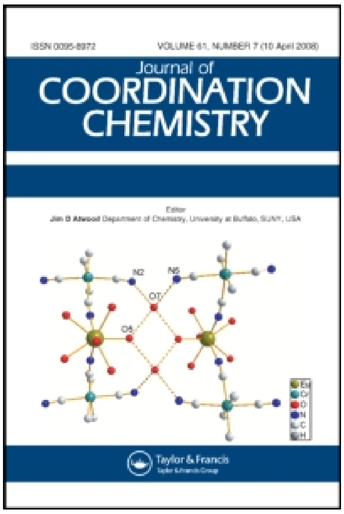

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Synthesis, structure and spectroscopic study of Cu(II) polypyridine complexes with phenylcyanamide derivative ligands

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Synthesis, structure and spectroscopic study of Cu(II) polypyridine complexes with phenylcyanamide derivative ligands

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Several new mononuclear copper(II) complexes, $[Cu(phen)_2L]PF_6$, where phen = 1,10-phenanthroline and L = monoanions of phenylcyanamide (pcyd), 2,5-dichlorophenylcyanamide (2,5-Cl_2pcyd), 2-dichlorophenylcyanamide (2-Clpcyd) and 4-methylphenylcyanamide (4-Mepcyd), have been prepared and characterized by elemental analysis, UV–Vis, IR and ^{1}H NMR spectroscopies and cyclic voltammetry. $[Cu(phen)_2(2,5\text{-}Cl_2pcyd)]PF_6$ crystallized with a molecule of acetone with empirical formula of $C_{31}H_{20}N_6OF_6Cl_2PCu$ in a triclinic crystal system and space group $P\bar{1}$ with $a = 9.2086(6)$ Å, $b = 13.3117(9)$ Å, $c = 15.5313(10)$ Å, $\alpha = 107.8210(10)^\circ$, $\beta = 104.6180(10)^\circ$, $\gamma = 104.1670(10)^\circ$, $V = 1643.21(19)$ Å^3 and $Z = 2$. The structure was refined using 7555 Mo-Kα reflections with $I > 2\sigma(I)$ and $R_1 = 0.0276$ and $Rw = 0.0692$. The results are consistent with a mostly σ bonding interaction between Cu(II) and cyanamide anion. The LMCT band intensity and electrochemical potentials are compared with ruthenium phenylcyanamide analogues.

Keywords: Mononuclear; Copper(II) complexes; Phenylcyanamide ligand; Cyclic voltammetry

1. Introduction

Coordination chemistry of phenylcyanamide has been the subject of a recent review [1]. Interest in cyanamide ligands arises from the discovery by Hünig and co-workers [2] of a radical anion copper salt of *N*,*N′*-dicyano-p-benzo-2,5-dimethylquinone diimine with increasing conductivity as the temperature is reduced (high value $5 \times 10^5\,S\,cm^{-1}$ at 3.5 K). Since the discovery of this π-electron/metal system, further research has shown that both the nature of the cation and that of the substituents on the ligand have important effects on the electronic properties of these new conductors [3]. Crutchley *et al.* [4] have investigated the coordination chemistry of phenylcyanamide ligands (which may be viewed as reduced forms of DCNQIs) in both neutral and anionic forms with copper.

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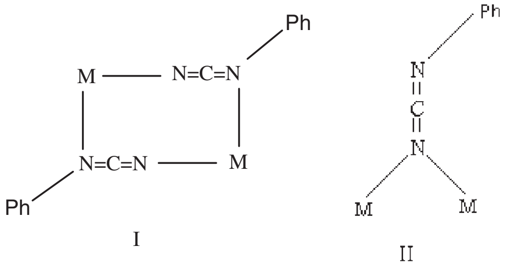

Scheme 1. (I) Neutral and (II) anionic phenylcyanamide as bridging ligands.

Phenylcyanamides are ambidentate ligands whether neutral or anionic, coordinating to a metal ion through either the nitrile or amine nitrogen (side-on). Side-on coordination is sterically crowded by phenyl and so terminal coordination to the nitrile is expected, particularly for electron-rich metal centers. Metal ions that behave as π-acceptors are expected to favor the anionic phenylcyanamide in order to take advantage of the ligand's π-donor properties. Neutral or anionic phenylcyanamide can also function as bridging ligands, although this has been observed only for anionic cyanamide (scheme 1). Both bridging modes I and II have been observed in copper(II) complexes [5].

