Synthesis, Electrochemical Properties and Spectroscopic Studies of Mono and Dinuclear Zn(II) Polypyridyl Complexes with Phenylcyanamide Ligands

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ABSTRACT: *Several novel mononuclear Zn(II) complexes, [Zn(bpy)L₂], where bpy=2,2'-bipyridine and L=monoanions of phenylcyanamide (pcyd), 4-methylphenylcyanamide (4-Mepcyd), 3,5-dimethylphenylcyanamide (3,5-Me₂pcyd), 4-methoxyphenylcyanamide (4-MeOpcyd), 3,5-dimethoxyphenylcyanamide (3,5-MeO₂pcyd), 3-chlorophenylcyanamide (3-Clpcyd), 2,3-dichlorophenyl-cyanamide (2,3-Cl₂pcyd), 4-bromophenylcyanamide (4-Brpcyd), 1-naphthylcyanamide (1-ncyd), azophenylcyanamide (apcyd) and a dinuclear Zn(II) complex, [{Zn(terpy)}₂(μ-adicyd)](PF₆)₂, where terpy = 2,2':6',2''-terpyridine and adicyd = azodi (phenylcyanamide) dianion have been synthesized and characterized by elemental analysis, UV-vis, IR, ¹H-NMR spectroscopic techniques and cyclicvoltammetry.The presence of only one sharp and intense absorption band for υ(N=C=N) around 2100-2180 cm⁻¹ for all the monomer complexes provide evidence that both cyanamide legend are equivalent in the solid state and coordinated end-on by nitride nitrogen to Zn(II). This is also indicated by ¹H-NMR spectra of the complexes. UV-vis spectra show one MLCT band that are associated with Zn(II)-pyridyl chromophores(t₂g⁶ →π*). Blue shift of this band with increasing the polarity of solvent from CH₃OH to DMSO is the reason for this assignment. The Zn(II) ion is redox innocent therefore, two irreversible oxidation peaks at positive potential and one reduction couple at the negative potential are assigned to sequential oxidation of two phenylcyanamide ligands and reduction of bipyridine, respectively.*

KEY WORDS: *Phenylcyanamide, Zinc (II) complex, Polypyridyl, Spectroscopy, Cyclicvoltammetry.*

INTRODUCTION

Phenylcyanamide coordination chemistry has been the subject of a recent review [1]. Phenylcyanamide ligands are pseudohalides. However, the attachment of a phenyl ring to the cyanamide group (NCN) adds an extra dimension not present in azide or thiocyanate ligands. An extensive π conjugation between the cyanamide group

and the phenyl ring provides an energetically favorable means by which a metal ion can couple into a conjugated organic π system.

In our previous studies [2-14], we reported the metal-cyanamide and metal-metal coupling in mono and dinuclear transition metal complexes were affected both by the nature of outer and inner-coordination spheres. The electronic properties of the metal-cyanamide LMCT chromospheres have been probed by varying the nature of the cyanamide ligands and the metal ions as well as by the outer-sphere perturbation of solvent molecules.

The coordination chemistry of phenylcyanamide ligands still requires much effort to complete. At this point in time, phenylcyanamide complexes of Ru(II) [4-6, 11, 15], Ru (III) [16], Ni(II) [17], Pd (II) [18,19], Cu(II) [20,21], Cu(I) [22], Ag(I) [23], Co(III) [3, 7,13] , Fe(III) [14], Mn(III) [10] and Rh(III) [9] have been fully studied.

It is well known that the nature of the spectator ligands can play an important role in adjusting the energy and size of metal orbitals and can therefore be used to significantly perturb the metal-cayanamide chromophores [24]. In addition to the factors mentioned above, the nature of the metal ion should also play an important role.

In order to study these factors, a series of the novel mononuclear Zn(II) complexes, $[Zn(bpy)L_2]$, where L =phenylcyanamide anion ligands and dinuclear $[\{Zn(terpy)\}_2(\mu-L)](PF_6)_2$, where L = azodi (phenyl-cyanamide) dianion have been synthesized and characterized.

