(Terpyridine)palladium(II) Complexes of Phenylcyanamide Ligands

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(Terpyridine)palladium(II) complexes of phenylcyanamide anion ligands have been prepared and characterized by UV-vis, IR, and ^{1}H-NMR spectroscopies. A crystal structure determination of the complex [Pd(terpy)(2,6-Cl_2-pcyd)][PF_6] has been performed. The overall geometry of the complex is approximately planar with a dihedral angle of 2.16(16)° between the best plane fit of the palladium coordination sphere and that for the phenyl ring of the phenylcyanamide ligand. Crystal structure data for the complex: $C_{22}H_{14}N_5Cl_2PF_6Pd$, monoclinic crystal system and space group $P2_1/n$, with $a = 8.185(5)$ Å, $b = 13.606(7)$ Å, $c = 21.163(5)$ Å, $\beta = 90.50(3)°$, $V = 2356.8(20)$ Å^{-3}, and $Z = 4$. The structure was refined by using 3233 Mo Kα reflections with $I > 2.5\sigma(I)$ to an R factor of 0.034. The UV-vis spectra of the complexes showed a broad band centered at approximately 400 nm which has been assigned to a $\pi_{nb} \rightarrow \sigma^*$ LMCT transition of the Pd(II)-NCN chromophore.

Introduction

The purposeful synthesis of novel solid-state materials requires a fundamental understanding of the molecular origins of macroscopic properties and the means by which molecular units can be assembled to express the desired property. One successful example has been the construction of molecular metals based on organic charge-transfer salts.[1] A characteristic feature in the crystal lattice of these materials is the orientation of conjugated planar organic molecules on top of one another to form "pancake" stack structures. Under the right conditions, π interactions between the molecules that make up the stack result in conductivity in the direction of the π-stack. A relatively recent development was the discovery of molecular metals based on copper and dicyanoquinonediimine (DCNQI) acceptor molecules.[2] These Cu(DCNQI)$_2$ molecular metals show evidence of being three-dimensional conductors in that they have conductivity not only in the direction of the π-stacks but also in the direction of the Cu-cyanamide links between the π-stacks.[3] The coordination of an organic acceptor molecule to a transition metal has additional importance to the design of novel molecular metals.

The electronic properties of a π-stack are largely dependent on the properties of its component planar molecules. However, if a planar molecule within a π-stack is bound to a transition metal, subtle variations in its molecular properties can be introduced by varying the nature of the π interaction between itself and the metal ion. Any variation in conductivity of the molecular metal can then be ascribed to these molecular perturbations, provided the π-stack structure remains unchanged.

There are two types of π interactions possible between a metal and an organic planar molecule: metal to ligand where the ligand functions as a π acceptor and ligand to metal where the ligand functions as a π donor. The extent of these π interactions can be significantly perturbed by the nature of the spectator ligands in the metal coordination sphere. For example, the oxidation couple of the Ru(II) ion is dramatically affected by the nature and number of π-acceptor ligands in its inner coordination sphere. In the electronic absorbance spectra of these complexes, this effect is paralleled by changes in the energies of the metal to ligand charge-transfer (MLCT) transitions.[4]

We hope to synthesize molecular metals based on the planar π donor 1,4-dicyanamidobenzene dianion (the two-electron reduction product of DCNQI). As a first step, this study describes the synthesis of mononuclear palladium(II) complexes of phenylcyanamide ligands. The overall planarity of these complexes is judged by a crystal structure of one of the complexes, and the existence of a Pd-NCN interaction is demonstrated by the observation of an LMCT band in the visible region.

Experimental Section

Reagents. All chemicals and solvents were reagent grade or better and were used as received. The phenylcyanamide ligands and their thallium salts have been previously prepared.[5] The chloro(2,2′,2″-terpyridine)palladium(II) chloride dihydrate starting complex was prepared by following a literature procedure.[6] To increase its solubility in organic solvents, the complex was converted to [Pd(terpy)Cl][PF_6] by metathesis with ammonium hexafluorophosphate.

The syntheses of the complexes are very similar, and so only one example preparation is given.

