

## The Electrochemical and Spectroscopic Studies of *trans*-[LCo((DO)(DOH)pn)L'] Complexes

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**ABSTRACT:** Six new complexes of the type *trans*-[LCo((DO)(DOH)pn)L'] where (DO)(DOH)pn = N<sup>2</sup>, N<sup>2</sup>'-propanediolbis(2,3-butanedione 2-imine 3-oxime), L=Cl and L'=mono-anion of phenylcyanamide (pcyd), 2,5-dichlorophenylcyanamide (2,5-Cl<sub>2</sub>pcyd), 2,4-dimethyl phenylcyanamide (2,4-Me<sub>2</sub>pcyd) and L=L'=pcyd, 2,5-Cl<sub>2</sub>pcyd, 2,4-Me<sub>2</sub>pcyd, have been synthesized and characterized by elemental analysis, spectroscopy and cyclic voltammetry. The electronic absorption spectra of the Co(III) complexes show two low-energy ligand to metal charge transfer band that are associated with Co(III)-NCN chromophore. The cyclic voltammogram of these complexes exhibit two subsequent quasi-reversible reduction couple related to Co(III)/Co(II) and Co(II)/Co(I), respectively.

**KEY WORDS:** Oxime, Phenylcyanamide, Cyclic voltammetry, LMCT, Quasi-reversible reduction

### INTRODUCTION

Many aspects of the chemistry of cobaloximes have been studied extensively in recent years, with the emphasis on their electrochemical properties [1-5]. The electrochemical behavior of the Co(III)/Co(II) redox couple is largely dependent on its axial ligands [6]. However, the Co(II)/Co(I) redox couple is sensitive to the properties of the equatorial ligands.

In order to determine the possible role played by electronic effects of the ligand on the cobalt redox couples, we have synthesized some novel cobalt complexes, *trans*-[LCo((DO)(DOH)pn)L'] where (DO)-(DOH)pn is an equatorial ligand and the axial ligands are the phenylcyanamide derivatives and chloride ion (Fig. 1).

Interest in cyanamide ligands began with the discovery of copper salts of radical anion N, N'-dicyanoquinonediimine derivatives (DCNQI). These Cu(DCNQI)<sub>2</sub> molecular models show evidence of being three dimensional conductors in that they have conductivity not only in the direction of the  $\pi$ -stacks but also in the direction of the Cu-cyanamide links between the  $\pi$ -stacks [7,8].

Phenylcyanamide ligands are far more stable and can be prepared in high yields. When deprotonated, these ligands behave like pseudohalides and prefer coordination to  $\pi$ -acid metal ions [9]. In previous studies, wereported the synthesis and characterization of mononuclear and dinuclear Ru complexes with phenylcyana-

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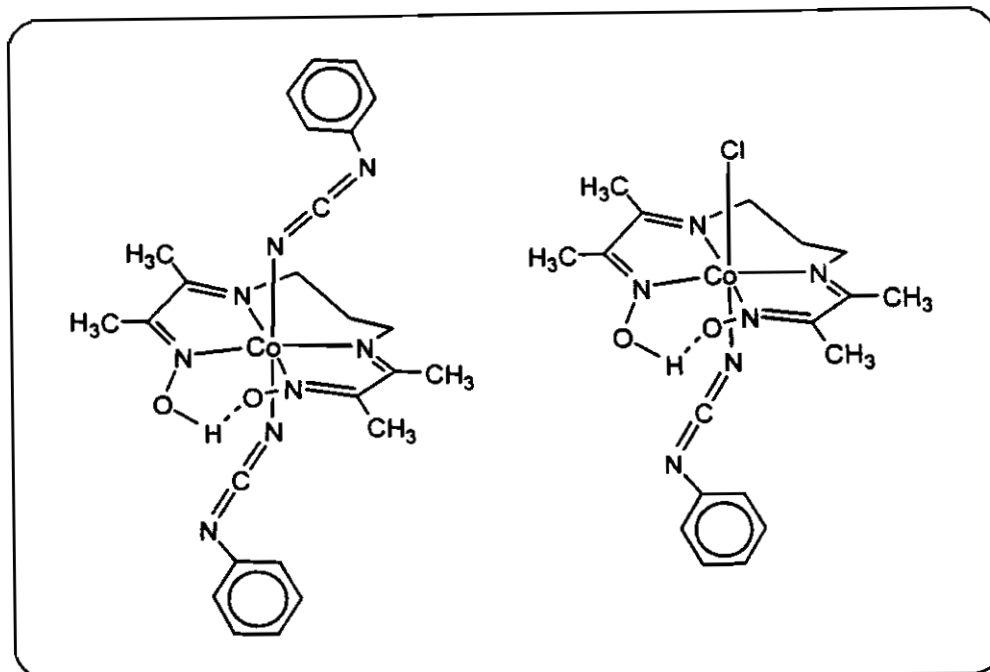


