

Synthesis, isolation and characterization of alkyl(aquo) and alkyl(ligand)cobaloximes

M. Bhoopal and S. Satyanarayana*

Department of Chemistry, Osmania University, Hyderabad-500 007, India

E-mail : ssnirasani@yahoo.com

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Alkyl(aquo)cobaloximes, $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$ ($\text{R} = \text{CH}_3$ and C_2H_5) have been prepared. These aquo complexes upon reacting with pyridine and substituted pyridines give alkyl(ligand)cobaloximes $[\text{RCo}(\text{DH})_2\text{L}]$, where L = pyridine, 4-methylpyridine, 4-ethylpyridine and 4-aminopyridine. These cobaloximes are characterized by electronic, IR, ^1H NMR and ^{13}C NMR spectral data.

Organocobalt B_{12} and B_{12} model complexes with diverse alkyl derivatives are necessary for elucidating the fundamental relationships between structure and spectra relationships helpful in understanding structural and/or ligating group changes that may occur in B_{12} dependent processes. Organocobalt compounds are relevant to the chemistry and biochemistry of vitamin B_{12} coenzymes and because there is a large *trans* influence of the axial alkyl ligands, an extensive background exists on the solution and solid state structural properties of B_{12} model compounds² with considerable range in axial bond lengths ligand dissociation rates etc. Results from studies on organocobalt compounds are potentially useful in improving our fundamental knowledge of factors influencing the properties of metal complexes in general. Organocobalt compounds are often serve as test case for method development.

Studies using model compounds of vitamin B_{12} have shown that the nature of the ligand *trans* to the Co-C can play a role in the kinetic and thermodynamic stability of this bond³. Recently, $[\text{SCN}(\text{pyridine})\text{cobaloximes}]$ were synthesized by Reddy *et al.*⁴. Equilibrium constants of benzyl(aquo)cobaloxime, synthesis and characterization of benzyl(ligand)cobaloximes (where ligands are imidazole and substituted imidazoles) were reported by Reddy *et al.*⁵. Sridhar *et al.*⁶, studied the equilibria and kinetics for pH dependent axial ligation of alkyl(aquo)cobaloximes with various N donor ligands. Synthesis of $[\text{RCo}(\text{DH})_2(\text{OH}_2)]$ ($\text{R} = \text{BrCH}_2$, CH_3 , C_2H_5) and $[\text{RCo}(\text{DH})_2(\text{L})]$ (L = imidazole, substituted imidazoles, histamine and histidine) were reported by Sridhar *et al.*⁷. Recently equilibrium constants for pH dependent axial ligation of methyl and ethyl(aquo)cobaloximes by various pyridines were reported by Bhoopal *et al.*⁸. In the present work we have isolated

and characterized various alkyl(ligand)cobaloximes.

Results and discussion

Electronic spectra of alkyl(aquo)cobaloximes in MeOH show spin-allowed $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ transition⁹ in the region of 22000 cm^{-1} due to $\text{R}^- \rightarrow \text{Co}^{\text{III}}$ sigma donation. This band disappears or intensity is drastically decreased in alkyl(ligand)cobaloximes. The $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ bands are masked by intense charge transfer bands. Charge transfer spectra of the complexes $[\text{RCo}(\text{DH})_2\text{L}]$ show bands at around 33000 cm^{-1} due to intra ligand $\pi \rightarrow \pi^*$ transition of the coordinated DH(dimethylglyoxime); bands occurring at around 29000 cm^{-1} are assigned to the $\text{L} \rightarrow \text{Co}^{\text{III}}$ in these complexes. The $\sigma \text{ DH} \rightarrow \sigma^* \text{ Co}^{\text{III}}$ band appears at around 25000 cm^{-1} , in some cases these are masked by intense short wavelength bands of alkyl(ligand)cobaloximes¹⁰. Electronic spectral data is compiled in Table 1.

