

Synthesis and Characterization of *trans*-[Co((BA)₂en)(amine)(CN)] and *trans*-K[Co((BA)₂en)(CN)₂] Complexes: Indication of Cobalt-cyanid π -Back Bonding Interaction

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The structure of vitamin B₁₂ (cyano cobalamin) was determined in the laboratory of Hodgkin and co-workers in the mid-1960s.^{1,2} In the equatorial plane the central six coordinate cobalt (III) ion is surrounded by four pyrrole nitrogen atoms of a corrin ligand. While one of the axial sites is occupied by a 5,6-dimethyl benzimidazol- α -D-ribofuranose-3-phosphate, the second axial ligand position is occupied by a cyanide group.² The vitamin can be converted *in vivo* to active alkylcobalamin coenzymes.^{3,4} These alkylcobalamin are known naturally occurring compounds with a biologically active carbon-metal bond.⁵

The macrocyclic tetradentate ligands with four nitrogen donor or Schiff base ligands (N₂O₂) which coordinated to four equatorial position octahedral structure of cobalt (III) center are considered as models for vitamin B₁₂.⁶⁻¹⁰ The effect of axial ligation (amine) on properties of cyano group with an organic monoanion ligand has played an important role in our knowledge of the properties of vitamin B₁₂ and of model compounds.

The coordination of the amine ligand in *trans* position can lead to cyano activation barrier of dissociation.¹¹⁻¹⁴ A variety of physical methods such as infrared and NMR have been used to study of π -back bonding from the cobalt (III) metal center into cyano ligand.^{11-14,15} Infrared and NMR spectroscopy allows one to investigate the effect amines on the cyano ligand π -back bonding in complexes. These results were indicative of the existence of $d\pi-p\pi$ back bonding in cyano cobalt species (Scheme 1).

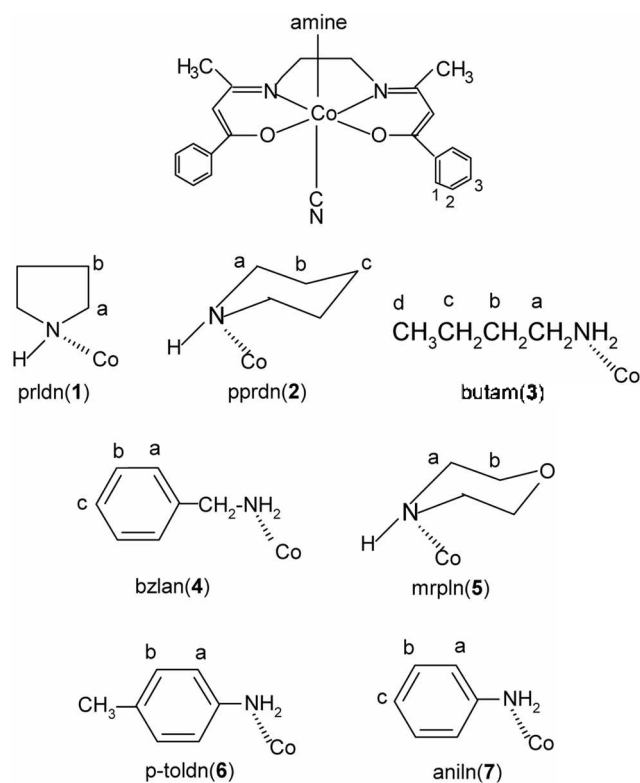
The effect of *trans* axial ligands on the cyanide chemical shifts and stretching properties can influence the relative stabilization of I and II species by the axial ligand. In this paper, we report result of ¹H NMR and IR study of a series of *trans*-(Schiff base)CN(amine)cobalt(III) complexes with different axial ligands (Scheme 2), which permits a more detailed analysis of these properties.

Experimental Section

UV-Vis spectra in solution were recorded on a Jasco 7800 spectrophotometer. IR spectra were recorded as KBr pellets in an Equinox 55 Bruker spectrophotometer. All NMR measurements were made in CDCl₃ or DMSO-*d*₆ on a Bruker Avancer 500 (500 MHz) NMR spectrometer. Proton chemical shifts are reported in parts per million (ppm) relative to an



Scheme 1



Scheme 2

internal TMS standard. Elemental analyses were performed by using a Heraeus CHN-O-RAPID elemental analyzer.