Preparation of [(2-Chlorophenyl)cyanamido](2,2′,2″-terpyridine)-palladium(II) Hexafluorophosphate, [Pd(terpy)(2-Cl-pcyd)][PF_6]. A yellow solution of 0.26 g (0.5 mmol) of [Pd(terpy)Cl][PF_6] in acetonitrile was brought to a boil. When [Tl][2-Cl-pcyd] (0.18 g, 0.5 mmol) was added, the solution turned immediately orange. After boiling for 40 min, the reaction mixture was filtered and the filtrate cooled to room temperature, precipitating orange crystalline product. The product was recrystallized by allowing ether to diffuse into an acetonitrile solution. The red-orange needles obtained were washed with ether and vacuum-dried. Yield: 0.23 g (70%). Anal. Calcd for $C_{22}H_{15}N_5ClPF_6Pd$: C, 41.53; H, 2.38; N, 11.01. Found: C, 41.18; H, 2.36; N, 10.95. ν(NCN) = 2142 cm^{-1}.

Physical Data. (Phenylcyanamido)(2,2′,2″-terpyridine)palladium(II) Hexafluorophosphate, [Pd(terpy)(pcyd)][PF_6]. Red cubes. Yield: 49%. Anal. Calcd for $C_{22}H_{16}N_5PF_6Pd$: C, 43.91; H, 2.66; N, 11.63. Found: C, 43.32; H, 2.67; N, 11.76. ν(NCN) = 2091 (s), 2145 (m) cm^{-1}.

[(2,3-Dichlorophenyl)cyanamido](2,2′,2″-terpyridine)palladium(II) Hexafluorophosphate, [Pd(terpy)(2,3-Cl_2pcyd)][PF_6]. Red-orange needles. Yield: 63%. Anal. Calcd for $C_{22}H_{14}N_5Cl_2PF_6Pd$: C, 39.39; H, 2.11; N, 10.44. Found: C, 38.92; H, 2.15; N, 10.34. ν(NCN) = 2178 cm^{-1}.

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[(2,6-Dichlorophenyl)cyanamido](2,2′,2″-terpyridine)palladium(II) Hexafluorophosphate, [Pd(terpy)(2,6-Cl$_2$pcyd)][PF$_6$]. Red-orange cubes and rectangular needles. Anal. Calcd for C$_{22}$H$_{14}$N$_5$Cl$_2$PF$_6$Pd: C, 39.39; H, 2.11; N, 10.44. Found: C, 39.54; H, 2.14; N, 10.41. ν(NCN) = 2116 (m), 2156 (s) cm^{-1}.

[(2,4,6-Trichlorophenyl)cyanamido](2,2′,2″-terpyridine)palladium(II) Hexafluorophosphate, [Pd(terpy)(2,4,6-Cl$_3$pcyd)][PF$_6$]. Yellow hairlike crystalline form. Yield: 64%. Anal. Calcd for C$_{22}$H$_{13}$N$_5$Cl$_3$PF$_6$Pd: C, 37.47; H, 1.86; N, 9.93. Found: C, 36.69; H, 2.00; N, 9.74. ν(NCN) = 2184 cm^{-1}.

[(2,3,4,5-Tetrachlorophenyl)cyanamido](2,2′,2″-terpyridine)palladium(II) Hexafluorophosphate, [Pd(terpy)(2,3,4,5-Cl$_4$pcyd)][PF$_6$]. Orange needles. Yield: 59%. Anal. Calcd for C$_{22}$H$_{12}$N$_5$Cl$_4$PF$_6$Pd: C, 35.72; H, 1.64; N, 9.47. Found: C, 35.75; H, 1.65; N, 9.49. ν(NCN) = 2169 cm^{-1}.

[(Pentachlorophenyl)cyanamido](2,2′,2″-terpyridine)palladium(II) Hexafluorophosphate, [Pd(terpy)(Cl$_5$pcyd)][PF$_6$]. Orange plates. Yield: 48%. Anal. Calcd for C$_{22}$H$_{11}$N$_5$Cl$_5$PF$_6$Pd: C, 34.13; H, 1.43; N, 9.05. Found: C, 34.37; H, 1.55; N, 9.08. ν(NCN) = 2180 cm^{-1}.

Physical Measurements. Infrared spectra (KBr disks) were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer, electronic absorbance spectra were recorded with a Cary 5 spectrophotometer, and ^{1}H-NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer at ambient temperature. Chemical shifts were referenced to tetramethylsilane (0.00 ppm). The instrumentation used to perform cyclic voltammetry has been described previously.[7] Ferrocene ($E°$ = 400 mV vs NHE) was used as an internal reference[8] at a constant electrochemical cell temperature of 25 °C. Acetonitrile for electrochemistry was first dried with activated alumina[9] and then distilled under nitrogen. Dimethylformamide (DMF, glass distilled, Anachemia) was used as received. Elemental analyses were performed by Canadian Microanalytical Services Ltd.

