

## Synthesis, $^{13}\text{C}$ and $^{15}\text{N}$ NMR and infrared studies of cyano(ligand) cobaloximes

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**Abstract.** Mixed ligand complexes of  $[\text{CNCo}(\text{D}_2\text{H}_2)\text{L}]$  (where  $L$  = imidazoles, benzimidazoles, thiourea or hydroxylamine) were prepared by treating the  $[\text{CNCo}(\text{D}_2\text{H}_2)\text{SCN}]$  with 'L' in alcohol. Imidazoles and benzimidazoles bind to Co(III) through  $\text{N}_3$ , thiourea through  $S$  and hydroxylamine through  $N$  of  $\text{NH}_2$ . The analogous series of complexes enriched in  $^{13}\text{C}$  and  $^{15}\text{N}$  of the cyanide ligand have been used to locate the cyanide's  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR resonances and the cyanide stretching frequencies in the infrared spectra. As the *trans* axial ligand is varied, an inverse dependence of the  $^{15}\text{N}$  chemical shift on the  $^{13}\text{C}$  chemical shift is observed. This data together with trends in  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and  $\nu_{\text{CN}}$  with the basicity of the *trans* axial ligand are interpreted to indicate that the cobalt to cyanide  $\pi$  bonding is important in these cyano (ligand) complexes.

**Keywords.** Cobaloximes; imidazole; benzimidazole; thiourea; *trans* axial ligand; chemical shift.

### 1. Introduction

Cobaloximes (*bis*-dimethylglyoximato cobalt (III)) have been used as models of vitamin  $\text{B}_{12}$  and its derivatives<sup>1</sup>. The similarities of numerous chemical and physical properties of cobaloximes with those of various derivatives of coenzymes  $\text{B}_{12}$  have been emphasized especially by Schrauzer and coworkers<sup>2,3</sup>. Among the ligand substitution reactions of vitamin  $\text{B}_{12}$ , its derivatives and model compounds, the cobaloximes are of interest<sup>4,5</sup>. The organo cobalt compounds known as cobaloximes were originally studied as models for vitamin  $\text{B}_{12}$  and its coenzymes. However, now these simple compounds represent the most extensively studied class of metal compounds with both organometallic members such as  $\text{L Co}(\text{D}_2\text{H}_2) \text{R}$  and non-organometallic members such as  $\text{L Co}(\text{D}_2\text{H}_2) \text{X}$ , where  $L$  is a neutral ligand and  $R$  and  $X$  are mononegative alkyl and non-alkyl ligands respectively. In view of this, we have prepared a series of cyano ( $L$ ) cobaloximes from cyano ( $\text{SCN}$ ) cobaloximes. The study of simple models of vitamin  $\text{B}_{12}$  coenzymes, such as so-called cobaloximes,  $\text{L Co}(\text{D}_2\text{H}_2) \text{R}$  (where  $L$  = neutral ligand,  $\text{DH}$  = mono anion of dimethylglyoxime and  $R$  = alkyl group) has furnished a significant amount of data<sup>1,2</sup>; that have provided a foundation for understanding the behaviour of the more complex cobalamins<sup>3</sup>.

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## 2. Material and methods

Imidazole, 1-methylimidazole, 2-methylimidazole, 2-ethylimidazole and  $K^{13}C^{15}N$  were obtained from Aldrich Chemical Co., USA. Cobalt acetate, dimethyl glyoxime, potassium thiocyanate, potassium cyanide, hydroxylamine, thiourea, benzimidazole, 5,6-dimethyl benzimidazole etc., were obtained from BDH, India. The complex  $NCS Co(D_2H_2) SCN$  was prepared by the method of Ablov and Syrtsova<sup>3,4,6</sup>. This was converted to  $H_3N Co(D_2H_2) SCN$  by treatment with concentrated  $NH_4OH$  as described by Crumbliss and Gaus<sup>7</sup>. This ammonia complex was then treated with an equimolar amount of  $KCN$ <sup>7</sup> to obtain the salt,  $K [CNCo(D_2H_2) SCN]$  in 80% yield.