Bis(benzoylacetone)ethylenediimine H₂(BA)₂en was prepared according to the literature by condensation of benzoylacetone in hot methanol with anhydrous ethylenediamine (1 : 2 mol stoichiometric ratio) and was purified by recrystallization from hot methanol.¹⁶ Bis(benzoylacetone)ethylenediiminocobalt(II) complex ([Co((BA)₂en)]) was synthesized by the method of McCarty.¹⁶

Synthesis of *trans*-[Co((BA)₂en)(amine)(CN)] Complexes (1-7). Those complexes were synthesized by a

modification of the route of us^{17,18} by the following general method. The appropriate amine (1 mmol) and of solid KCN (0.065 g) were added to stirring solution of 1 mmol (0.405 g) of the [Co(BA)₂en] complex in 60 mL acetone: dichloromethane (5 : 1 v/v) and air was bubbled slowly through the reaction mixture for 4 hours. The resulting clear brown solution was left overnight to give a brown precipitate. The following complexes, which were recrystallization as shown below, were filtered off and wash with ethanol and dried in vacuum at room temperature.

– *trans*-[Co(BA)₂en](prldn)(CN)] complex (1): recrystallization from dichloromethane-ethanol (2 : 1 v/v) gave brown crystals. Yield 0.1709 g (34%). Anal. found: C, 64.50; H, 6.19; N, 11.20. Calcd. For C₂₇H₃₃N₄O₂Co (MW 502.50): C, 64.54; H, 6.22; N, 11.15.

– *trans*-[Co(BA)₂en](pprdn)(CN)] complex (2): the crystalline form of this complex was recrystallized from dichloromethane-ethanol (3 : 1 v/v). The complex is dark brown. Yield 0.1550 g (30%). Anal. found: C, 65.20; H, 6.51; N, 10.80. Calcd. For C₂₈H₃₃N₄O₂Co (MW 516.53): C, 65.11; H, 6.44; N, 10.85.

– *trans*-[Co(BA)₂en](butam)(CN)] complex (3): this complex which was recrystallized from dichloromethane-ethanol (2 : 1 v/v) gave brown crystals. Yield 0.1362 g (27%). Anal. found: C, 64.35; H, 6.66; N, 11.07. Calcd. For C₂₇H₃₃N₄O₂Co (MW 504.52): C, 64.28; H, 6.59; N, 11.11.

– *trans*-[Co(BA)₂en](bzlan)(CN)] complex (4): this complex was obtained as needle like brown crystals by recrystallization from acetone-ethanol (2 : 1 v/v). Yield 0.2046 g (38%). Anal. found: C, 66.84; H, 5.73; N, 10.44. Calcd. For C₃₀H₃₁N₄O₂Co (MW 538.53): C, 66.91; H, 5.80; N, 10.40.

– *trans*-[Co(BA)₂en](mrpln)(CN)] complex (5): this complex was recrystallized as complex 4 with acetone-ethanol (2 : 1 v/v) gave brown crystals. Yield 0.1452 g (28%). Anal. found: C, 62.62; H, 5.98; N, 10.85. Calcd. For C₂₇H₃₁N₄O₂Co (MW 518.50): C, 62.55; H, 6.03; N, 10.81.

– *trans*-[Co(BA)₂en](p-toldn)(CN)] complex (6): this brown complex was recrystallized as from acetone-ethanol-toluene (6 : 2 : 1 v/v/v). Yield 0.1723 g (32%). Anal. found: C, 66.95; H, 5.74; N, 10.35. Calcd. For C₃₀H₃₁N₄O₂Co (MW 538.53): C, 66.91; H, 5.80; N, 10.40.

– *trans*-[Co(BA)₂en](aniln)(CN)] complex (7): this complex was recrystallized from acetone-2-propanol (2 : 1 v/v) gave dark brown crystals. Yield 0.1626 g (31%). Anal. found: C, 66.50; H, 5.62; N, 10.74. Calcd. For C₂₉H₂₉N₄O₂Co (MW 524.51): C, 66.41; H, 5.57; N, 10.68.