IR spectra of the complexes investigated contain peaks at around 1235 cm^{-1} and 1087 cm^{-1} were assigned¹⁵ to N-O stretching vibrations. These two bands are shifted to lower wave numbers when fifth ligand changes in the order $4\text{-NH}_2\text{py} > 4\text{-Etpy} > 4\text{-Mepy} > \text{Py}$. This is in the approximate order of electron donating strength of ligand. The band at around 1570 cm^{-1} is assignable to $>\text{C}=\text{N}$ of the dimethyl-glyoxime^{11,12}. This band undergoes lower wave numbers, when H_2O of alkyl(aquo)cobaloxime replaced by strong sigma donor ligand (in the present case pyridine and substituted pyridines). Similar trends were reported by Burger *et al.*¹³ based on frequency shifts of $>\text{C}=\text{N}$ vibration, they concluded that lower the $>\text{C}=\text{N}$ vibrational frequency the stronger the $\text{M}-\text{C}=\text{N}$ donor pi bond. Similar trends were observed in our present study. Another important IR peak is observed at around 510 cm^{-1} , which is due

Table 1. Analytical and UV-visible data for methyl(ligand)cobaloxime and ethyl(ligand)cobaloxime

CH ₃ Co(DH) ₂ L L =	Fórmula	UV-visible data (cm ⁻¹)			
		Peak-1	Peak-2	Peak-3	Peak-4
Water	C ₉ H ₁₉ CoN ₄ O ₅	22675	25641	-	32258
Pyridine	C ₁₄ H ₂₂ CoN ₅ O ₄	-	25720	28850	32750
4-Methylpyridine	C ₁₅ H ₂₅ CoN ₅ O ₄	-	25740	28855	32770
4-Ethylpyridine	C ₁₆ H ₂₇ CoN ₅ O ₄	-	25770	28870	32890
4-Aminopyridine	C ₁₄ H ₂₃ CoN ₆ O ₄	-	25780	28890	32890
C ₂ H ₅ Co(DH) ₂ L L =					
Water	C ₁₀ H ₂₁ CoN ₄ O ₅	22172	25575	-	32573
Pyridine	C ₁₅ H ₂₄ CoN ₅ O ₄	-	25585	29230	32850
4-Methylpyridine	C ₁₆ H ₂₆ CoN ₅ O ₄	-	25590	29235	32865
4-Ethylpyridine	C ₁₇ H ₂₈ CoN ₅ O ₄	-	25600	29250	32890
4-Aminopyridine	C ₁₅ H ₂₅ CoN ₆ O ₄	-	25630	29270	32890

*Calculated and experimental values for C, H, N, are in good agreement.

to Co-N stretching (N of DMG)¹¹. In alkyl(ligand)cobaloximes this is observed at higher wave numbers when compared to alkyl(aquo)cobaloximes. This is because of increased back donation from Co^{III}→N of DMG makes

Co^{III}→N bond stronger. Increase in back donation is due to replacement of water by strong ligands. The band at around 760 cm⁻¹ is due to C=N-O deformation mode. IR spectral data is given in Table 2.

Methyl and ethyl(aquo)cobaloximes shows characteristic band due to water molecule coordinated to the Co^{III} atom at around 3200 cm⁻¹. Disappearance of this band in methyl and ethyl ligand cobaloximes indicates that water is replaced by ligand (py and substituted pyridines). Appearance of a new band at around 460 cm⁻¹ is assignable to ligand N→Co^{III} stretching mode. These complexes are stable and non-electrolytes in different solutions¹⁴(10⁻³ M) of MeOH, conductance being in the range of 10–20 Ω⁻¹ cm² mol⁻¹.

In the pyridine free ligand the H₂ (H₆), H₃ (H₅) and H₄ proton chemical shifts appear at 7.60, 7.25 and 7.75 ppm, respectively. In the 4-substituted pyridines the H₂ (H₆) and H₃ (H₅) proton peaks are observed in the region 7.25–7.50 and 6.30–6.90 ppm. In addition to these peaks the substituent group proton signals like C₄-CH₃ (2.35 ppm), C₄-(CH₂-CH₃) (2.55 ppm, 1.15 ppm) and C₄-NH₂ (5.65 ppm) are also observed. However, coordination of pyridine to Co^{III} of alkyl cobaloxime renders the H₂ (H₆) protons shift to

Table 2. IR Spectral data* for methyl(ligand)cobaloximes-[CH₃Co(DH)₂(L)] and ethyl(ligand)cobaloximes-[CH₃CH₂Co(DH)₂(L)]