Fig. 1: Proposed structure for  $trans\text{-[ClCo((DO)(DOH)pn)(pcyd)]}$  and of  $trans\text{-[Co((DO)(DOH)pn)(pcyd)_2]}$  (both pcyd ligands are equivalent) complexes

mide and 1,4-dicyanamidobezene ligands [10,11].

These new complexes permit an examination of the effect of the substituent present on the phenyl ring of the phenylcyanamide ligand located in the axial position on electronic properties and the redox chemistry.

## EXPERIMENTAL

### Materials

All of chemicals and solvents used were reagent grade. Acetone, acetonitrile, benzene, diethyl ether, dichloromethane, aniline, ethanol, methanol, diacetyl monoxime, 1,3-propanediamine were purchased from Merck (Darmstadt, Germany), Glacial acetic acid, thallium acetate, tetrabutylammonium hexafluorophosphate (TBAH), cobalt(II) nitrate hexahydrate, lead acetate, 2,4-dimethylaniline, 2,5-dichloroaniline were purchased from Aldrich (Milwaukee, WI, USA) and used without further purification. The neutral phenylcyanamide derivatives and their thallium salts, pcyd, 2,4-Me<sub>2</sub> pcyd, 2,5-Cl<sub>2</sub>pcyd [10-12] and  $trans\text{-[Co((DO)(DOH)pn)Cl_2]}$  complex were prepared by literature method [13].

### Measurements

UV-vis spectra were taken on a JASCO 7850 spectrophotometer. The spectra were measured in acetonitrile solution at room temperature. The IR spectra (KBr disks) were obtained on a Shimadzu 460 spectrophotometer. <sup>1</sup>H-NMR spectra were recorded on a Bruker DRX-500 MHz AVANCE spectrometer at ambient temperature in deuterated chloroform. Elemental analyses were performed by Heraeus CHN-O-Rapid elemental analyzer (Heraeus, Germany). Cyclic voltammograms recorded by using a Metrohm 694 apparatus (Switzerland). Three electrodes were utilized in this system, a platinum disk working electrode (RDE), a platinum wire auxiliary electrode and Ag/AgCl reference electrode. The platinum disk working electrode was manually cleaned with 1-μm diamond polish prior to each scan. The supporting electrolyte, 0.1M tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol and vacuum-dried at 110°C overnight. Acetonitrile was distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry.

Solutions were de-aired by bubbling with argon (Ar) for 15 min and blanketed with argon prior to each scan.

**Trans-chloro (phenylcyanamido)( $N^2, N^2'$ -propanediyl bis (2,3- butanedione 2- imine 3- oxime)) cobalt(III) , *trans*-[Co((DO)(DOH)pn)(pcyd)Cl] complex (I)**

A mixture of deprotonated phenylcyanamide (TI salt) ( $2 \times 10^{-3}$  mol) and *trans*-[Co((DO)(DOH)pn)Cl<sub>2</sub>] ( $2 \times 10^{-3}$  mol) dissolved in 100 ml acetonitrile was stirred for 5h at the reflux temperature. The resulting reaction mixture was allowed to cool to room temperature and then left in a refrigerator overnight. A white solid (TiCl) was filtered off. The filtrate was then transferred to a 500 ml round- bottom flask and the solvent removed on a rotary evaporator. The brown product precipitated. For further purification, the complex was recrystallized by diffusing ether into an acetonitrile solution, yielding deep brown crystals. Yield 62%. Anal. calcd. for C<sub>18</sub>H<sub>24</sub>ClN<sub>6</sub>O<sub>2</sub>Co requires C, 47.96; H, 5.37; N, 18.64%. Found: C, 48.10; H, 5.47; N, 18.72.