$^1H$  and  $^{13}C$  NMR spectra were recorded on Varian Gemini 200 NMR spectrometer and  $^{15}N$  NMR spectra were obtained on GE QE 300 NMR spectrometer. Samples were prepared by dissolving 25–50 mM of  $^{15}N^{13}C Co(D_2H_2)L$  in  $DMSO-d_6$ .  $^1H$  and  $^{13}C$  NMR spectra were referenced to external TSP in  $DMSO-d_6$ .  $^{15}N$  spectra were referenced to external  $CH_3NO_2$  locked to  $DMSO-d_6$  in a concentric insert (Wilmad).  $^{15}N$  chemical shifts were reported relative to  $NH_3$  using  $\delta CH_3NO_2 = 380.23$  ppm relative to  $NH_3$ <sup>8</sup>. Infrared spectra were obtained on Perkin Elmer FTIR instrument using KBr pellets. Microanalysis of complexes were performed on Perkin Elmer 240C elemental analyser and the metal analysis on AAS, Perkin-Elmer 2380. Co(III) was also estimated iodometrically by using standard hyposolution<sup>9</sup>.

## 3. Preparation of $[CNCo(D_2H_2)L]$ complexes

The ligand (L) is predissolved in minimum quantity of ethanol or water. To this,  $K[(CN)Co(D_2H_2)(SCN)]$  complex already dissolved in ethanol is added. The mixture is stirred and refluxed for 24 h, while heating up to  $70^\circ C$ . Ethanol was removed under reduced pressure and water was added to induce precipitation. The product was recrystallized from ethanol and water. It was then washed with water, ethanol and ether and dried in vacuo. Yield is 60–70%.

## 4. Results and discussion

$^1H$  NMR spectra of  $CN Co(D_2H_2) SCN$  showed signal at 2.20 ppm corresponding to equatorial methyls.  $^{13}C$  NMR spectra of  $CN Co(D_2H_2) SCN$  showed signal for the equatorial methyls (14–14 ppm) and equatorial oxime carbons (152). Whereas  $^{13}C^{15}N Co(D_2H_2) SCN$  in addition to the equatorial methyl and oxime carbon signals, it shows a very broad and prominent resonance attributed to the cyanide carbon at 120.82 ppm. The absence of the signal in unlabelled CN complex confirms that the signal at 120.82 is due to  $^{13}C$  of CN bound to Co(III). The broadness of the  $^{13}C$  resonance of CN is generally attributed to the quadrupolar relaxation by the  $^{59}Co$  nucleus ( $I = 7/2$ )<sup>10–15</sup> and completely obscured the anticipated  $^{15}N$ – $^{13}C$  coupling. The  $^{15}N$  NMR spectra of the  $^{15}N^{13}C Co(D_2H_2) SCN$  complex consisted of a signal relatively sharp doublet at 304.55 ppm. The unenriched equatorial and axial nitrogens are unobservable under these conditions. Coordination of  $^{13}C^{15}N$  ( $\delta^{13}C = 166.9$  ppm,  $\delta^{15}N = 272.4$  ppm) to the cobaloxime cobalt centre causes  $^{13}C$  resonance to shift upfield ( $\delta = 120$  ppm) but the  $^{15}N$  resonance to shift downfield ( $\delta = 305$  ppm).

In the infrared spectra of the  $CN Co(D_2H_2) L$  complexes, the cyanide stretching band was readily identified by comparison to the spectra of the  $^{15}N^{13}C Co(D_2H_2)L$  complexes. There is not much difference in the IR spectral features of labelled and

unlabelled cyano (ligand) cobaloximes. But  $\nu$  CN in labelled complexes appear at  $\sim 2060\text{ cm}^{-1}$  which is about  $80\text{ cm}^{-1}$  shift away compared to unlabelled complexes which appear at  $\sim 2140\text{ cm}^{-1}$ . The ratio of  $\nu$  CN to  $^{13}\text{C}^{15}\text{N}$  was nearly constant across the series of four imidazoles with an average value of 1.0380. This value is very close to the square root of the ratio of the reduced masses (1.0393).