EXPERIMENTAL
Materials

All of the chemicals and solvents were reagent grade or better and used without further purification. Acetone, absolute ethanol, diethylether and DMF were purchased from Merck. Glacial acetic acid, 2,2´:6´,2´´-terpyridine, 2,2'-bipyridine, thallium(I) acetate, Tetrabutylammonium hexaflourophosphate, lead(II) acetate, zinc(II) chloride, 4-methylaniline, 3,5-dimethylaniline, 3, 5-dimethoxy-aniline, 4-methoxy aniline, 3-chloroaniline,aniline, 4-bromoaniline, 2,3-dichloroaniline, α-aminonaphtalene and 4,4'-azophenyl aniline were purchased from Aldrich. 4,4´- Azodianiline was purchased from Kodak. The neutral phenylcyanamide derivatives and their thallium salts, Tl(pcyd), Tl(4-Mepcyd), Tl(3,5-Me$_2$pcyd), Tl(4-MeOpcyd), Tl(3,5-MeO$_2$pcyd), Tl(3-Clpcyd), Tl(2,3-l$_2$pcyd), Tl(4-Brpcyd), Tl(1-ncyd) , and Tl(apcyd) were prepared according to established procedure [25,26].

Measurements

The IR spectra (KBr-disks) were obtained on a Shimadzu 460 spectrophotometer. ^{1}H-NMR spectra were recorded on a Bruker DRX-500 MHz AVANCE spectrometer at ambient temperature in deuterated dimethylsulfoxide (DMSO-d$_6$). UV-vis spectra were taken on a JASCO 7850 spectrophotometer. The spectra were measured in dimethylformamide. Elemental analyses were performed by CHNS-O 2400TI Perkin-Elmer elemental analyzer. Cyclic voltammograms were recorded by using a Metrohm 694 apparatus. 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 0.1 M tetrabutylammonium hexaflourophosphate (TBAH), was recrystallized twice from ethanol and vacuum-dried at 110 °C overnight. Dimethylformamide (DMF) was distilled over calcium hydride and degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by bubbling with argon for 15 min and blanketed with argon prior to each scan.

SYNTHESIS
Preparation of (bipyridine)dichlorozinc(II), [Zn(bpy)Cl$_2$]

681 mg (5 mmol) of ZnCl$_2$ dissolved in 50 mL absolute ethanol was stirred at 40 °C. To the resulting colorless solution, a solution of 780 mg (5 mmol) bipyridine in 50 mL absolute ethanol was added dropwise and stirred for 1 h at mild temperature (40 °C). The resulting white precipitate [Zn(bpy)Cl$_2$] was filtered off. The product was washed several times with 30 mL portions of absolute ethanol followed by 10 mL ether and air-dried. Yield 1.34 g (92 %).

Caution: To avoid of formation of by-product of [Zn(bpy)$_2$]Cl$_2$, bipyridine solution must be added very slowly.

Preparation of Zn(II) phenylcyanamide complexes
General Methods

A mixture of thallium(I) phenylcyanamide (Tlpcyd) (2100 mg, 2.82 mmol) and [Zn(bpy)Cl$_2$] (410 mg, 1.41

mmol) dissolved in 10 ml DMF was stirred for 24 h at 40 °C. The resulting reaction mixture was allowed to cool to room-temperature and then left in a refrigerator overnight. A white solid (TlCl) was filtered off . Then 200 mL ether was added to the filtrate and left in a refrigerator overnight. The yellow color product was precipitated and filtered off. Yield 0.47 g (84 %). Anal. Calcd for $ZnC_{24}H_{18}N_6$: C, 64.30; H, 4.04; N, 19.12. Found: C, 63.75; H, 3.98; N, 18.87.

[Zn(bpy)(apcyd)$_2$]: Yield 1.9 g (79 %). Anal. Calcd for $ZnC_{36}H_{26}N_{10}$: C, 65.79; H, 3.86; N, 20.89. Found: C, 65.11; H, 3.91; N, 21.09.