Synthesis of *trans*-K[Co(BA)₂en(CN)₂](8) complex. A solid KCN (0.13 g, 2 mmol) was added under continuous stirring to suspension of 1 mmol (0.405 g) of the [Co(BA)₂en] complex in 70 mL acetone. Air was then bubbled through the reaction mixture for about 4 h. The resulting brown solution was left overnight to give a brown precipitate. This complex was recrystallized from acetone-methanol-toluene (4 : 2 : 1 v/v/v) gave dark brown powder. The powders were filtered off and wash with methanol and dried in vacuum at room temperature. Yield 0.0745 g (15%). Anal. found: C,

57.98; H, 4.52; N, 11.35. Calcd. For C₂₄H₂₂N₄O₂KCo (MW 496.50): C, 58.06; H, 4.47; N, 11.28.

Results and Discussion

The *trans*-[Co(BA)₂en(amine)(CN)] was synthesized by air oxidation of [Co^{II}(BA)₂en] in acetone: dichloromethane (5 : 1 v/v) solvent in the presences of KCN salt and the appropriate amine. The air oxidation was continued for a period of 4 h, during which time the solution changed from red to brown. Dark brown crystals of these complexes were obtained in yield 27-38%. All complexes reported here are diamagnetic as expected for a low-spin d⁶-configuration.

The absorption spectrum of free ligand exhibits bands in the regions of 350 nm ($\epsilon \approx 34000 \text{ M}^{-1} \cdot \text{cm}^{-1}$) and 243 nm ($\epsilon \approx 19000 \text{ M}^{-1} \cdot \text{cm}^{-1}$) corresponding to $\pi \rightarrow \pi^*$ transition, which involving the azomethine chromophore and $\pi \rightarrow \pi^*$ transitions involving the phenyl rings respectively.¹⁹ These transitions in *trans*-[Co(BA)₂en(amine)(CN)] complexes are red shifted relative to free ligand (Table 1). The nature of axial amine does not show any significant influence on the position of these bands.

The ¹H NMR spectrum of H₂(BA)₂en ligand exhibits signal at $\delta = 11.6$ assigned to intramolecular hydrogen band formation and disappears upon coordination of ligand to cobalt. The ¹H NMR spectrum of *trans*-[Co(BA)₂en(amine)(CN)] complexes exhibit singlet at ~ 5.6 ppm due to two =CH groups (Table 2) and indicates that the equatorial coordination sites are occupied by the (BA)₂en ligand and leading to the magnetically equivalent =CH protons.²⁰ The -CH₃ protons in the complexes all resonate to give a singlet at ~ 2.2 ppm and the aromatic protons of the phenyl rings in the Schiff base appear as a complex multiplet at ~ 7.3 to 8.0 ppm. The ethylenediamine protons appear as a multiplet at ~ 3.3 ppm. The axially coordinated amine (NH) proton(s) appear at 1.36 to 4.23 ppm (depending on the type of amine). The chemical shifts of axial amine proton(s) and other protons of the axial amines are listed in Table 2.

The IR spectrum of the free ligand exhibits a strong band at 1540 cm⁻¹ due to $\nu_{\text{C=N}}$ of imine,^{21,22} which are shifted to lower frequency by $\sim 30 \text{ cm}^{-1}$ and appears at about 1510 cm⁻¹. The fairly broad band of medium intensity appearing

Table 1. electronic absorption data of *trans*-[Co(BA)₂en(amine)(CN)] complexes in CH₃OH solution, ν_{CN} and Pk_b of the amines

amine	$\lambda_{\pi \rightarrow \pi^*}$ (nm) ($\epsilon, \text{M}^{-1} \cdot \text{cm}^{-1}$) ^a	$\lambda_{\pi \rightarrow \pi^*}$ (nm) ($\epsilon, \text{M}^{-1} \cdot \text{cm}^{-1}$) ^b	Pk _b ^c	ν_{CN} (cm ⁻¹)
prldn (1)	378 (8840)	248 (44200)	2.73	2123.7
pprdn (2)	378 (8520)	250 (45100)	2.88	2124.0
butam (3)	377 (8680)	247 (44600)	3.23	2124.3
bzlan (4)	375 (9210)	260 (50700)	4.67	2125.0
mrpln (5)	377 (10980)	246 (49500)	5.60	2126.0
p-toldn (6)	377 (9120)	244 (50400)	8.92	2127.3
aniln (7)	376 (8960)	245 (49500)	9.30	2129.3