**(*Trans*- [Co((DO)(DOH)pn)(2,5- Cl<sub>2</sub>pcyd)Cl] complex (II)**

This complex was prepared from 2,5-dichlorophenylcyanamide (TI salt, 2,5-Cl<sub>2</sub>pcydTI) ( $2 \times 10^{-3}$  mol) by using the general procedure described above as brown microcrystals. Yield 75%. Anal. calcd. for C<sub>18</sub>H<sub>22</sub>Cl<sub>3</sub>N<sub>6</sub>O<sub>2</sub>Co requires C, 41.60; H, 4.27; N, 16.17%. Found: C, 41.74; H, 4.38; N, 16.29.

***Trans*- [Co((DO)(DOH)pn) (2,4-Me<sub>2</sub> pcyd)Cl] complex (III)**

This complex was prepared from 2,4-dimethylphenylcyanamide (TI salt) ( $2 \times 10^{-3}$  mol) by using the general procedure described above and obtained as brown microcrystals. Yield 79%. Anal. calcd. for C<sub>20</sub>H<sub>28</sub>ClN<sub>6</sub>O<sub>2</sub>Co requires C, 50.16; H, 5.90; N, 17.55%. Found: C, 50.31; H, 6.03; N, 17.70.

***Trans*-[Co ((DO)(DOH)pn)(pcyd)<sub>2</sub>] complex (IV)**

This complex was prepared from phenylcyanamide (TI salt) ( $4 \times 10^{-3}$  mol) by using the general procedure described above and obtained as brown microcrystals. Yield 58%. Anal. calcd. For C<sub>25</sub>H<sub>29</sub>N<sub>8</sub>O<sub>2</sub>Co requires C,

56.39; H, 5.49; N, 21.04%. Found: C, 56.72; H, 5.61; N, 21.17.

***Trans*-[Co((DO)(DOH)pn)(2,4-Me<sub>2</sub> pcyd)<sub>2</sub>] complex (V)**

This complex was prepared from 2,4-dimethylphenylcyanamide (TI salt) ( $2 \times 10^{-3}$  mol) by using the general procedure described above and obtained as brown microcrystals. Yield 67%. Anal. calcd. For C<sub>29</sub>H<sub>37</sub>N<sub>8</sub>O<sub>2</sub>Co requires C, 59.18; H, 6.34; N, 19.04%. Found : C, 59.50; H, 6.47; N, 19.19.

***Trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] complex (VI)**

This complex was prepared from 2,5-dichlorophenylcyanamide (TI salt, 2,5-Cl<sub>2</sub>pcydTI) ( $4 \times 10^{-3}$  mol) by using the general procedure described above and obtained as brown microcrystals. Yield 75%. Anal. calcd. For C<sub>25</sub>H<sub>25</sub>Cl<sub>4</sub>N<sub>8</sub>O<sub>2</sub>Co requires C, 44.80; H, 3.76; N, 16.72%. Found: C, 45.02; H, 3.84; N, 16.88 .

## RESULTS AND DISCUSSION

### Absorption spectra

All complexes were prepared from the metathesis reaction of *trans*-[Co((DO)(DOH)pn)Cl<sub>2</sub>] with the thallium salt of a phenylcyanamide derivatives. The elemental analysis of the complexes are consistent with their structural formula Fig. 1, and confirmed by the following spectroscopic and electrochemical characterizations.

Quantitative electronic spectra of the complexes were taken in acetonitrile. The data and spectroscopic assignments are summarised in Table 1.

A representative spectrum of *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] is shown in Fig.2. Two ligand field transition for Co(III) complexes (<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub>) and (<sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub>) are expected[14]. However, the intensity of the two absorption bands in the visible region (407 to 850 nm) in comparison to Ru(III) and Co(III) phenylcyanamide complexes[11-13,15], allow these two intense absorption bands to be assigned to the ligand to metal charge transfer (LMCT) with minor contributions to band intensity from the underlying ligand field transition. These two bands are associated with Co(III)-cyanamide chromophore. The reason for this is the dependence of charge transfer energy on solvent polarity

which is a well-known phenomenon [16,17]. For the *trans*-[LCo((DO)(DOH)pn)L'] complexes (I-VI) changing the solvent from dichloromethane (lower polarity solvent) to dimethylsulfoxide (higher polarity solvent) cause the low-energy LMCT bands to shift to higher energy levels (Fig. 3). This behavior is consistent with ground-state stabilization of the complexes' permanent dipoles by the solvent [16].