[Zn(bpy)(4-Mepcyd)$_2$]: Yield 0.31 g (82 %). Anal. Calcd for $ZnC_{26}H_{22}N_6$: C, 64.89; H, 4.61; N, 17.52. Found: C, 64.54; H, 4.58; N, 17.37.

[Zn(bpy)(3,5-Me$_2$pcyd)$_2$]: Yield 0.66 g (87 %). Anal. Calcd for $ZnC_{28}H_{26}N_6$: C, 66.41; H, 4.97; N, 17.00. Found: C, 66.89; H, 5.11; N, 16.62.

[Zn(bpy)(4-MeOpcyd)$_2$]: Yield 0.45 g (85 %). Anal. Calcd for $ZnC_{26}H_{22}N_6O_2$: C, 61.33; H, 4.30; N, 16.93. Found: C, 60.72; H, 4.39; N, 16.29.

[Zn(bpy)(3,5-MeO$_2$pcyd)$_2$]: Yield 0.66 g (87 %). Anal. Calcd for $ZnC_{26}H_{28}N_6O_4$: C, 59.11; H, 4.60; N, 14.63. Found: C, 58.59; H, 4.55; N, 14.59.

[Zn(bpy)(3-Clpcyd)$_2$]: Yield 0.39 g (76 %). Anal. Calcd for $ZnC_{24}H_{16}N_6Cl_2$: C, 53.95; H, 3.10; N, 16.62. Found: C, 54.93; H, 3.07; N, 16.01.

[Zn(bpy)(2,3-Cl$_2$pcyd)$_2$]: Yield 0.88 g (88 %). Anal. Calcd for $ZnC_{24}H_{14}N_6Cl_4$: C, 49.06; H, 2.41; N, 14.50. Found: C, 48.56; H, 2.38; N, 14.16.

[Zn(bpy)(1-ncyd)$_2$]: Yield 0.43 g (78 %). Anal. Calcd for $ZnC_{32}H_{22}N_6$: C, 70.19; H, 4.01; N, 14.97. Found: C, 69.43; H, 3.96; N, 15.17.

Preparation of (terpyridine)chloro zinc(II) hexa-flourophosphate, [Zn(terpy)Cl]PF$_6$

This was prepared by the method of *Doughlas et al.* [27] with a small modification. 470 mg (3.5 mmol) of $ZnCl_2$ dissolved in 50 mL absolute ethanol was stirred at 40 °C. To the resulting colorless solution, a solution of 780 mg (3.5 mmol) of 2,2',2'',6'-terpyridine in 50 mL absolute ethanol was added dropwise and was stirred for 1 h at mild temperature(40 °C). The mixture was left in fridge for 5 h and resulting white precipitate, [Zn(terpy)Cl]Cl, was filtered off. The product was dissolved in 25 mL double distilled water. To the resulting colorless solution, a solution of 1 g NH_4PF_6

in 2 mL water was added and stirred for 15 min, then cooled in fridge. The white product, [Zn(terpy)Cl]PF$_6$, was filtered off and washed with water and air-dried. Yield 0.35 g (60 %).

Preparation of μ-(4,4´-azodiphenylcyanamide)bis ((terpyridine)zinc(II))hexafluorophosphate,[{Zb(terpy)}$_2$ (μ-adicyd)](PF$_6$)$_2$