Complex [CH ₃ Co(DH) ₂ (L)] where L =	νCo-N (N of L)	νCo-N (N of DH)	νC=N-O	νOH	νN-O	νCH ₃ (of DH)	νC=N	νH-O...H	νCH ₂	νCH ₃
(H ₂ O)	-	511.5	750.2	971.4	1083.0	1373.2	1571.6	1774.0	-	2900.0
Water						1231.0 1447.2				
C ₅ H ₅ N Pyridine	450.0	517.3	766.7	974.0	1091.0 1235.0	1369.1 1444.3	1557.0	1735.0	-	2895.0
C ₅ H ₄ N-CH ₃ 4-Methylpyridine	456.4	512.3	736.8	975.6	1089.1 1234.4	1369.3 1438.0	1559.9	1737.2	-	2917.6
C ₅ H ₄ N-C ₂ H ₅ 4-Ethylpyridine	456.4	518.0	744.5	976.5	1089.5 1233.0	1375.0 1431.8	1558.8	1720.2	-	2852.08
C ₅ H ₄ N-NH ₂ 4-Aminopyridine	460.2	517.2	739.0	974.4	1090.0 1234.5	1374.2 1421.8	1560.0	1740.2	-	2892.0
Complex [CH ₃ CH ₂ Co(DH) ₂ (L)] where L =										
(H ₂ O)	-	513.1	749	971.4	1085.7	1375.6	1568.4	1776.0	2922.0	3134.0
Water						1229.7 1445.9				
C ₅ H ₅ N Pyridine	446.0	517.9	744	973.5	1090.5 1235.9	1374.0 1449.5	1558.2	1748.0	2916.2	3139.0
C ₅ H ₄ N-CH ₃ 4-Methylpyridine	448.4	517.5	727	974.0	1090.5 1234.5	1374.4 1436.1	1555.2	1737.0	2915.9	3143.0
C ₅ H ₄ N-C ₂ H ₅ 4-Ethylpyridine	453.2	517.3	742	976.9	1088.8 1232.1	1375.2 1431.7	1560.0	1729.0	2976.6	3142.0
C ₅ H ₄ N-NH ₂ 4-Aminopyridine	458.0	517.9	733	980.0	1087.6 1218.8	1333.8 1435.7	1552.6	1720.0	3075.0	3148.0

*Recorded as KBr discs and values in cm⁻¹.

down field and observed at 8.50 ppm. The chemical shifts are observed at 7.2 and 7.9 ppm for H₃ (H₅) and H₄ protons respectively. In these complexes the electron donation from N to Co^{III} leads to a pronounced deshielding of the proton adjacent to the hetero atom of pyridines. The other protons are also shifted to down field but not as much as H₂ (H₆) protons. The characteristic signals for various substituted pyridines are assigned and reported. In case of 4-Mepy complex C₄-CH₃ proton signal was observed at 2.40 ppm, C₂ (C₆)-H at 8.40 ppm and C₃ (C₅)-H at 7.15 ppm. 4-Ethylpyridine shows a triplet at 1.15 ppm corresponding to CH₃ group and quartet at 2.75 ppm corresponding to -CH₂ of 4-ethyl group at pyridine ring. Two more signals at down field corresponding to C₂, (C₆)-H (8.40 ppm) and C₃, (C₅)-

H at 7.20 ppm are observed. ¹H NMR spectral data is given in Table 3.

¹³C NMR spectrum of [CH₃CH₂Co(DH)₂(H₂O)] showed signals for the equatorial methyl groups (12.22 ppm) and equatorial oxime carbons (152 ppm) and a signal at 13.30 ppm corresponding to CH₃ of CH₂CH₃. ¹³C signal of CH₂ bonded Co^{III} could not be seen due to quadrupolar relaxation by the ⁵⁹Co nucleus (*I* = 7/2). The coordination of pyridines by replacement of H₂O shows three more signals at 149.2 (C₂, C₆) 124.98 (C₃, C₅) and 131.5 ppm (C₄). The C₂ and C₆ signals are shifted to more downfield than C₄ and C₃ signals upon coordination of nitrogen of pyridine to Co^{III}. Similar down field shifts were observed for other substituted pyridine complexes also (Table 4) in