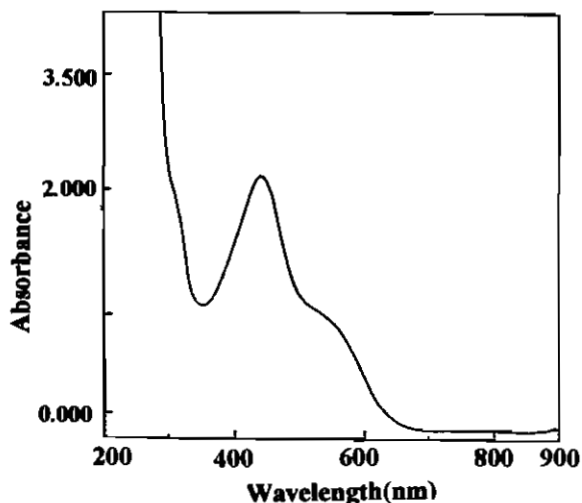


Fig. 2: UV-vis spectra of *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pyd)<sub>2</sub>], 1 × 10<sup>-3</sup> M in acetonitrile

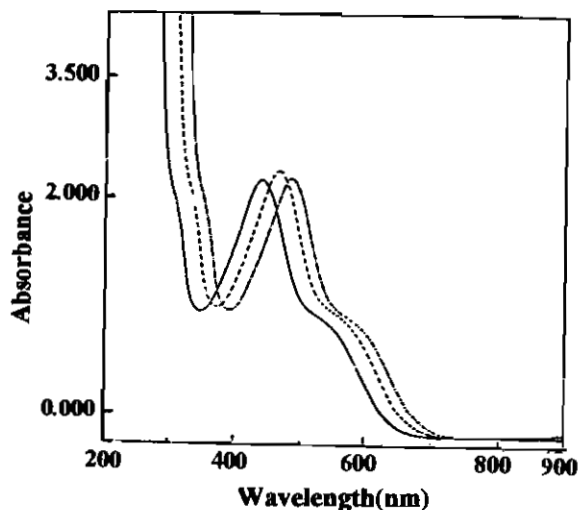


Fig. 3: The LMCT band of *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pyd)<sub>2</sub>], 1 × 10<sup>-3</sup> M in a) acetonitrile (—), b) acetone (---), c) dichloromethane (· · ·)

These two LMCT transitions arise from two non-degenerate pairs of nonbonding electrons ( $\pi_{nb}$ ) that are delocalized in to the cyanamide three-atom  $\pi$  system and their qualitative molecular orbitals can be represented in (Fig. 4a) [18]. An extended Huckel calculation of phenylcyanamide anion show that  $\pi_{nb2}$  is more stable by 0.49 eV than  $\pi_{nb1}$  (Fig. 4b) because only the  $\pi_{nb1}$  MO has the correct symmetry to interact with the phenyl  $\pi$  system [19]. Since the  $t_{2g}$  orbitals in Co(III) are full occupied, the LMCT bands originate from the ligand  $\pi$  orbital to a metal  $e_g^*$  ( $\sigma^*$ ) orbitals ( $\pi \rightarrow \sigma^*$ ) [16].