[Zn(terpy)Cl]PF$_6$ (160 mg, 0.33 mmol) was dissolved in 10 mL DMF in a 100 ml two neck round bottom flask. Tl$_2$(adicyd) (110 mg, 0.165 mmol) was added. The orange color solution was stirred while heated to about 40 °C for 24 h. The resulting reaction mixture was allowed to cool to room temperature and then left in a refrigerator over night. A white solid (TlCl) was filtered off. Then 200 mL ether was added to filtrate, and the solution was placed in the refrigerator overnight. The orange color product, [{Zb(terpy)}$_2$(μ-adicyd)](PF$_6$)$_2$, which precipitated was filtered off and washed with 20 mL ether. For further purification, the complex was recrystallized by diffusing ether into a saturated solution of the complex in DMF. Yield: 100 mg (55 %). ^{1}H-NMR (500 MHz, DMSO-d$_6$, 298 K, relative to TMS): for terpy protons, 7.03(t, 4H), 7.42(t, 2H), 7.43(t, 4H), 7.74(unresolved d, 8H), 8.59(t, 4H); adicyd protons, 6.94(d, 4H), 7.49(d, 4H). Anal. Calcd for $Zn_2C_{44}H_{30}N_{12}F_{12}P_2$: C, 48.84; H, 2.77; N, 15.54. Found C, 49.19; H, 2.81; N, 15.83. IR (KBr disk): v(N=C=N) = 2076 cm^{-1} ; v(P-F) = 840 cm^{-1}. UV-vis (in DMF) : λ_{max} (MLCT) = 491 nm (log ε = 3.860).

RESULTS AND DISCUSSION

The synthetic strategy to prepare [Zn(bpy)Cl$_2$] was based on a modification of the literature methods to increase the yield and the purity of the complex [28]. The bipyridinebis(phenylcyanamide) zinc(II) complexes, [Zn(bpy)L$_2$], were prepared from the metathesis reaction of [Zn(bpy)Cl$_2$] with thallium salt of a phenylcyanamide anion derivatives at a mild temperature in dimethylformamide (Scheme 1).

The coordination mode of terpy as a tridentate ligand depends on the synthesis sequence. If the metal ion bound to a tetradentate, pentadentate or two bidentate ligands such as a Schiff base, the terpy ligand can behave as monodentate or bidentate ligand. In this present work, the Zn-terpy complex is primarily prepared from $ZnCl_2$. Therefore, due to the chelating effect, the terpy ligand has
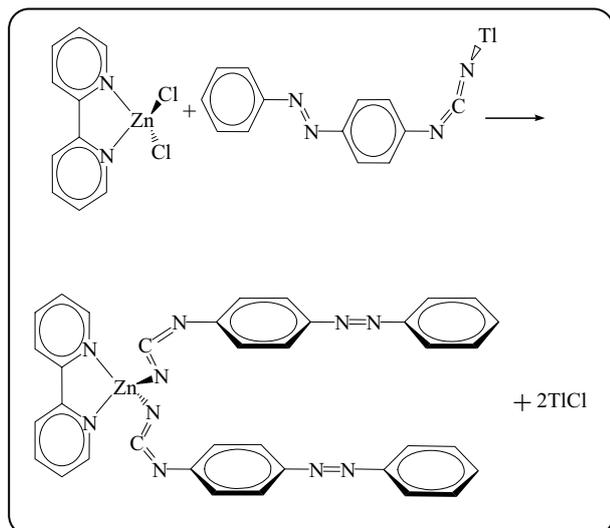
Scheme 1.
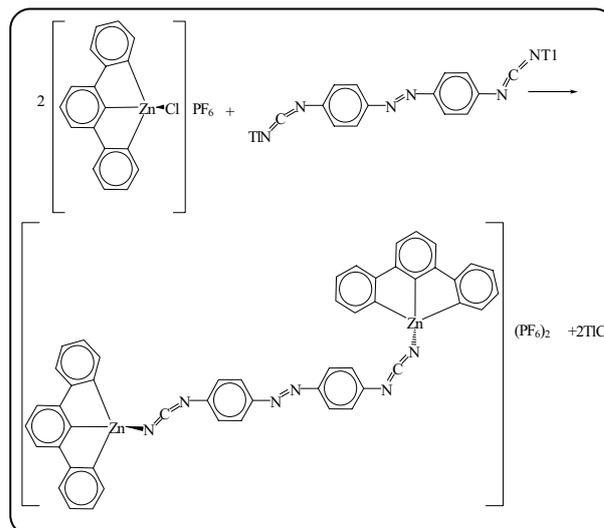
Scheme 2.

to act as a tridentate ligand and forms [Zn(terpy)Cl]Cl. There are many Zn(II)-terpy complexes that the terpy ligand is coordinated to Zn(II) via its three pyridyl rings. In these complexes, the pyridyl rings of terpy ligands are not coplanar and show a skew conformation. Therefore, the geometry around Zn(II) in the dinuclear complex is distorted tetrahedron and the pyridyl rings are not coplanar [29-31].