Inspection of the values of  $\nu$  CN and  $\nu$   $^{13}\text{C}^{15}\text{N}$  (table 2) shows that  $\nu$  CN and  $\nu$   $^{13}\text{C}^{15}\text{N}$  tend to increase with increasing basicity of imidazoles. Brown et al.<sup>16</sup> studied the effect of *trans* ligand ( $L$  = various 4-substituted pyridines and primary amines) on  $\text{C}\equiv\text{N}$  stretching frequency. Within each series of ligand, as basicity of *trans* ligand increases, the  $\text{C}\equiv\text{N}$  stretching frequency is decreased and Co stretching frequency lowered as the donor power of *trans* ligand is increased<sup>17</sup>. So, the increase in CN stretching frequency in our studies may be due to steric hindrance caused by the  $-\text{CH}_3$  and  $-\text{C}_2\text{H}_5$  substituents on the  $\text{C}_2$  of imidazole. This makes imidazole to bind weakly to Co(III). If we observe carefully, the  $^{13}\text{C}$  and  $^{15}\text{N}$  chemical shifts of  $^{15}\text{N}^{13}\text{C}$   $\text{Co}(\text{D}_2\text{H}_2)\text{L}$  complexes with imidazoles and thiocyanate  $^{13}\text{C}$  resonance shifted to upfield and  $^{15}\text{N}$  resonance to downfield compared to free cyanide as observed in corrin<sup>18</sup>. Changes in the *trans* axial ligand cause opposite changes in the  $^{13}\text{C}$  and  $^{15}\text{N}$  chemical shifts, though there is no correlation between basicity of *trans* ligand and chemical shift. The opposite shift of  $^{13}\text{C}$   $^{15}\text{N}$  resonance is due to anisotropic effect<sup>16,18</sup> which is due to the existence of  $d\pi-p\pi$  back bonding as depicted in (1)



The increased electron density on the cyanide carbon and the hybridization of II suggest that stabilization of the species II should cause the  $^{15}\text{N}$  resonance to shift downfield and  $^{13}\text{C}$  upfield. If  $\text{CN}^-$  binds to  $\text{H}^+$  ( $\text{HCN}$ ) both  $^{13}\text{C}$  and  $^{15}\text{N}$  shifted upfield as  $\text{H}^+$  is incapable of  $d\pi$  donation<sup>18</sup>. The terminal nitrogen of diazo compounds ( $\text{RCH}=\text{N}^+=\text{N}^-$ ) resonates downfield (364–447 ppm) from the terminal nitrogen of diazonium salts ( $\text{R}-\text{N}^+\equiv\text{N}$  range 316–364 ppm)<sup>11</sup>.

All the complexes show broad peaks in the region  $3600\text{--}3900\text{ cm}^{-1}$  assigned to  $\nu(\text{N}-\text{H})$  and  $\text{OH}$  stretching frequencies. The peak shifts due to  $\nu(\text{C}=\text{C})$  and  $\nu(\text{C}=\text{N})$  frequencies of the complexes in the region  $1450\text{--}1650\text{ cm}^{-1}$  indicate that at least one of the ring nitrogens of imidazole or benzimidazole is involved in metal ion coordination. The  $\nu(\text{C}=\text{S})$  and  $\nu\text{NH}_2$  modes are observed around  $755\text{ cm}^{-1}$  and  $1618\text{ cm}^{-1}$ . Upon coordination,  $\text{NH}_2$  deformation did not change but  $\text{C}-\text{S}$  stretching shifted to lower frequency ( $8\text{ cm}^{-1}$ ) indicating thiourea coordinated to the metal through sulphur, whereas in  $\text{NH}_2\text{OH}$  complex,  $\text{NH}_2$  deformation vibrations ( $1637\text{ cm}^{-1}$ ) shifted to lower frequencies. So  $\text{NH}_2\text{OH}$  coordinated to metal through N of  $\text{NH}_2\text{OH}$ .

