]$	$CoC_{10}H_{17}N_7O_4Br$ (438)	13.42 (13.47)	18.27 (18.26)	27.39 (27.35)	3.82 (3.88)	22.35 (22.37)	12.41	> 240
$[Co(DH)_2indBr]$	$CoC_{16}H_{21}N_5O_4Br$ (486)	12.11 (12.13)	16.42 (16.46)	39.51 (39.50)	4.33 (4.32)	14.42 (14.40)	16.01	> 240
$[Co(DH)_2bmzBr]$	$CoC_{15}H_{20}N_6O_4Br$ (487)	12.14 (12.11)	16.40 (16.42)	36.92 (36.96)	4.08 (4.10)	17.22 (17.24)	11.02	> 240
$[Co(DH)_2PbtzBr]$	$CoC_{14}H_{19}N_7O_4Br$ (488)	12.12 (12.09)	17.36 (17.39)	34.40 (34.42)	3.96 (3.98)	20.07 (20.08)	9.33	> 240
$[Co(DH)_2carBr]$	$CoC_{20}H_{22}N_5O_4Br$ (536)	11.02 (11.00)	14.89 (14.92)	44.42 (44.77)	4.08 (4.10)	13.03 (13.05)	13.41	

Conductance values in ohm^{-1} cm^2 mol^{-1} at room temperature. py = pyridine, pi = piperidine, qui = quinoline, isoqui = isoquinoline, tria = triazole, ind = indole, bmz = benzimidazole, btz = benzotriazole, car = carbazole, DH = dimethylglyoximato anion.

^{13}C NMR Spectra: In free uncoordination dimethylglyoxime the signal for methyl group appears at 9.2 ppm[11]. This signal shifts downfield on coordination and appears at 12.91 ppm. The signal for imine carbon atom appears at 154 ppm. This signal shifts upfield and appears at around 151.5 ppm in all the complexes. Due to limitation of our instrument the individual peak for carbon atom in heterocyclic ligand cannot be ascertained. In all the complexes a broad peak has been obtained.



trans-[$Co(DH)_2LBr$]

DH = dimethylglyoximato anion, L = pyridine, piperidine, quinoline, isoquinoline, triazole, indole, benzimidazole, benzotriazole, carbazole.

TABLE-2
IR BANDS (cm^{-1}) OF *trans* -[$Co(DH)_2LBr$] COMPLEXES

Complexes	ν(N—O)		ν(C=N)	ν(Co—N)		—O—H . . . O—
[$Co(DH)_2$pyBr]	1238	1085	1562	511	418	3420
[$Co(DH)_2$piBr]	1236	1087	1568	516	422	3410
[$Co(DH)_2$pipBr]	1242	1092	1588	517	425	3412
[$Co(DH)_2$quiBr]	1235	1086	1574	514	419	3416
[$Co(DH)_2$isoquiBr]	1243	1091	1585	522	428	3405
[$Co(DH)_2$triaBr]	1245	1095	1605	520	430	3400
[$Co(DH)_2$indBr]	1239	1088	1602	518	431	3404
[$Co(DH)_2$bmzBr]	1240	1086	1589	517	427	3415
[$Co(DH)_2$PbtzBr]	1242	1093	1592	513	424	3419
[$Co(DH)_2$carBr]	1239	1094	1574	519	431	3410

DH = dimethylglyoximato anion, py = pyridine, pi = piperidine, qui = quinoline, isoqui = isoquinoline, tria = triazole, ind = indole, bmz = benzimidazole, btz = benzotriazole, car = carbazole.

EXPERIMENTAL

All chemicals used were of analytical reagent or equivalent grade; cobalt bromide was prepared by literature method. The complexes were analyzed for their metal and bromine by standard procedures[12]. The carbon, hydrogen and nitrogen were estimated on a Carlo-Erba-1108 elemental analyzer. Electronic spectra were recorded on a Hitachi 320 Perkin-Elmer Lambda-15 spectrophotometer. The IR spectra were recorded in the 4000–400 cm^{-1} region by Shimadzu-8201 pc spectrophotometer using KBr pellet technique. ^1H and ^{13}C NMR spectra

were recorded in DMSO-d_6 by Bruker-DRX-300-NMR spectrometer using TMS as internal reference. Conductance measurements were taken in DMSO by Systronics-321 model.

Synthesis of the Complexes $[Co(DH)_2LBr$: To an ethanolic solution of $Co(NO_3)_2 \cdot 6H_2O$ (2 mmol) KBr (2 mmol) was added. KNO_3 was separated as precipitate. It was filtered off. The solution was somehow concentrated and taken as $CoBr_2$. The above solution was warmed and stirred. The dimethylglyoxime (4 mmole) was added to it. It was warmed, stirred for 2 min. and then cooled. Now 4 mmole of heterocyclic nitrogen donor ligands (pyridine, piperidine, piperazine, quinoline, isoquinoline, indole, benzimidazole, benzotriazole, triazole and carbazole) were dissolved in 2 mL of EtOH and then added. The whole solution was stirred for 5 min, slightly warrned and cooled . Then air was passed for 1–6 h. The compound separated was washed with diethyl ether and dried *in vacuo*.

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