In this study, a series of mononuclear complexes of $[Cu(phen)_2L]PF_6$, where L = phenylcyanamide derivative anionic ligand, have been synthesized and characterized by elemental analysis, IR, ^1H NMR and electronic absorption spectroscopies. A crystal structure determination of $[Cu(phen)_2(2,5\text{-}Cl_2pcyd)]PF_6$ has been performed and compared with the structures of other transition metal complexes of phenylcyanamides.

2. Experimental

2.1. *Materials and physical methods*

All chemicals and solvents were reagent grade or better and used without purification. The neutral phenylcyanamide derivatives and their thallium salts, (pcyd), ($2,5\text{-}Cl_2pcyd$), (2-Clpcyd), (4-Mepcyd) [6], and $[Cu(phen)_2Cl]PF_6$ [7], were synthesized as described in the literature.

Caution: Thallium salt is toxic.

Elemental analyses were performed by a Heraeus CHN-O-Rapid elemental analyzer. IR spectra were recorded as KBr pellets on a FT-IR JASCO 460 pulse spectrophotometer and UV-vis electronic spectra were taken on a JASCO 7850 spectrophotometer. The effective magnetic moments (μ_{eff}) of the complexes were measured by Evans method on a ^1H-NMR Bruker DRX-500 MHz, Avance spectrometer at ambient temperature. Cyclic voltammograms were recorded 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, tetrabutylammonium hexafluorophosphate (TBAH), was recrystallized twice from ethanol-water (1/1) and vacuum-dried at 110°C overnight. Acetonitrile was distilled over alumina and degassed under vacuum prior to use in cyclic voltammetry. The solutions were deoxygenated by bubbling with Ar for 15 min. Ferrocene ($E^\circ = 0.665$ V *versus* NHE) was used as internal reference [8].

2.2. *Synthesis*

The procedure to synthesize the four complexes is the same and, therefore, we only describe the synthesis of one complex as an example.

2.2.1. [Cu(phen)$_2$(4-Mepcyd)]PF$_6$•Me$_2$CO. To a solution of [Cu(phen)$_2$Cl]PF$_6$ (1 mmol) in 400 mL of acetonitrile was added (1 mmol) the thallium salt of anionic 4-methylphenylcyanamide, Tl(4-Mepcyd). The reaction mixture was stirred at room temperature for 24 h, during which the solution turned deep brown. The solution was cooled and filtered to remove a fine white TlCl precipitate. The filtrate evaporated to dryness and the crude product was dissolved in 20 mL of 1 : 2 CH_3CN/toluene, filtered, and purified by chromatography on a 40 cm × 2 cm diameter column containing 120 g grade III alumina (weakly acidic, 150 mesh). One band containing starting material was eluted with 1 : 2 CH_3CN/toluene. The second band was eluted with 1 : 1 CH_3CN/toluene and contained the target complex, [Cu(phen)$_2$(4-Mepcyd)]PF$_6$. The solution was evaporated to dryness. The brown product was recrystallized by slow ether diffusion into an acetone solution of the complex. Yield: 37%. Elemental analysis calcd for [Cu(phen)$_2$(4-Mepcyd)]PF$_6$ · Me$_2$CO ($CuC_{35}H_{29}N_6OPF_6$): C, 55.45; H, 3.85; N, 11.09. Found: C, 55.69; H, 3.91; N, 11.18%.

2.2.2. [Cu(phen)$_2$(pcyd)]PF$_6$•Me$_2$CO. Yield: 41%. Elemental analysis Calcd for Cu(phen)$_2$(pcyd)]PF$_6$ · Me$_2$CO ($CuC_{34}H_{27}N_6OPF_6$): C, 54.88; H, 3.65; N, 11.29. Found: C, 54.74; H, 3.59; N, 11.37%.