Imidazole exhibit NMR signals due to  $\text{C}_2\text{-H}$ ,  $\text{C}_4\text{-H}$  and  $\text{C}_5\text{-H}$ . These ( $\text{C}_2\text{-H}$  and  $\text{C}_4\text{-H}$ ) signals are shifted downfield upon coordination to metal ion (table 1). Whereas in 2-methyl and 2-ethyl imidazoles, in addition to  $\text{C}_4\text{-H}$  and  $\text{C}_5\text{-H}$  protons, methyl and ethyl proton signals are exhibited in NMR and these  $\text{C}_4$  and  $\text{C}_5$  proton signals are shifted downfield upon coordination. In thiourea complex, the  $\text{NH}_2$  signal shifted downfield upon coordination to Co(III) complex. Similarly there is a downfield shift of  $\text{C}_2\text{-H}$  signal of benzimidazole and 5,6-dimethyl benzimidazole in their complexes as compared to the free ligand (table 1).

$^{13}\text{C}^{15}\text{N}$  NMR spectra were recorded for  $[^{13}\text{C}^{15}\text{NCo}(\text{D}_2\text{H}_2)\text{L}]$  complexes. Their signal positions are shown in table 2.

**Table 1.**  $^1\text{H}$  NMR spectral data of  $\text{K}[\text{CNCo}(\text{D}_2\text{H}_2)\text{SCN}]$  and  $[\text{CNCo}(\text{D}_2\text{H}_2)\text{L}]$  complexes

Complex/ligand	$\text{C}_4\text{-H}$	$\text{C}_5\text{-H}$	$\text{C}_2\text{-H}$	$\text{N-H}$	$\text{CH}_3$	$\text{CH}_2$	$\text{CH}_3(\text{eq})$
$\text{K}[\text{CNCo}(\text{D}_2\text{H}_2)\text{SCN}]$	—	—	—	—	—	—	2.21
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Imd}]$	7.42	7.22	7.85	12.73	—	—	2.20
Imidazole	7.15	7.15	7.73	12.43	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)1\text{-Meimd}]$	7.15	7.10	7.60	—	3.70	—	2.21
1-methyl imidazole	6.88	7.05	7.42	—	3.68	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)2\text{-Meimd}]$	7.48	7.05	—	11.95	2.45	—	2.20
2-methyl imidazole	6.98	6.98	—	11.91	2.43	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)2\text{-Etimd}]$	7.18	6.94	—	12.45	1.10(t)	2.78(q)	2.22
2-ethyl imidazole	6.90	6.90	—	12.19	1.04(t)	2.81(q)	—
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Bimd}]$	7.65	7.20	8.35	—	—	—	2.23
Benzimidazole	7.61	7.20	8.24	—	—	—	—
	$(\text{C}_5\text{C}_6)$	$(\text{C}_4\text{C}_7)$					
$[\text{CNCo}(\text{D}_2\text{H}_2)5,6\text{DMeimd}]$	7.35	7.2	7.95	—	2.8	—	2.21
5,6-dimethyl, benzimidazole	$(\text{C}_4)$	$(\text{C}_7)$	$(\text{C}_2)$	—	$(5,6\text{CH}_3)$	—	$(\text{CH}_3)$
	7.2	7.2	7.8	—	2.8	—	2.21
					$(5,6\text{CH}_3)$		
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Ha}]$	—	—	—	7.11	—	—	2.21
Hydroxylamine	—	—	—	6.9	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Thu}]$	—	—	—	$7.8(\text{NH}_2)_2$	—	—	2.25
Thiourea	—	—	—	7.6	—	—	—

**Table 2.** Cyanide  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR chemical shifts and infrared stretching frequencies of cyano (ligand) cobaloximes