The dinuclear complex, [{Zn(terpy)}$_2$(μ-adicyd)] (PF$_6$)$_2$, was achieved by the reaction of stoichiometric amounts of [Zn(terpy)Cl](PF$_6$) and thallium salt of the bridging ligand, Tl$_2$adicyd in the same conditions as mononuclear complexes in DMF (Scheme 2).

The complexes appeared stable in solution for days at a time and no evidence of decomposition was seen in the solid state. The elemental analysis of the complexes is consistent with their formulation as are the following spectroscopic and electrochemical characterizations.

The ^{1}H-NMR spectra data for mononuclear zinc (II) complexes are compiled in (table 1). The integration of phenyl protons and comparison with those of bipyridine suggests that both phenylcyanamide anion ligands occupy magnetically equivalent coordination environments. The two pyridine moieties in the bipyridine ligand in the mononuclear complexes have similar magnetically environment and should result in one ABCD pyridine proton patterns for a total of four chemical shift [4]. But only, three are observed (table 1), and that is because the chemical shifts of the 3,3′-protons are nearly equivalent.

The ^{1}H-NMR spectra of the free bridging ligand azodiphenylcyanamide dianion (adicyd) show two separate doublet about 7-8 ppm. The integration of the bridging ligand protons and comparison with those of terpyridine confirmed the formation and the purity of dinuclear complex (see Experimental section).

The infrared data for the free phenylcyanamide ligands (neutral and Tl salt) have been reported elsewhere [25,26]. The IR spectra of the neutral ligands show a strong band at 2245 cm^{-1} that is assigned to $\upsilon(C{\equiv}N)$ of the cyanamide group. Organic carbodiimdes have $\upsilon(N{=}C{=}N)$ ranging from 2100 to 2150 cm^{-1}. Thus, the strong band at 2102 cm^{-1} in the IR spectrum of the thallium salt of the anion ligand is assigned to $\upsilon(N{=}C{=}N)$ [32,33]. When a phenylcyanamide ligand coordinates to a transition metal ion, $\upsilon(N{=}C{=}N)$ shifts to higher energies [4, 25, 32-33], but in Zn(II) phenylcyanamide complexes, this band shifts to lower energy probably due to π-back bonding from metal to cyanamide moiety. The presence of only one sharp and intense absorption band for the cyanamide stretching frequency (table 2) for both phenylcyanamide ligands in all the mononuclear complexes and in the free bridging ligand azodiphenyl-cyanamide dianion (adicyd) as wall as dinuclear complex, [{Zn(terpy)}$_2$(μ-adicyd)](PF$_6$)$_2$ provides evidence that both cyanamide moieties on the phenyl rings are equivalent in the solid state.   When the cyanamide ligands are equivalent, multiple $\upsilon(N{=}C{=}N)$ bands are observed [22].

Table 1: ^{1}H-NMR spectral data for [Zn(bpy)L$_2$] complexes in dimethylsulfoxide-d$_6$.