2.2.3. [Cu(phen)$_2$(2-Clpcyd)]PF$_6$•Me$_2$CO. Yield: 43%. Elemental analysis Calcd for Cu(phen)$_2$(2-Clpcyd)]PF$_6$ · Me$_2$CO ($CuC_{34}H_{26}N_6OPF_6Cl$): C, 52.45; H, 3.36; N, 10.79. Found: C, 52.33; H, 3.18; N, 10.83%.

2.2.4. [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$•Me$_2$CO. Yield: 44%. Elemental analysis calcd for [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ · Me$_2$CO ($CuC_{34}H_{25}N_6OPF_6Cl_2$): C, 50.23; H, 3.10; N, 10.34. Found: C, 50.29; H, 3.05; N, 10.49%.

2.3. *Single crystal X-ray diffraction*

Dark brown crystals of [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ · Me$_2$CO were grown by ether diffusion into an acetone solution of the complex. Single-crystal X-ray diffraction measurements were carried out on a Bruker Apex II using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 100(2) K. Unit cell parameters were determined by least-squares calculation with θ ranging from 1.47 to 29.00°. Intensities of 33107 reflections were measured using a Bruker Apex II CCD area detector giving 8656 unique reflections. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation. All hydrogen atoms were located from the difference Fourier syntheses and placed in geometrically calculated positions. All hydrogen atom positions were refined in isotropic approximation in riding model with $U_{\mathrm{iso}}(\mathrm{H})$ parameters equal to $1.5U_{\mathrm{eq}}(\mathrm{Ci})$ for methyl groups and $1.2U_{\mathrm{eq}}(\mathrm{Ci})$ for other carbon atoms, where $U(\mathrm{Ci})$ are the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded. All calculations were performed on an IBM PC/AT using SHELXTL version 5.1 software [9] giving a final $\mathrm{R1} = 0.0276$, $\mathrm{WR2} = 0.0692$ [for 7555 reflections with $I > 2\sigma(I)$]. The largest diffraction peak and hole on the final difference-Fourier map were 0.432 and $-0.374\,\mathrm{e\,Å^{-3}}$.

Further details of the structural analyses are given in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and structure refinement summary for $[\mathrm{Cu(phen)_2(2,5\text{-}Cl_2pcyd)}]\mathrm{PF_6 \cdot Me_2CO}$.

Empirical formula	$C_{34}H_{25}C_{l2}CuF_6N_6OP$
Formula weight	813.01
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.2086(6)
b	13.3117(9)
c	15.5313(10)
α	107.8210(10)
β	104.6180(10)
γ	104.1670(10)
V (Å^3)	1643.21(19)
Z	2
D_{Calcd} (g cm^{-3})	1.643
Crystal dimensions (mm^3)	0.20 × 0.13 × 0.10
λ (Mo-Kα) (Å)	0.71073
Number of collected reflections	33107
Independent reflections	8656 [$R_{\mathrm{(int)}} = 0.0256$]
Parameters	462
R factor[a]	0.0276
R_{w} factor[a]	0.0692
Goodness-of-fit ratio	1.019

Table 2. Selected bond lengths (Å) and angles (°) for $[\mathrm{Cu(phen)_2(2,5\text{-}Cl_2pcyd)}]$ $\mathrm{PF_6 \cdot Me_2CO}$.

Cu(1)–N(5)	1.9822(12)	Cu(1)–N(2)	2.0443(11)
Cu(1)–N(1)	2.0124(11)	Cu(1)–N(4)	2.1736(11)
Cu(1)–N(3)	2.0130(11)		
N(3)–Cu(1)–N(2)	97.33(4)	N(5)–Cu(1)–N(4)	104.50(5)
N(1)–Cu(1)–N(2)	81.68(4)	N(1)–Cu(1)–N(4)	96.26(4)
N(5)–Cu(1)–N(2)	149.43(5)	N(3)–Cu(1)–N(4)	79.82(4)
N(1)–Cu(1)–N(3)	175.56(4)	N(2)–Cu(1)–N(4)	106.01(4)
N(5)–Cu(1)–N(1)	93.25(5)	C(25)–N(5)–Cu(1)	140.27(11)
N(5)–Cu(1)–N(3)	89.78(4)	C(25)–N(6)–C(26)	121.69(12)

3. Results and discussion

All the complexes were prepared from metathesis of [Cu(phen)$_2$Cl]PF$_6$ with thallium salts of phenylcyanamide derivatives. Purification by column chromatography was required. The final product was recrystallized by ether diffusion in acetone solution giving a deep brown crystal.