Crystal Structure Determination. Red-orange cubes of the complex [Pd(terpy)(2,6-Cl$_2$pcyd)][PF$_6$] were grown by ether diffusion into an acetonitrile solution of the complex. All the measurements were made on a Rigaku diffractometer with Mo Kα radiation, at a temperature of −90 °C. No decay of the crystal was observed. The standards were measured after every 150 reflections. The data were corrected for Lorentz and polarization effects,[10] and no absorption correction was made.

The structure was solved by direct methods. All the atoms were refined anisotropically except hydrogen. The hydrogen atoms were found by a difference Fourier map. The final cycle of full-matrix least-squares refinement was based on 2546 observed reflections ($I > 2.5\sigma(I)$) and 335 variable parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final difference Fourier map were found to be 0.410 and −0.750 e Å^{-3}, respectively. All the calculations were performed with the NRCVAX crystallographic software package.[11]

Results and Discussion

The palladium complexes of phenylcyanamide ligands were prepared by reacting [Pd(terpy)Cl][PF$_6$] with the thallium salt of a phenylcyanamide anion ligand. This methathesis reaction precipitates TlCl, which can be readily separated from the reaction solution. Recrystallization of the complexes yields orange to red crystals in good yield and purity, as judged by their elemental analyses and ^{1}H-NMR spectra. The numbering scheme of the terpyridine protons for the ^{1}H-NMR data in the supplementary material has been published.[12]

The ORTEP diagram of the complex [Pd(terpy)(2,6-Cl$_2$pcyd)][PF$_6$] is shown in Figure 1. Crystal structure data (Table I), atomic parameters (Table II), and selected bond lengths and angles (Table III) are given. The coordination sphere about Pd(II) has a distorted square planar geometry (Table III), and the overall geometry of the complex cation is also approximately planar. For example, the dihedral angle between the best plane equation for the palladium coordination sphere and the phenyl ring of the cyanamide ligand (planes A and B, respectively, in Table III) is only 2.16(16)°. This is in contrast to the structure of [Ni(dip)(2-Cl-pcyd)], where dip is the tridentate ligand 1,3-bis(2′-pyridylimino)isoindolinato.[13] In this complex, not only is the distortion of the coordination sphere from square planarity greater but the phenyl ring is perpendicular to the best plane of the Ni(II) coordination sphere and the approximately planar dip ligand. The fourth coordination site on Ni(II) is sterically hindered by the dip ligand, and this forces the cyanamide group out of the same plane as the dip ligand and twists the phenylcyanamide ligand down and away. For the Pd(terpy) complexes, there is far greater space available in the fourth coordination site and the extra space is needed because of the small Pd–NCN bond angle (137.9(4)°).

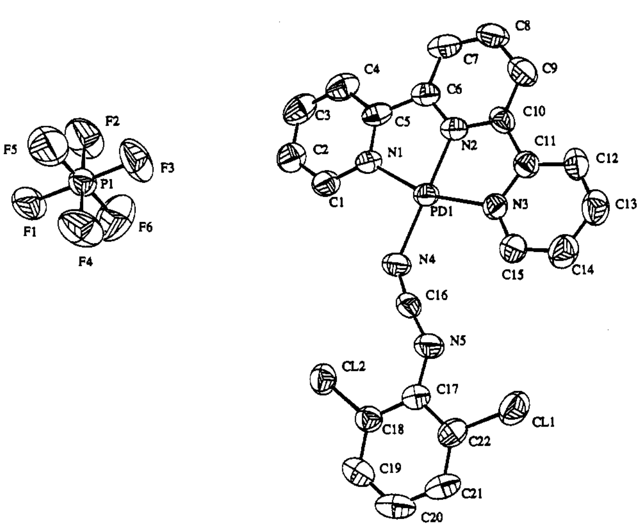

Figure 1. ORTEP diagram of the complex [Pd(terpy)(2,6-Cl$_2$pcyd)][PF$_6$].