^a $\pi \rightarrow \pi^*$ transition azomethine chromophore. ^b $\pi \rightarrow \pi^*$ transition involves the imine C=N group. ^cReference 24

Table 2. ^1H NMR data for *trans*-[Co((BA)₂en)(X)(CN)]^{0 or -} complexes^{a,b}

X	CH ₃	(CH ₂) ₂	=CH ₂	H ₁	H _{2,3}	NH	Other peaks
PrlIn ^c	2.24 (6H, s)	3.35 (4H, br s)	5.65 (2H, s)	7.92 (4H, br s)	7.37 (6H, d) (J = 6)	3.70 (1H, br s)	1.74 (4H, m, H _b) 2.35 (4H, m, H _a)
PprdIn ^c	2.17 (6H, s)	3.35 (4H, br s)	5.57 (2H, s)	7.87 (4H, br s)	7.37 (6H, d) (J = 7)	3.63 (1H, br s)	2.45 (4H, br t, H _a) 1.74-1.80 (6H, m, H _{b,s})
Butam ^c	2.30 (6H, s)	3.31 (4H, br s)	5.54 (2H, s)	7.87 (4H, br s)	7.36 (6H, d) (J = 7)	1.36 (2H, br s)	0.75 (3H, br s, H _a) 1.84 (2H, br s, H _c) 2.15 (2H, br s, H _b) 2.30 (2H, br s, H _a)
Bzlan ^c	2.15 (6H, s)	3.33 (4H, br s)	5.59 (2H, s)	7.91 (4H, br s)	7.37 (6H, d) (J = 6)	3.45 (2H, br t)	2.82 (2H, s, -CH ₂ -) ^e 7.09 (2H, br s, H _c) 7.20 (3H, br s, H _{b,s})
Mrpln ^c	2.24 (6H, s)	3.47 (4H, br s)	5.64 (2H, s)	7.90 (4H, br d) (J = 6)	7.38 (6H, br d) (J = 7)	3.70 (1H, br t) (J = 4.5)	2.50 (4H, m, NCH ₂) 3.69 (4H, m, OCH ₂)
<i>p</i> -toldn ^c	2.25 (6H, s)	3.31 (4H, br s)	5.68 (2H, s)	7.96 (4H, br s)	7.38 (6H, br s)	4.23 (2H, br s)	2.07 (3H, s, CH ₃) ^f 6.56 (2H, d, H _a) (J = 6) 6.96 (2H, d, H _b) (J = 7)
Aniln ^c	2.22 (6H, s)	3.31 (4H, br s)	5.66 (2H, s)	7.97 (4H, br s)	7.38 (6H, br s)	4.26 (2H, br s)	6.66 (2H, d, H _a) (J = 5.5) 7.05 (2H, d, H _b) (J = 7) 7.16 (1H, t, H _c) (J = 6)
CN ^d	2.29 (6H, s)	3.55 (4H, br s)	5.83 (2H, s)	7.99 (4H, br s)	7.44 (6H, br s)	—	—

^appm relative Me₄Si. ^bs = singlet, d = doublet, t = triplet, m = multiplet. ^cCD₃Cl solvent. ^dDMSO-d₆ solvent. ^eph-CH₂-NiI₂. ^fH₂N-C₆H₄-CH₃

at 3285 cm⁻¹ corresponds to the intramolecular hydrogen bonding in the free ligand,²¹ this band is absent in the complexes.

The axial amine N-H stretching vibrations and cyano ligand stretching vibrations (ν_{CN}) appears in the range of 3200-3300 and 2120-2127 cm⁻¹ respectively (Table 2).