The elemental analyses of the complexes are consistent with their formulation, as are the X-ray structure, spectroscopic and electrochemical characterizations.

The ORTEP drawing of [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ · Me$_2$CO with atom numbering is depicted in figure 1. The complex possesses five-coordinate environment with a CuN$_5$ chromophore. The geometry about the Cu(II) is distorted square-pyramidal, where two nitrogen atoms of the phen ligand, N(1) and N(2), the cyano nitrogen N(5) of the 2,5-Cl$_2$pcyd ligand and one nitrogen atom of the other phen ligand, N(3) are in basal positions. The N–Cu bond lengths Cu–N(1), Cu–N(2), Cu–N(3) and Cu–N(5) are 2.0124(11), 2.0443(11), 2.0130(11) and 1.9822(12) Å, respectively. The remaining nitrogen N(4) of phen is in the axial position with Cu–N(4) = 2.1736(11) Å, considerably larger than that of the basal pyridyl nitrogens. The average bond length between Cu(II) and each nitrogen [N(1), N(2), N(3) and N(5)] in the basal plane is 2.0130 Å. Due to different π-donor ability of Cl$^-$ and 2,5-Cl$_2$pcyd$^-$, the difference between the longest and shortest Cu–N bond distances for [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ (ΔCu–N = 0.191 Å) is considerably larger than ΔCu–N for [Cu(phen)$_2$Cl]PF$_6$ (0.156 Å) [7].

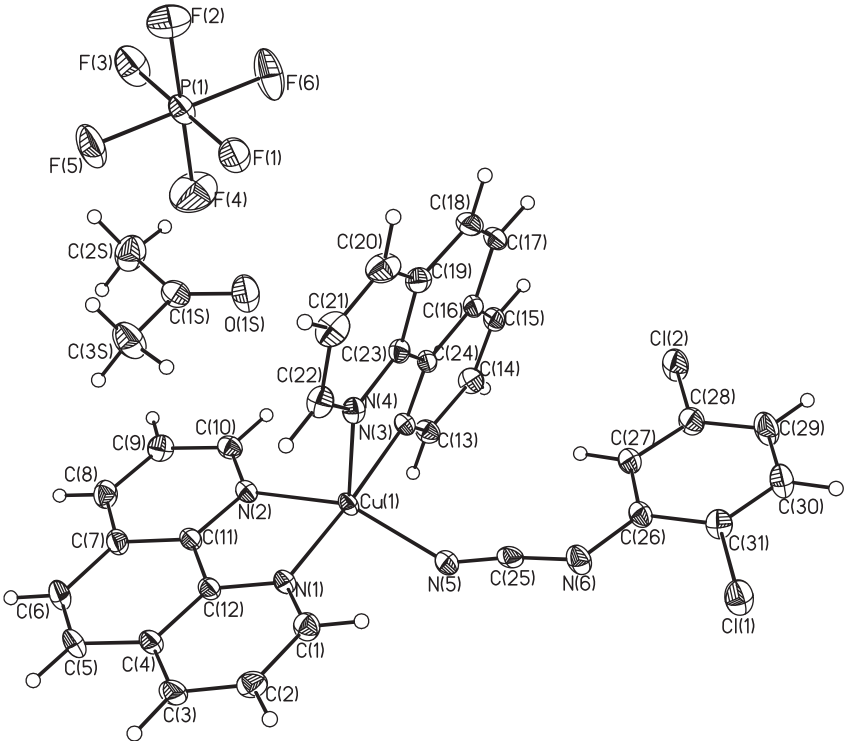

Figure 1. ORTEP structure of [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ · Me$_2$CO.