Table I Crystal Data for [Pd(terpy)(2,6-Cl$_2$pcyd)][PF$_6$]

formula	PdPCl$_2$F$_6$N$_5$C$_{22}$H$_{14}$
mol wt	670.65
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	8.185(5)
b, Å	13.606(7)
c, Å	21.163(5)
β, deg	90.50(3)
V, Å^3	2356.8(20)
Z	4
D_c, g/cm^3	1.890
cryst dimens, mm^3	0.20 × 0.20 × 0.20
radiation (λ, Å)	Mo Kα (0.709 30)
μ (mm^{-1})	1.06
no. of reflns measd	3509
no. of unique reflns	3233
no. of sig reflns ($I > 2.5\sigma(I)$)	2546
R^a	0.034
$R_w{}^a$	0.041
goodness-of-fit ratio	3.15

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

The phenylcyanamide anion ligand is itself planar,[14] and this is suggested to arise from π coupling between cyanamide and phenyl ring groups. For a significant number of phenylcyanamide transition metal complexes, crystal structures have shown the retention of planarity upon cyanamide ligand coordination.[5b,7,13,15] The palladium complex of this study is no different, and this is important because it is the first instance of a coordinated

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Table II. Atomic Parameters and B_{iso} for $[Pd(terpy)(2,6\text{-}Cl_2pcyd)][PF_6]$[a]

	x	y	z	B_{iso}[b]
Pd1	0.18408(5)	0.00064(3)	0.960592(17)	3.578(17)
Cl1	0.55885(23)	−0.22536(11)	1.17246(8)	5.91(9)
Cl2	0.51020(19)	0.17057(10)	1.16622(8)	4.97(7)
P1	0.71274(19)	0.56392(11)	0.88872(8)	4.27(7)
F1	0.7544(5)	0.67075(23)	0.91381(17)	6.66(19)
F2	0.5581(5)	0.6037(3)	0.85352(22)	8.56(24)
F3	0.6746(5)	0.4573(3)	0.86244(21)	8.09(23)
F4	0.8691(5)	0.5237(3)	0.92416(21)	8.55(23)
F5	0.8201(6)	0.5845(3)	0.82880(19)	9.5(3)
F6	0.6106(6)	0.5425(3)	0.94909(22)	10.0(3)
N1	0.1083(5)	0.1347(3)	0.93050(19)	3.69(19)
N2	0.0559(5)	−0.0392(3)	0.88791(19)	3.74(20)
N3	0.2227(5)	−0.1473(3)	0.96573(19)	3.79(5)
N4	0.3098(6)	0.0451(3)	1.03794(20)	4.68(22)
N5	0.4500(7)	−0.0412(3)	1.12008(23)	6.0(3)
C1	0.1433(7)	0.2215(4)	0.9580(3)	4.4(3)
C2	0.0835(8)	0.3082(4)	0.9328(3)	5.3(3)
C3	−0.0120(8)	0.3047(4)	0.8785(3)	6.0(3)
C4	−0.0476(8)	0.2158(5)	0.8509(3)	5.5(3)
C5	0.0133(6)	0.1306(4)	0.87797(24)	4.1(3)
C6	−0.0167(7)	0.0308(4)	0.85313(24)	4.1(3)
C7	−0.1100(7)	0.0033(5)	0.8011(3)	5.3(3)
C8	−0.1251(8)	−0.0956(5)	0.7874(3)	5.6(3)
C9	−0.0522(7)	−0.1660(4)	0.8243(3)	5.3(3)
C10	0.0434(6)	−0.1366(4)	0.87575(24)	3.94(25)
C11	0.1374(6)	−0.1981(4)	0.92049(25)	3.96(25)
C12	0.1485(7)	−0.2990(4)	0.9155(3)	4.7(3)
C13	0.2485(8)	−0.3491(4)	0.9566(3)	5.5(3)
C14	0.3351(8)	−0.2977(4)	1.0023(3)	5.5(3)
C15	0.3194(7)	−0.1969(4)	1.0049(3)	4.5(3)
C16	0.3835(7)	0.0095(4)	1.07916(24)	4.03(24)
C17	0.5448(6)	−0.0280(4)	1.17236(24)	3.71(23)
C18	0.5841(6)	0.0637(4)	1.20016(25)	3.9(3)
C19	0.6827(7)	0.0700(4)	1.2534(3)	5.0(3)
C20	0.7452(8)	−0.0151(5)	1.2809(3)	6.3(4)
C21	0.7083(7)	−0.1049(4)	1.2554(3)	5.2(3)
C22	0.6085(7)	−0.1105(4)	1.2029(3)	4.2(3)