L	Bipyridine Protons	Phenyl Protons	Methyl	Methoxy
apcyd	7.42(2H,t), 8.25(2H,t), 8.64(4H, d)	6.92(4H,d), 7.41(4H,t), 7.48(2H,t), 7.68(4H,d), 7.74(4H,d)	—	—
4- Mepcyd	7.75(2H,t), 8.27(2H,t), 8.64(4H,d)	6.71(4H,d), 6.86(4H,d)	2.1(6H,s)	—
3,5- Me$_2$pcyd	7.75(2H,t), 8.26(2H,t), 8.64(4H,t)	6.44(4H,s), 6.31(2H,s)	2.1(12H,s)	—
4- MeOpcyd	7.73(2H,t), 8.25(2H,t), 8.64(4H,d)	6.66(4H,d), 6.75(4H,d)	—	3.61(6H,s)
3,5- MeO$_2$pcyd	7.73(2H,t), 8.25(2H,t), 8.64(4H,d)	6.00(4H,s), 5.84(2H,)	—	3.59(12H,s)
Pcyd	7.74(2H,t), 8.27(2H,t), 8.64(4H,d)	6.66(2H,t),6.80(4H,d),7.05(4H,t)	—	—
3- Clpcyd	7.75(2H,t), 8.27(2H,t), 8.67(4H,d)	6.67(2H,d),6.73(2H,d),6.70(2H,s), 7.05(2H,t)	—	—
2,3- Cl$_2$pcyd	7.71(2H,t), 8.23(2H,t), 8.63(4H,d)	6.81(2H,d),6.84(2H,d), 6.96(2H,t)	—	—
4- Brpcyd	7.72(2H,t), 8.24(2H,t), 8.63(4H,d)	6.70(4H,d), 7.16(4H,d)	—	—
1- ncyd	7.68(2H,d),8.22(2H,d), 861(4H,d)	6.95(4H,d),7.17(6H,d),7.31(2H,t), 7.37(2H,t)	—	—

Data in ppm vs TMS reference at 0.00ppm. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet.

Table 2: Infrared spectra^a data for [Zn(bpy)L$_2$] complexes (KBr disk).

Complex	ν(N=C=N) /cm^{-1}
[Zn(bpy)(apcyd)$_2$]	2120
[Zn(bpy)(4-Mepcyd)$_2$]	2100
[Zn(bpy)(3,5- Me$_2$pcyd)$_2$]	2150
[Zn(bpy)(4- MeOpcyd)$_2$]	2175
[Zn(bpy)(3,5- MeO$_2$pcyd)$_2$]	2134
[Zn(bpy)(pcyd)$_2$]	2175
[Zn(bpy)(3-Clpcyd)$_2$]	2135
[Zn(bpy)(2,3-Cl$_2$ pcyd)$_2$]	2135
[Zn(bpy)(4-Brpcyd)$_2$]	2180
[Zn(bpy)(l-ncyd)$_2$]	2125

^{a} Strong absorption.

Table 3: Electronic spectroscopy data for [Zn(bpy)L$_2$] complexes in DMF.

Complex	MLCT(λ_{max}) /nm	Log(ε)
[Zn(bpy)(apcyd)$_2$]	491	3.790
[Zn(bpy)(4-Mepcyd)$_2$]	337	3.255
[Zn(bpy)(3,5- Me$_2$pcyd)$_2$]	455	3.602
[Zn(bpy)(4-MeOpcyd)$_2$]	462	3.845
[Zn(bpy)(3,5- MeO$_2$pcyd)$_2$]	340	3.240
[Zn(bpy)(pcyd)$_2$]	459	3.740
[Zn(bpy)(3-Clpcyd)$_2$]	413	3.090
[Zn(bpy)(2,3-Cl$_2$pcyd)$_2$]	386	3.146
[Zn(bpy)(4-Brpcyd)$_2$]	458	3.653
[Zn(bpy)(l-ncyd)$_2$]	475	3.699

A small positive shift in υ(N=C=N) is observed, as the electron-withdrawing ability of the substituents on the phenyl ring increased.

Quantitative electronic spectral data for the both mono and dinuclear Zn(II) complexes were taken in dimethylformamide. The data and spectroscopic assignments are assembled in (table 3). The absorption bands seen in the UV region are assigned to ligand-centered ($\pi \rightarrow \pi^*$) transitions [34,35]. In contrast to other transition metal phenylcayanamide complexes, for the Zn(II) complexes with d^{10} electronic configuration, both t_{2g} and e_g are full, therefore, it is only expected the MLCT band and not a ligand field transition. So the intense band at visible region is assigned to metal to ligand charge-transfer (MLCT) that are associated with Zn(II)-pyridyl chromophores. The reason for this case is the solvent dependence of charge transfer energy on solvent polarity which is a well-known phenomenon [34,35].