The Cu–N(phen) bond distances are consistent with values in previously reported structures [10–14]. The largest angle around the Cu(II) center [β: N(1)–Cu–N(3) $= 175.56(4)^\circ$] for [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ is considerably different from the second-largest one [α: N(2)–Cu–N(5) $= 149.43(5)^\circ$], implying that the geometry around Cu(II) is distorted square-pyramidal or distorted trigonal-bipyramidal. The angular structural index parameter, $\tau = (\beta - \alpha)/60$, distinguishes between trigonal-bipyramidal and square-pyramidal and is evaluated by the two largest angles ($\alpha < \beta$) in the five-coordinate geometry ($\tau = 0$ for an ideal square-pyramid and $\tau = 1$ for an ideal trigonal-bipyramid) [7, 15, 16]. The value of $\tau = 0.43$ for [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ indicates a distorted square-pyramidal geometry. The bond angle between cyanamide (N=C=N) and a metal ion is largely determined by the π-acceptor properties of the metal ion. Ru(III), a strong π-acceptor, has been shown to coordinate to 2,3-C1$_2$pcyd$^-$ with a bond angle of $171.4(10)^\circ$ [17]; (Cu–NCN) bond angle is $140.27(11)^\circ$ in [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$, bent due to far weaker π-acceptor property of Cu(II) compared to Ru(III). Free anionic phenylcyanamides are expected to be planar in the absence of steric effects [1, 18] due to strong coupling of the cyanamide with the phenyl ring π system. Crystal structures of Ru(II), Ru(III), Ni(II), Pd(II), Rh(III), Cu(II), Cu(I), Ag(I) and Co(III) phenylcyanamide complexes show that the phenylcyanamide is approximately planar and that the preferred coordination of the cyanamide is by its terminal nitrile nitrogen [1, 18–30]. This is likely due to the greater steric hindrance of coordination to the amide nitrogen. In contrast, a crystal structure of [{Cu(phen)(3-Clpcyd)(CH$_3$CO$_2$)}$_2$]$\cdot$2H$_2$O dimerization is achieved via the terminal nitrogen of the 3-chlorophenylcyanamide anion which asymmetrically bridges two coppers and hence is an example of a third type of coordination for phenylcyanamide. The shorter bond length to the cyanamide ligand [Cu–N $= 1.950(6)$ Å] is similar to the Cu–NCN distances found in [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$ [5]. A longer apical bond to the cyanamide ligand of the other half of the dimer [Cu–N(1′) $= 2.454(6)$ Å] in [{Cu(phen)(3-Clpcyd)(CH$_3$CO$_2$)}$_2$]$\cdot$2H$_2$O is considerably shorter than Cu(1)$\cdots$N(5) in mononuclear [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$. As shown in the dimeric fragment (figure 2) and the unit cell of [Cu(phen)$_2$(2,5-Cl$_2$pcyd)]PF$_6$$\cdot$Me$_2$CO (figure 3), dimerization occurs between two adjacent cationic complexes via nitrile nitrogens [N(5) and N(5A)].

Semicoordination takes place between each copper and neighboring nitrile nitrogen with Cu(1A)$\cdots$N(5) $= 3.377$ Å and Cu(1)$\cdots$N(5A) $= 3.377$ Å, significantly longer than normal coordination bonds, but shorter than the sum of non-bonded radii. The reason dimerization does not occur for this complex may be the greater steric crowding of the Cl atoms on the phenyl ring and the inductive effect of chlorine which makes the cyanamide less basic, and therefore, a poorer bridging ligand.

Infrared data for free phenylcyanamide (neutral and Tl salt) have been reported elsewhere [1]. The neutral ligands have a sharp and intense absorption at 2250 cm^{-1} assigned to υ_{NCN}. When a phenylcyanamide coordinates to a transition metal ion, υ_{NCN} shifts to higher energies [31]. Although Cu(II) should be able to coordinate to either nitrogen of the phenylcyanamide ligands, υ_{NCN} indicates bonding to only the nitrile nitrogen (table 3) [5, 32–34]. The presence of a strong absorption at 842 cm^{-1} in all the complexes, assigned to υ(P–F), demonstrates the existence of PF$_6^-$ as counterion [35].