[a] Estimated standard deviations are given in parentheses. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid, $Å^2$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Pd(terpy)(2,6\text{-}Cl_2pcyd)][PF_6]$[a]

Bond Lengths			
Pd–N1	2.027(4)	Pd–N2	1.932(4)
Pd–N3	2.040(4)	Pd–N4	2.018(4)
N4–C16	1.162(7)	N5–C16	1.231(7)
N5–C17	1.358(7)		
Bond Angles			
N1–Pd–N3	162.01(16)	N1–Pd–N2	80.79(17)
N1–Pd–N4	97.92(17)	N2–Pd–N3	81.27(17)
N2–Pd–N4	177.63(18)	N3–Pd–N4	100.06(18)
Pd–N4–C16	137.9(4)	N4–C16–N5	170.3(6)
Distances to the Best Plane (A) Described by the Coordination Sphere			
Pd	−0.0002(5)	N1	−0.017(5)
N2	0.034(5)	N3	−0.018(5)
N4	0.033(6)	C16	0.078(7)
N5	0.186(8)		
Distances to the Best Plane (B) Described by the Cyanamide Phenyl Ring			
N4	−0.172(13)	N5	−0.017(9)
C16	−0.122(11)		

[a] The atom numbers are shown in Figure 1, and estimated standard deviations are given in parentheses.

phenylcyanamide ligand in which both ortho positions relative to the cyanamide group are substituted. That planarity is retained despite an increase in steric crowding upon coordination of phenylcyanamide ligands is a basic assumption of the theoretical analysis of antiferromagnetic superexchange found in dinuclear Ru(III) complexes which incorporate dicyanamidobenzene dianion bridging ligands.[7]

To a significant extent, the bond angle between palladium and the cyanamide group is determined by the resonance

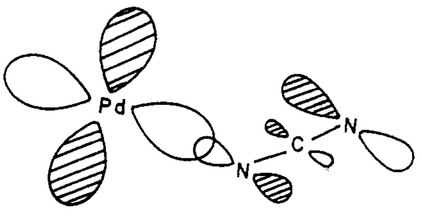
$$\underset{\textbf{A}}{Ph{-}N^{-}{-}C{\equiv}N} \longleftrightarrow \underset{\textbf{B}}{Ph{-}N{=}C{=}N^{-}}$$

and the bonding properties of the metal ion.[15a] The coordination of the cyanamide group by its terminal nitrogen is expected to polarize electron density and give preference to resonance form **B**. Nevertheless, the NCN bond angle in the Pd complex was found to be 170.3(6)°, and this indicates a small contribution from resonance form A. Ru(III) is a strong π acceptor and prefers a linear coordination mode in order to optimize its π interaction with the cyanamide's π nonbonding electrons.[5b] Pd(II) has little in the way of π-acceptor properties, and so the bent Pd–NCN bond is largely determined by the σ-bonding interaction of a cyanamide nonbonding electron pair in an sp^2 hybrid orbital.

The unit cell shown in Figure 2 shows evidence of dimerization of the Pd complex in the solid state. The distance between Pd and the amide nitrogen from the neighboring complex is 3.265 Å, which is significantly closer than a van der Waals contact. This same type of interaction has also been observed in the crystal structures of [Pd(terpy)Cl][Cl][16] and $[Pt(terpy)(HET)][NO_3]$, where HET is 2-hydroxyethanethiolato.[17]

The UV-vis spectrum of $[Pd(terpy)(2,6\text{-}Cl_2pcyd)][PF_6]$ is given in Figure 3, and spectral data for all the complexes have been compiled in Table IV. The bands that appear below 300 nm are assigned to $\pi \rightarrow \pi^*$ transitions of terpy and phenylcyanamide ligands. The bands between 320 and 380 are similar to those found for $[Pd(terpy)L]^{n+}$ (where L = imidazole, histidine, and chloride), and these have been assigned previously to metal to ligand charge-transfer (MLCT) transitions.[18] An extra absorption feature is seen centered at approximately 400 nm in the spectra of the palladium phenylcyanamide complexes that is not seen in the spectrum of $[Pd(terpy)(Cl)]^+$ and is assigned to a ligand to metal charge-transfer (LMCT) transition. This absorption band is unlikely to be a d–d transition, since for PdN_4 systems, d–d transitions occur at wavelengths smaller than 400 nm and with lower intensity.[19] In a previous study, $[Cu(bpy)_2(pcyd)]^+$ complexes were shown to possess cyanamide to Cu(II) $\pi \rightarrow \sigma^*$ LMCT transitions,[15a] and the same assignment is given to the palladium phenylcyanamide complexes of this study.