For the mono and dinuclear Zn(II) complexes, changing the solvent from methanol to DMSO shows an increase in solvent polarity and causes the low-energy MLCT bands to shift to higher energy. A representative spectrum of the mononuclear complex, [Zn(bpy)(apcyd)$_2$] in three solvents, CH$_3$OH, DMF and DMSO is shown in (Fig. 1). This behavior is consistent with ground-state stabilization of the complexes's permanent dipoles by the solvent. This metal to ligand charge transfer transition arises from the (t$_{2g}^6$) on the Zn(II) to the empty π^* orbitals on the phenylcyanamide ligands (t$_{2g}^6 \rightarrow \pi^*$).

In comparison to azodi(phenylcynamide) ruthenium(II) analogous complexes [16], another electronic transition from cyanamide moiety (-N=C=N) to the azo group (-N=N-) is expected but in azodic(phenylcynamide) Zn(II) complexes, this transition is covered by intense MLCT band. However, this transition is seen in free neutral bridging ligand (H$_2$adicyd).

The electrochemical properties of mononuclear complexes have been investigated by cyclic voltammetry. The electrochemical data of these complexes in dimethylformamide are summarized in (table 4) and representative voltammogram of [Zn(bpy)(4-Brpcyd)$_2$] appears in (Fig. 2). The cyclic voltammograms of the mononuclear complexes display two irreversible oxidation waves at the positive potentials and one quasi-reversible reduction couple at the negative potentials.

[Zn(bpy)(pcyd)$_2$] $\leftrightarrows$ [Zn(bpy)(pcyd)(pcyd^0)]$^+$ + ē

[Zn(bpy)(pcyd)(pcyd^0)]$^+$ $\leftrightarrows$ [Zn(bpy)(pcyd^0)(pcyd^0)]$^{2+}$ + ē
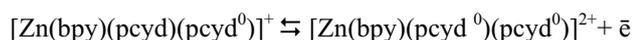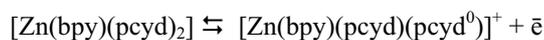
In view of the redox inactive nature of Zn(II) [36,37] and comparison with other transition metal phenylcyanamide analogous as well as the observation that the oxidation waves appear to vary with the nature of the phenylcyanamide ligands, the two oxidation waves are tentatively assigned to the two phenylcyanamide ligand-centered oxidation. The quasi-reversible reduction wave at negative potentials is assigned to the reduction of the bipyridine-centered reduction processes by analogy to M(bpy)$_n$ [4].

[Zn(bpy)(pcyd)$_2$] + ē $\leftrightarrows$ [Zn(bpy^{0-})(pcyd)$_2$]$^-$
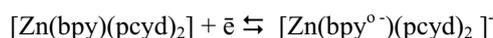
Cyclic voltammetry of the free azodiphenylcyanamide dianion (adicyd^{2-}) showed two redox couples corresponding to adicyd$^{-1/2-}$ adicyd$^{0/-1}$ [38]. In dinuclear Zn(II) complex,[{Zb(terpy)}$_2$(μ-adicyd)](PF$_6$)$_2$, two irreversible waves at positive potential are assigned to

Table 4: Electrochemical data for [Zn(bpy)L$_2$] complexes in DMF.