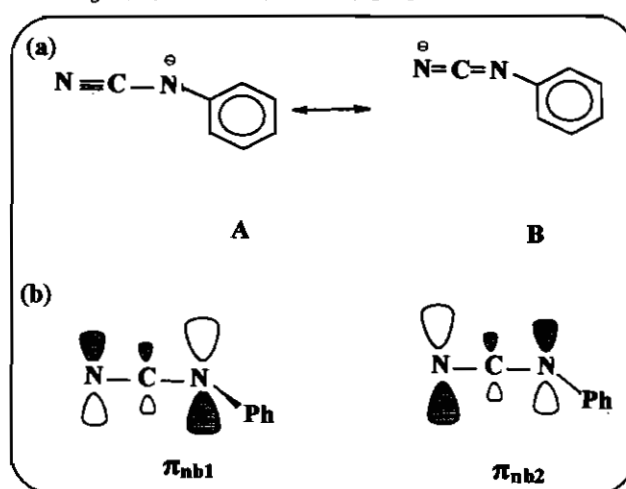


Fig. 4: a) Resonance stabilized phenylcyanamide anion ligand b)  $\pi$ -symmetry orbitals ( $\pi_{nb1}$  is orthogonal to  $\pi_{nb2}$ ) resulting from the delocalization of two bonding electron pairs as in form B. The size of atomic orbitals approximate their contribution to the molecular orbital

The IR spectra of these complexes show similar absorption patterns in 1800-400 cm<sup>-1</sup> region, indicating the existence of (DO)(DOH)pn as the common equatorial ligand [20]. The O-H stretching vibration of the (DO)(DOH)pn ligand appears at about 3400 cm<sup>-1</sup> for all six complexes.

The infrared data for the free phenylcyanamide ligand (neutral and TI salt) have been reported elsewhere [18,21-22]. The IR spectrum of the neutral ligand shows a strong band at 2245 cm<sup>-1</sup> that is assigned to  $\nu$  (C≡N) of cyanamide group. Organic carbodiimides have  $\nu$ (N=C=N) ranging from 2050 to 2150 cm<sup>-1</sup> [21]. Thus,

Table 1: Electronic <sup>a</sup> and IR Absorption <sup>b</sup> Data for *trans*-[L Co((DO)(DOH)pn)L] complexes.

No.	Complex	LMCT	$\nu(\text{N}=\text{C}=\text{N})$
I	[Co((DO)(DOH)pn)(pcyd)Cl]	453(3.65), 553(3.32)	2050
II	[Co((DO)(DOH)pn)(2,5-Cl <sub>2</sub> pcyd)Cl]	444(3.15), 546 (3.18)	2063
III	[Co((DO)(DOH)pn)(2,4-Me <sub>2</sub> pcyd)Cl]	465(3.05), 571(3.10)	2045
IV	[Co((DO)(DOH)pn)(pcyd) <sub>2</sub> ]	450(3.90), 562 (3.69)	2065
V	[Co((DO)(DOH)pn)(2,5- Cl <sub>2</sub> pcyd) <sub>2</sub> ]	441(3.98), 550(3.64)	2083
VI	[Co((DO)(DOH)pn)(2,4-Me <sub>2</sub> pcyd) <sub>2</sub> ]	463(4.02), 568(3.87)	2057

<sup>a</sup>  $\lambda$  in nm (log $\epsilon$ ) ; in acetonitrile solution, <sup>b</sup> IR data (KBr) in cm<sup>-1</sup>, strong absorption.

the sharp and strong band at 2050 cm<sup>-1</sup> in the IR spectrum of the anion phenylcyanamide ligand is assigned to  $\nu(\text{N}=\text{C}=\text{N})$ . Coordination of the neutral and anionic phenylcyanamide to metal ion can occur via amine or nitrile nitrogens. This may be due to the  $\pi$  back-bonding and donor properties of the nitrile group and the steric hindrance that would be experienced upon coordination to the amine of N-alkyl-substituted cyanamides. When a phenylcyanamide ligand coordinates to a transition metal ion,  $\nu(\text{N}=\text{C}=\text{N})$  is shifted to higher energies [23,24]. The presence of only one sharp and intense absorption band for the cyanamide stretching frequency (Table 1) in all the complexes provides the evidence that both cyanamide ligands are equivalent in the solid state (Fig. 5). When cyanamide ligands are non-equivalent, multiple  $\nu(\text{N}=\text{C}=\text{N})$  bands are observed [23]. A small positive shift in  $\nu(\text{N}=\text{C}=\text{N})$  is observed, as the electron-withdrawing ability of the substituents on the phenyl ring increases.