These $\pi \rightarrow \sigma^*$ transitions will be observed only when there is significant mixing of the cyanamide π nonbonding electron pairs with the σ^* $d_{x^2-y^2}$ orbital of Pd(II). Extended Huckel calculations[20] of the protonated resonance form B show that the phenylcyanamide ligand has two nondegenerate π_{nb} orbitals; the HOMO is orthogonal to $d_{x^2-y^2}$, and the SHOMO is in the same plane. The bending of the Pd–NCN bond allows for mixing of the oribtals in the same plane:



The 2p orbital contributions of the cyanamide group are indicated where lobe size is drawn in proportion to the relative contribution of that atomic orbital to the π_{nb} SHOMO. Minor atomic orbital

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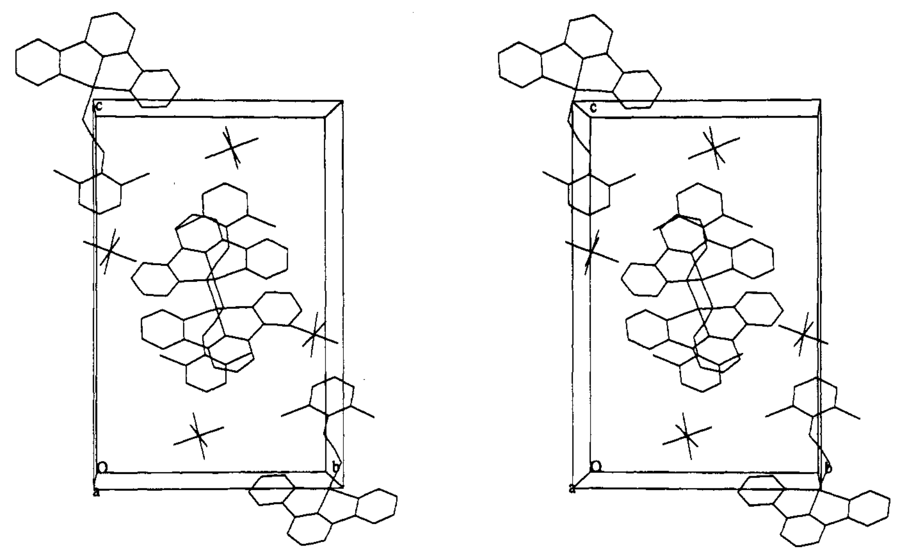

Figure 2. Crystal packing of the unit cells from the crystal structure of $[Pd(terpy)(2,6\text{-}Cl_2pcyd)][PF_6]$.

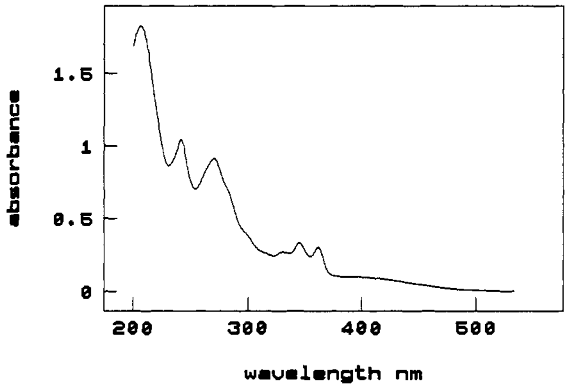

Figure 3. UV–vis electronic absorption spectrum of $[Pd(terpy)(2,6\text{-}Cl_2pcyd)][PF_6]$, 2.9×10^{-5} M in acetonitrile.

contributions of the cyanamide group and all of those of the phenyl ring are omitted for clarity.