Complex/ligand	$\nu(\text{C} \equiv \text{N})$	$\nu(^{13}\text{C} \equiv ^{15}\text{N})$	$^{13}\text{C}(\text{CN}^-)$	$^{15}\text{N}$
$\text{K}[\text{CNCo}(\text{D}_2\text{H}_2)\text{SCN}]$	2142	—	—	—
$\text{K}[^{13}\text{C}^{15}\text{NCo}(\text{D}_2\text{H}_2)\text{SCN}]$	2143	2065	120.82	304.55
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Imd}]$	2138.2	2059	117.0	307.0
Imidazole	—	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)1\text{-Meimd}]$	2144.9	2065	118.5	307.5
1-methyl imidazole	—	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)2\text{-Meimd}]$	2158	2067	118.0	306.5
2-methyl imidazole	—	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)2\text{-Etimd}]$	2154	2064	118.0	307.8
2-ethyl imidazole	—	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Bimd}]$	2145	2060	—	—
Benzimidazole	—	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)5,6\text{-DMeimd}]$	2135	2058	—	—
5,6-dimethyl benzimidazole	—	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Ha}]$	2122	2065	121.1	303.0
Hydroxylamine	—	—	—	—
$[\text{CNCo}(\text{D}_2\text{H}_2)\text{Thu}]$	2141	2060	119.5	304.5
Thiourea	—	—	—	—

**Table 3.** Analytical data of cyano (ligand) cobaloximes

Complex/ligand	Colour	(Found) Calc % of			
		C	H	N	Co
K[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )SCN]	Wine red	29.13 (29.11)	3.42 (3.90)	20.38 (20.35)	14.20 (14.21)
[ $^{13}\text{C}^{15}\text{N}$ Co(D <sub>2</sub> H <sub>2</sub> )SCN]	Wine red	29.3 (29.14)	3.42 (3.90)	20.39 (20.36)	14.30 (14.21)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )Imd]	Pale Yellow	37.59 (37.60)	4.34 (4.34)	25.59 (25.55)	15.3 (15.36)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )1-Meimd]	Pale Yellow	39.29 (39.30)	5.08 (5.08)	24.68 (24.69)	14.8 (14.86)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )2-Meimd]	Bright yellow	39.30 (39.29)	5.07 (5.09)	24.68 (24.69)	14.8 (14.86)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )2-Etimd]	Bright brown	40.87 (40.89)	5.39 (5.39)	23.84 (23.87)	14.3 (14.38)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )Bimd]	Wine red	44.33 (44.35)	4.65 (4.66)	22.63 (22.66)	13.6 (13.69)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )5,6-DMeimd]	Wine red	46.84 (46.87)	5.25 (5.28)	21.26 (2.29)	12.7 (12.9)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )Ha]	Wine red	31.04 (31.05)	4.92 (4.95)	24.14 (24.16)	16.9 (16.98)
[CNC <sub>o</sub> (D <sub>2</sub> H <sub>2</sub> )Thu]	Light brown	30.69 (30.69)	4.64 (4.65)	25.06 (25.09)	15.06 (15.08)

The electronic spectra of imidazole and substituted imidazoles exhibit a strong band around 200–215 nm which is assigned to the  $\pi-\pi^*$  transition of the ligand. On complexation of the ligand to [CNC<sub>o</sub>(D<sub>2</sub>H<sub>2</sub>)SCN] to give [CNC<sub>o</sub>(D<sub>2</sub>H<sub>2</sub>)L], a slight shift occurs and this band is observed in all the complexes. In addition to this, three more bands are observed for complexes of imidazole between 200 to 242 nm, 1-methyl imidazole between 243 to 371 nm and 2-methyl imidazole between 343 to 311 nm. These may be assigned as  $^1\text{A}_1 \rightarrow \text{E}$ ,  $^1\text{A}_1 \rightarrow ^1\text{A}_2$ ,  $^1\text{A}_1 \rightarrow ^1\text{T}_2$ .

## 5. Conclusion

Mixed ligand complexes of the type [CNC<sub>o</sub>(D<sub>2</sub>H<sub>2</sub>)L] are prepared and changes in the  $^{13}\text{C}$  and  $^{15}\text{N}$  shifts with varying 'L' were studied. These studies reveal that there is an inverse dependence of  $^{13}\text{C}$  and  $^{15}\text{N}$  chemical shift. IR studies show that the cyanide stretching frequencies are changed with the change of *trans* ligand 'L'. All these confirm that there is a back bonding between cobalt to cyanide ion.

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