The <sup>1</sup>H-NMR spectral data of compounds 1–VI were collected in chloroform-d, and relevant chemical

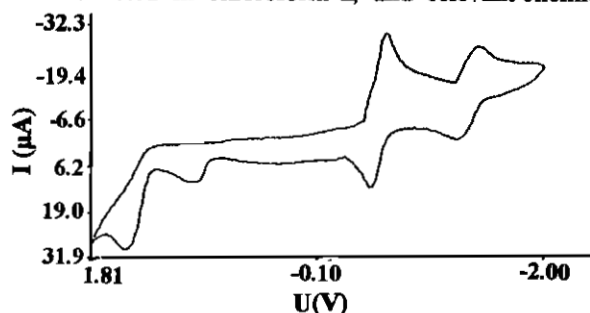
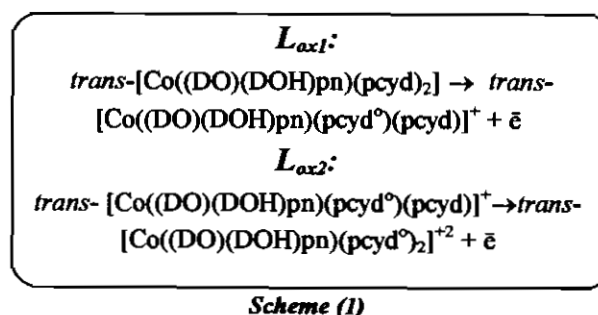


Fig. 5: Cyclic voltammetry of *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>], 1×10<sup>-3</sup> M in dry acetonitrile (0.1 M TBAH) at a scan rate of 100 mV/s

shifts of the O—H—O signals, equatorial methyl signals and phenylcyanamide signals are reported in Table 2. The *trans*-[Co((DO)(DOH)pn)Cl<sub>2</sub>] complex is also included for comparison[3].

#### Electrochemistry

The electrochemical data for the six complexes are collected in Table 3 and a representative voltammogram of *trans*-[Co((DO)(DOH)pn)(2,5-Cl<sub>2</sub>pcyd)<sub>2</sub>] is shown in Fig. 5. The electrochemical measurements were made on acetonitrile solutions of the complexes with 0.1 M TBAH as a supporting electrolyte and 2×10<sup>-3</sup> M complex. E<sub>1/2</sub> values were calculated from the average of the anodic and cathodic peak potentials (E<sub>1/2</sub>=(E<sub>pc</sub>+E<sub>pa</sub>)/2) at the scan rate of 100 mV/s. The two irreversible oxidations and only the anodic current peaks at positive potentials in IV–VI are assigned to the sequential oxidation of the two coordinated phenylcyanamide anion ligands as shown in the scheme(1).



The irreversible oxidation at the positive potentials in the voltammogram of I–III complexes is assigned to oxidation of the one phenylcyanamide ligand, scheme (2).

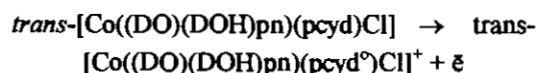
Table 2: <sup>1</sup>H-NMR Spectral Data for *trans*-[LCo((DO)(DOH)pn)L] Complexes<sup>a</sup>

No.	Complex	O-H—O	C-N=C-CH <sub>3</sub>	O-N=C-CH <sub>3</sub>	phenyl protons	Methyl protons
I	[Co((DO)(DOH)pn)(pcyd)Cl]	19.28(s)	2.38(s)	2.30(s)	6.31(t), 6.58(d), 6.90(t)	—
II	[Co((DO)(DOH)pn)(2,5-Cl <sub>2</sub> pcyd)Cl]	19.19(s)	2.35(s)	2.30(s)	6.70(d), 6.91(d), 7.06(s)	—
III	[Co((DO)(DOH)pn)(2,4-Me <sub>2</sub> pcyd)Cl]	19.29(s)	2.34(s)	2.29(s)	6.46(s), 6.64(d), 6.70(d)	2.19(s), 2.23(s)
IV	[Co((DO)(DOH)pn)(pcyd) <sub>2</sub> ]	19.26(s)	2.38(s)	2.30(s)	6.30(t), 6.60(d), 6.88(t)	—
V	[Co((DO)(DOH)pn)(2,5-Cl <sub>2</sub> pcyd) <sub>2</sub> ]	19.08(s)	2.36(s)	2.30(s)	6.74(d), 6.90(d), 7.11(s)	—
VI	[Co((DO)(DOH)pn)(2,4-Me <sub>2</sub> pcyd) <sub>2</sub> ]	19.30(s)	2.35(s)	2.28(s)	6.45(s), 6.61(d), 6.67(d)	2.17(s), 2.19(s)
	[Co((DO)(DOH)pn)Cl <sub>2</sub> ] <sup>b</sup>	19.4(s)	2.58(s)	2.51(s)	—	—