L	L$_{ox1}$(mV)[a]	L$_{ox2}$(mV)[a]	L$_{red}$(mV)[b]
acyd	1181	1939	-1272
4-Mepcyd	1168	1428	-1448
3,5-Me$_2$pcyd	1073	1658	-1463
4-MeOpcyd	640	1200	-1560
3,5-MeO$_2$pcyd	830	1498	-1442
Pcyd	1059	1434	-1540
3-Clpcyd	1057	1365	-1500
2,3-Cl$_2$pcyd	954	1579	-1475
4-Brpcyd	919	1409	-1478
1-ncyd	619	754	-1446

Data mV vs NHE (0.1 M TBAH DMF solution) at a scan rate of 100 mV/s. a) anodic wave only. b) bipyridine reduction couple.
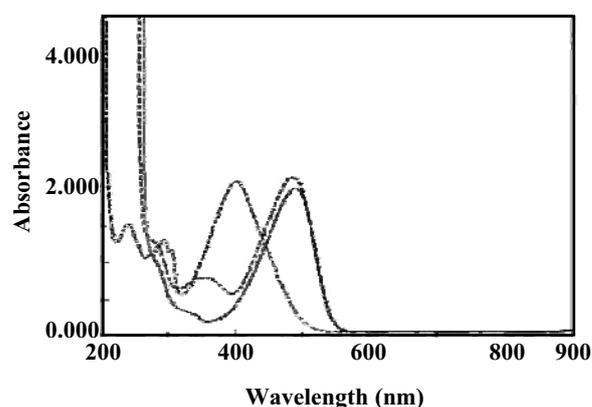

Fig. 1: The MLCT band of [Zn(bpy)(apcyd)$_2$], 2 × 10^{-4} M in (a) CH$_3$OH (——), (b) DMF (----) and (c) DMSO (_._ → _).
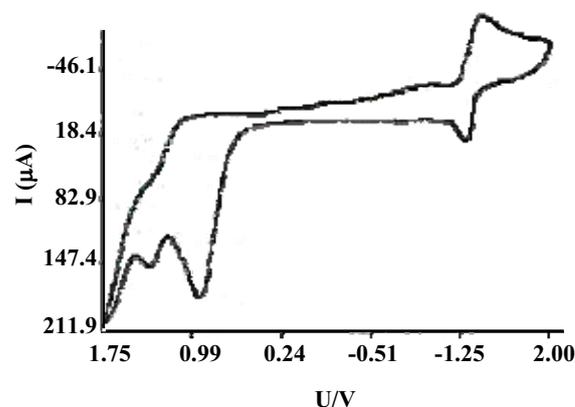
**Fig. 2: Voltammogram of [Zn(bpy)(4-Brpcyd)$_2$] in DMF at a scan rate of 100 mV/s; 0.1 M TBAH.**

the sequential oxidation of bridging ligang (adicyd) as shown in following reactions:

$$[\{Zn(terpy)\}_2(\mu\text{-adicyd})]^{2+} \leftrightarrows \{Zn(terpy)\}_2(\mu\text{-adicyd})]^{3+} + \bar{e}$$

$$[\{Zn(terpy)\}_2(\mu\text{-adicyd})]^{3+} \leftrightarrows \{Zn(terpy)\}_2(\mu\text{-adicyd})]^{4+} + \bar{e}$$
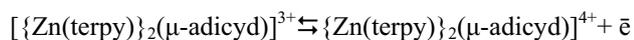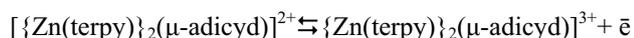
The two quasi-reversible reduction couples at negative potential are assigned to the sequential reductions of terpy ligands as shown in following reactions:
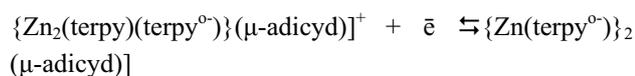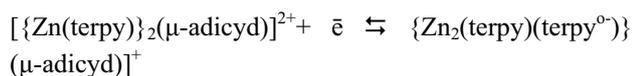
$$[\{Zn(terpy)\}_2(\mu\text{-adicyd})]^{2+} + \bar{e} \leftrightarrows \{Zn_2(terpy)(terpy^{o\text{-}})\}(\mu\text{-adicyd})]^{+}$$

$$\{Zn_2(terpy)(terpy^{o\text{-}})\}(\mu\text{-adicyd})]^{+} + \bar{e} \leftrightarrows \{Zn(terpy^{o\text{-}})\}_2(\mu\text{-adicyd})]$$

Acknowledgments

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