The intensity of this LMCT transition is therefore expected to be strongly dependent upon the overlap of cyanamide and Pd(II) orbitals[21] and may be the explanation for the anomalously small LMCT intensity found for $[Pd(terpy)(pcyd)]^+$ compared with that for the other complexes in Table IV. A crystal structure determination of the complex $[Pd(terpy)(pcyd)][PF_6]$ has been performed.[22] This crystal structure was not of high quality but nevertheless showed many of the same general features as the crystal structure of this study. However, the Pd–NCN bond angle (146.4(12)°) was larger, and on the basis of the orbital interaction shown above, this would significantly reduce the overlap.

Table IV. UV–Vis Absorption Data for $[Pd(terpy)L][PF_6]$ Complexes[a]

L	$\pi \rightarrow \pi^*$ (terpy)	$\pi \rightarrow \pi^*$ (pcyd)	MLCT	LMCT[b]
Cl	205 (57 500)		328 (8670)	
	246 (25 800)		345 (9050)	
	279 (23 900)		362 (8180)	
pcyd[c]	206 (43 300)		331 (7170)	417 (1820)
			345 (9640)	
			361 (9210)	
2-Cl-pcyd	206 (59 200)	268 (30 610)	330 (8740)	403 (3770)
	243 (36 600)		345 (10 700)	
			362 (9850)	
2,3-Cl_2pcyd	206 (59 000)	271 (36 500)	331 (9100)	400 (4130)
	243 (35 000)		345 (11 200)	
			362 (10 400)	
2,6-Cl_2pcyd	207 (62 900)	270 (31 040)	331 (9050)	398 (3540)
	242 (35 200)		345 (11 500)	
			362 (10 400)	
2,4,6-Cl_3pcyd	242 (35 100)	275 (42 600)	346 (12 000)	401 (4210)
			362 (11 100)	
2,3,4,5-Cl_4pcyd	232 (40 300)	278 (43 400)	329 (11 200)	392 (4370)
	242 (38 300)		346 (12 400)	
			362 (11 700)	
Cl_5pcyd	205 (62 600)	279 (36 100)	330 (11 500)	390 (4040)
	230 (46 500)		345 (12 200)	
			362 (11 000)	

[a] Acetonitrile solutions of the complexes at concentrations of 3.00×10^{-5} M. Extinction coefficients ($M^{-1}\ cm^{-1}$) are given in parentheses. [b] Broad bands. [c] The pcyd $\pi \rightarrow \pi^*$ absorptions are obscured by the terpy absorptions.

In general, the LMCT band intensities of the palladium complexes (Table IV) have values around 4000 $M^{-1}\ cm^{-1}$, and this is larger than expected for a formally forbidden transition. For example, LMCT bands of the copper phenylcyanamide complexes[15a] had extinction coefficients at band maxima that varied from 1280 to 1720 $M^{-1}\ cm^{-1}$. This difference can be almost entirely explained by recognizing that the LMCT transitions of the palladium complexes are doubly degenerate whereas the LMCT transitions of the copper complexes are singly degenerate.[21]

Conclusion

The main goal of this research was to construct a planar complex which incorporated a phenylcyanamide ligand, and this has been accomplished. The observation of cyanamide to palladium LMCT transitions in the UV–vis absorption spectra of the complexes results from an interaction between a π_{nb} MO of the cyanamide ligand and the $d_{x^2-y^2}$ orbital of Pd(II). The nature and extent of this interaction can be "tuned" depending on the properties and relative orientation of the orbitals concerned.

The next step will be to construct a novel molecular metal.

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(21) The oscillator strength $f = 1.085 \times 10^{11} G\nu k^2 S_{ad}^2 R^2$, where S_{ad} is the overlap between donor and acceptor wavefunctions and G is the degeneracy of the transition: Saleh, A. A.; Crutchley, R. J. *Inorg. Chem.* **1990**, *29*, 2132.

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The targeted molecular unit building block will be a planar dinuclear palladium complex in which the palladium ions are bridged by a dicyanamidobenzene dianion derivative. The proper choice of ligands and counterions may result in the assembly of these units in the crystal lattice in such a way as to cause the formation of π-stacks.

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Supplementary Material Available: Full listings of crystal structure data and experimental details, a structural diagram, and tables of atomic parameters, anisotropic thermal parameters, bond lengths, bond angles, and distances to least-squares planes for [Pd(terpy)(2,6-Cl_2pcyd)][PF_6] and a table of ^{1}H-NMR data for the complexes (14 pages). Ordering information is given on any current masthead page.