Since the equatorial Schiff base ligand is the same in all complexes, the ν_{CN} of cyano ligand is only influenced by the property of the axial amine. The dependence of ν_{CN} on amine ligand basicity supports an interaction between cobalt and cyanide (Table 1). The results indicate a correlation between the ν_{CN} of cyano ligand and σ -donor ability of the trans amine ligand. The values of ν_{CN} in Table 1 show that ν_{CN} tend to decrease with increasing basicity of the ligand amine (Fig. 1).

Since the cyanide ligand involves a transfer of electron density from a filled cobalt orbital into cyanide π^* -antibonding orbital, this interaction expected to be enhanced by stronger amine axial donor due to increase electron density on the cobalt.

The axial amine can influence the ν_{CN} of cyano ligand through enhance electron density on the cobalt. The increase of charge on the cobalt by stronger amine donor has been associated with increase of π -bonding in cobalt-cyanide, and therefore ν_{CN} shifts to lower frequency.²³ Indeed, amines with high basicity are able to increase the π -interaction of cobalt with carbon of cyanide and hence transfer of electron density from a filled metal orbital to the cyanide π^* antibonding orbital. Therefore, the CN bond order in cyanide

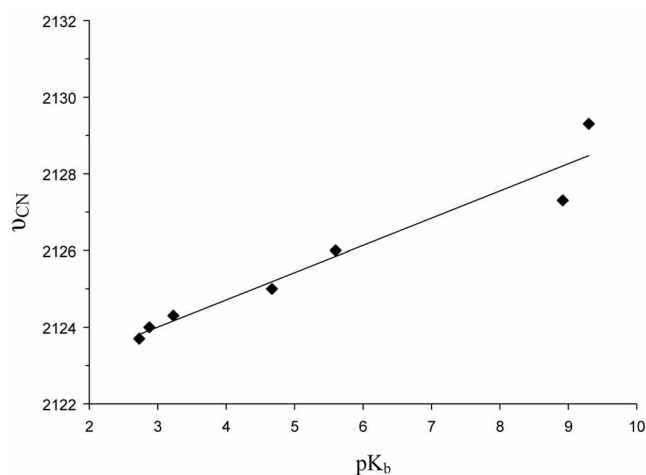


Figure 1. Dependence of ν_{CN} the *trans*-[Co((BA)₂en)(amine)(CN)] complexes on pK_b amines.

ligand decreases (stabilization II species in Scheme 1). In other word, the CN stretching frequency is displaced to a lower frequency indicating a decrease in the CN bond order due to π interaction of cyano ligand with cobalt(III).

The ν_{CN} is slightly displaced to a lower frequency due to increase basicity of amine ligand, similar behavior is reported for cyano(amines)cobaloximes complexes with σ -donor amines.¹¹

The amines are ligands with σ -donor ability in *trans*-[Co((BA)₂en)(amine)(CN)] complexes, therefore cyanide ligand establishes a strong π -back bonding with cobalt. Such

interaction is consistent with partial population of cyanide ligand π^* -antibonding orbital and therefore decrease ν_{CN} .

The influence of amine on cyanide stretching vibration frequency, which was the result of π cobalt-cyanide interaction, was confirmed by the synthesis of *trans*-K[Co(BA)₂en](CN)₂ (**8**) complex. In this complex, amine (no π interaction) was replaced with another cyanide group. Two *trans* cyanide groups compete with metal for π interaction, which is different in comparison with amine cyano complexes **1-7**; therefore, π cobalt-cyano interaction decreased in the dicyano complex **8**. As the amine ligands in all complexes **1-7** did not have π -interaction with cobalt, they should not be able to compete with cyanide for cobalt d_{π} -electron density, thus increasing cobalt to cyanide π -donation. Reduction in π interaction for each cyanide group tends to decrease the transfer of electron density from a filled metal orbital to the cyanide π^* antibonding orbital. Therefore, there is an increase in ν_{CN} of complex **8** ($\nu_{\text{CN}} = 2177 \text{ cm}^{-1}$) in comparison with complexes **1-7**. These results confirm the π cobalt-cyanide interaction and the influence of amine on this interaction.

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