<sup>a</sup> In chloroform - *d*; data in ppm vs TMS refrence at 0.00 ppm. Abbreviations: *s*, singlet; *d*, doublet; *t*, triplet.

<sup>b</sup> Ref.3.

*L*<sub>oxi</sub>:



Scheme(2)

These oxidation waves are shifted anodically due to their coordination to Co(III) ion[15].

Since the phenylcyanamide ligands behave like a pseudo halogen, consistent with *trans*-[Co((DO)(DOH)pn)Cl<sub>2</sub>], [6] the voltammogram of the compounds of this study, show two subsequent cathodic/ anodic peak systems due to the reduction couples corresponding to the Co(III)/Co(II) and Co(II)/Co(I). These two reduction couple are quasi-reversible and generally possess invariant anodic to cathodic peak separation from 90 to 120 mV for Co(III/II) and 70 to 85 mV at the scan between 100 to 500 mV/ S in acetonitrile. In comparison to other Schiff-base Co(III) complexes previously described [25-26], the Co(III/II) reduction couple depends on the nature of axial ligands. On the other hand, the Co(II)/ Co(I) reduction couple is relatively insensitive to the axial ligands, and is mainly influenced by the equatorial

chelate. Both the Co(III)/Co(II) reduction couple and ligand oxidation waves shift to more positive potentials as the electron-withdrawing ability of the substituent on the phenyl ring increases from CH<sub>3</sub> to Cl, (Table 3). This trend may be rationalized as being due to the stabilization of cyanamide ligand electrons which reduce the ligand's effectiveness in stabilizing the Co(II) oxidation state. This is consistent with the expected decrease in basicity of phenylcyanamide ligands.

## CONCLUSIONS

The presence of only one sharp and intense band for the  $\nu(\text{NCN})$  around 2100 cm<sup>-1</sup> provides evidence that both phenylcyanamide ligands are equivalent and coordinated to cobalt through the nitrile nitrogen. Electrochemical data of these complexes demonstrate that Co(III)/Co(II) reduction couple depends only to the nature of the axial phenylcyanamide ligands. On the other hand, the Co(II)/Co(I) reduction couple for all the complexes are almost constant. The energy of LMCT bands shift to lower-energy as the electron-donating ability of the substituent on the phenyl ring increased.

Table 3: Electrochemical <sup>a</sup> Data for trans-[LCo((DO)(DOH)pn)L'] Complexes

No.	Complex	Co (II/II)	Co (I/I)	L <sup>b</sup> <sub>ox1</sub>	L <sup>b</sup> <sub>ox2</sub>
I	[Co((Do) (DOH)pn)(pcyd) Cl]	-560	-1014	970	—
II	[Co((DO) (DOH)pn)(2,5-Cl <sub>2</sub> pcyd)Cl]	-407	-1009	1260	—
III	[Co((DO) (DOH)pn)(2,4-Me <sub>2</sub> pcyd)Cl]	-785	-1024	923	—
IV	[Co ((DO) (DOH)pn)(pcyd) <sub>2</sub> ]	-642	-1015	1020	1215
V	[Co ((DO) (DOH)pn)(2,5-Cl <sub>2</sub> pcyd) <sub>2</sub> ]	-476	-1028	1284	1511
VI	[Co ((DO)(DOH)pn)(2,4- Me <sub>2</sub> pcyd) <sub>2</sub> ]	-851	-1012	877	1120
	[Co ((DO)(DOH)pn)Cl <sub>2</sub> ] <sup>c</sup>	-610	-1020	—	—

<sup>a</sup> Data in mV vs Ag/AgCl(0.1 M TBAH acetonitrile solution).<sup>b</sup> Anodic wave only.<sup>c</sup> Ref.5.**Acknowledgment**

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