Table 3. ¹H NMR Spectral data* of alkyl(ligand)cobaloximes-[RCo(DH)₂(L)]

Sl. no.	Complex	eq CH ₃ *	CH ₃	CH ₂	Pyridine protons			
					H ₂ ,H ₆	H ₃ ,H ₅	H ₄	R'
1.	[CH ₃ Co(DH) ₂ (OH) ₂]	2.1 s	0.65 s	–	–	–	–	–
2.	[CH ₃ Co(DH) ₂ (py)]	2.1 s	0.65 s	–	8.5 d	7.4 t	7.9	–
3.	[CH ₃ Co(DH) ₂ (4-Mepy)]	2.0 s	0.57 s	–	8.45 d	7.18 d	–	2.7 s (CH ₃)
4.	[CH ₃ Co(DH) ₂ (4-Etpy)]	2.0 s	0.57 s	–	8.45 d	7.22 d	–	2.7 q (CH ₂) 1.25 t (CH ₃)
5.	[CH ₃ Co(DH) ₂ (4-NH ₂ py)]	2.0 s	0.4 s	–	7.75 d	6.39 d	–	5.75 s (NH ₂)
6.	[C ₂ H ₅ Co(DH) ₂ (OH) ₂]	2.20 s	0.5 t	1.5 q	–	–	–	–
7.	[C ₂ H ₅ Co(DH) ₂ (Py)]	2.0 s	0.25 t	1.2 q	8.3 d	7.1 t	7.9 t	–
8.	[C ₂ H ₅ Co(DH) ₂ (4-Mepy)]	2.2 s	0.32 t	1.42 q	8.38 d	7.12 d	–	2.38 s (CH ₃) 1.25 t (CH ₃)
9.	[C ₂ H ₅ Co(DH) ₂ (4-Etpy)]	2.15 s	0.38 t	1.60 q	8.40 d	7.2 d	–	2.70 q (CH ₂)
10.	[C ₂ H ₅ Co(DH) ₂ (4-NH ₂ py)]	2.1 s	0.30 t	1.55 q	7.85 d	6.4 d	–	5.65 s (NH ₂)

*Dissolved in DMSO-*d*₆ and values in ppm relative to TMS.

R' = CH₃, C₂H₅.

Table 4. ¹³C NMR Spectral data* of alkyl(ligand)cobaloximes-[RCo(DH)₂(L)]

Sl. no.	Complex	eq CH ₃ *	CH ₃	CH ₂	C=N	Pyridine Carbons			
						C ₂ ,C ₆	C ₃ ,C ₅	C ₄	R'
1.	[CH ₃ Co(DH) ₂ (py)]	11.54	–	–	148.49	149.2	124.98	131.50	–
2.	[CH ₃ Co(DH) ₂ (4-Mepy)]	11.50	–	–	148.00	147.0	124.20	137.00	21.00 (CH ₃)
3.	[CH ₃ Co(DH) ₂ (4-Etpy)]	11.48	–	–	147.5	147.5	123.8	136.00	28.10 (CH ₂) 15.4 (CH ₃)
4.	[CH ₃ Co(DH) ₂ (4-NH ₂ py)]	11.46	–	–	147.1	147.0	123.2	135.00	–
5.	[C ₂ H ₅ Co(DH) ₂ (py)]	11.52	13.36	–	148.8	148.0	124.45	154.5	–
6.	[C ₂ H ₅ Co(DH) ₂ (4-Mepy)]	11.51	13.40	–	149.0	153.54	128.8	153.7	21.9 (CH ₃)
7.	[C ₂ H ₅ Co(DH) ₂ (4-Etpy)]	11.41	13.34	–	148.8	148.89	124.95	154.0	15.29 (CH ₂) 27.43 (CH ₂)
8.	[C ₂ H ₅ Co(DH) ₂ (4-NH ₂ py)]	11.50	13.40	–	148.00	157.6	111.8	153.0	–

*Dissolved in DMSO-*d*₆ and values in ppm relative to TMS.

R' = CH₃, C₂H₅.

$[\text{CH}_3\text{Co}(\text{DH})_2(\text{L})]$ and $[\text{CH}_3\text{CH}_2\text{Co}(\text{DH})_2(\text{L})]$ where L = Py, 4-Mepy, 4-Etpy or 4-NH₂py. As an example, proposed structure of one of the complexes is given in Fig. 1.

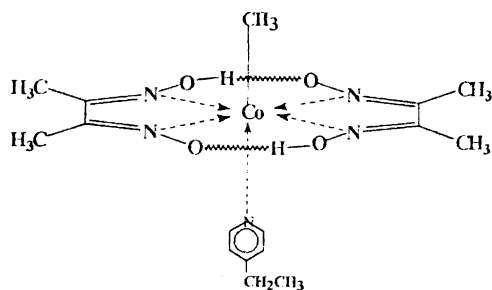


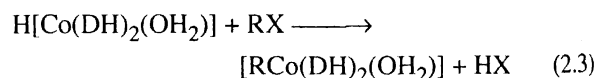
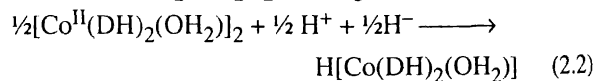
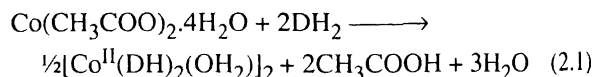
Fig. 1. Methyl(4-Etpy)cobaloxime.

Experimental

Pyridine, 4-aminopyridine, 4-methylpyridine and 4-ethylpyridine were obtained from S.D Fine Chemicals. Cobalt(II)acetate and dimethylglyoxime were obtained from B.D.H. ¹H NMR and ¹³C spectra were recorded on Varian Gemini XL 200 spectrometer at Indian Institute of Chemical Technology (IICT), Hyderabad, ¹H and ¹³C NMR were referenced to TMS in CDCl₃/DMSO-*d*₆. IR spectra were obtained on Perkin-Elmer FTIR-1605 spectrometer using KBr pellets and UV-visible spectra of complexes were recorded on Hitachi U-3410 spectrophotometer at the Department of Chemistry, Osmania University, Hyderabad.

Alkyl(aquo)cobaloximes were prepared by the procedure of Brown *et al.*¹⁵. All manipulations are performed in the dark due to the photolability of organocobalt complexes. In a well ventilated hood 200 ml of methanol is deaerated under a stream of nitrogen for 30 min in a three-neck round-bottomed flask fitted with a pressure equalizing addition funnel. Cobaltous acetate tetrahydrate (0.05 mole) and dimethylglyoxime (0.10 mole) are added and stirred magnetically under a continuous nitrogen purge. The orange aquocobalt(II) complex forms rapidly but remains only partially dissolved. The mixture is stirred for 30 min to insure complete formation of the cobalt(II) reagent. KOH (6.67g) in about 20 ml of deaerated water is then added to neutralize the acetic acid and the reaction mixture is cooled to 0° in ice. For the alkylation 0.055 mole alkyl iodide is added and then a total of 1.20 g sodium borohydride in about 40 ml of deaerated water in which 0.1 g KOH has been dissolved is added slowly over a period of about one hour. Formation of alkyl(aquo)cobaloxime is monitored by TLC. When product formation is virtually complete the reaction mixture is filtered, reduced in volume to under 100 ml with

a rotary evaporator, diluted with 100 ml water and allowed to crystallize over night at 4°. Filtered and dried over P₂O₅.



These cobaloximes are soluble in alcohol and DMSO, less soluble in chloroform or water and virtually insoluble in ether and hydrocarbon solvents.

Synthesis of $[\text{RCo}(\text{DH})_2\text{L}]$:

100 mg of $[\text{RCo}(\text{DH})_2(\text{H}_2\text{O})]$ (where R = CH₃ and C₂H₅) was dissolved in 20 ml of methanol and heated up to 40° and to this an equimolar quantity of ligand L (L = pyridines and substituted pyridines) was added. This mixture was heated at 40–50° by constant stirring for 1–2 h. Then minimum amount of distilled water was added to the above solution to get the precipitation and allowed it to settle. The resulting precipitate of yellow powder was filtered, washed with distilled water, ethanol and ether and dried *in vacuo*.

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