Electronic spectral data of the bis(1,10-phenanthroline)copper(II) (phenylcyanamido) complexes, in acetonitrile, are found in table 3, and a representative spectrum of [Cu(phen)$_2$(2-Clpcyd)]PF$_6$ is shown in figure 4. The absorption bands in the UV region are assigned to ligand-centered transitions ($\pi \rightarrow \pi^*$) [30, 36]. The visible absorption

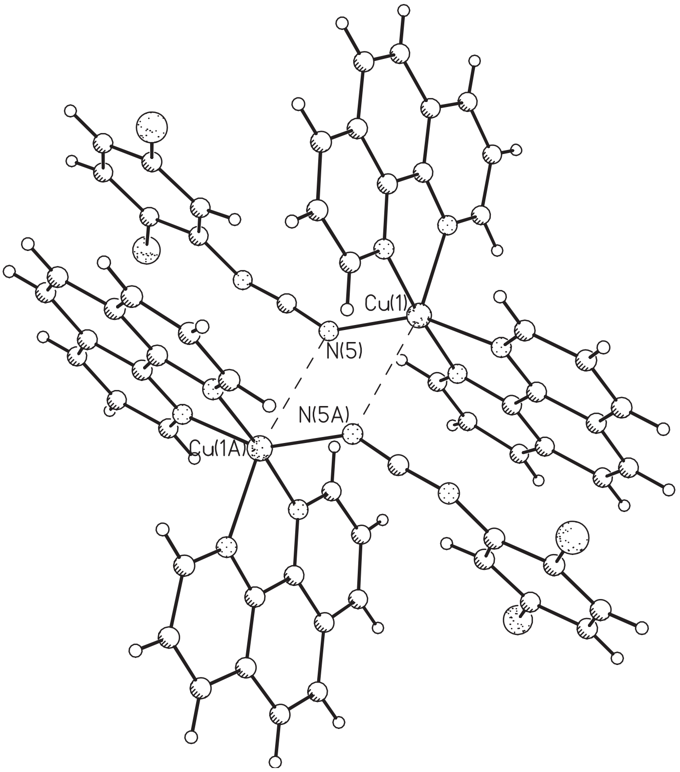

Figure 2. Dimeric fragment of $[Cu(phen)_2(2,5\text{-}Cl_2pcyd)]PF_6 \cdot Me_2CO$. The interaction $Cu(1) \cdots N(5)$ $(2-x, 1-y, 1-z)$ (3.377 Å) is significantly longer than a normal coordination bond, but shorter than the sum of non-bonded radii.

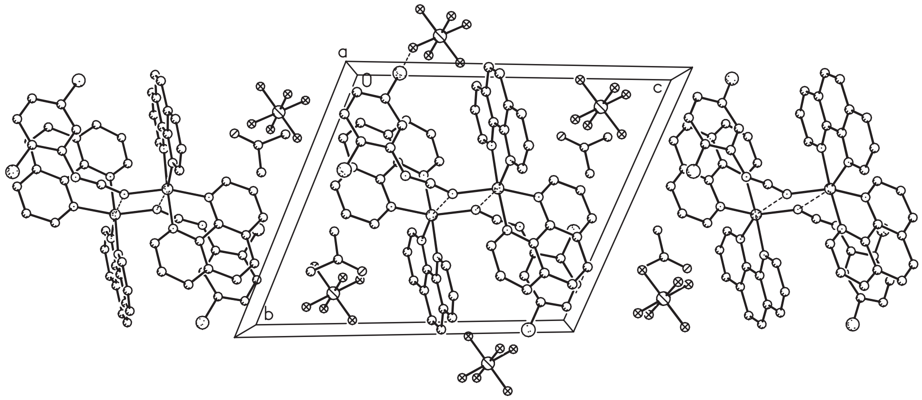

Figure 3. Unit cell of $[Cu(phen)_2(2,5\text{-}Cl_2pcyd)]PF_6 \cdot Me_2CO$ (columns along the *a* axis formed by dimeric dications are surrounded by anions and acetone molecules).

spectrum shows two major peaks, in contrast to the visible spectrum of $[Cu(phen)_2Cl]PF_6$, which has only one broad absorption band. The low energy band at wavelengths >700 nm is assigned as a predominantly d–d transition by analogy with $[Cu(phen)_2Cl]PF_6$. The high-energy and more intense band in the region <550 nm shifts

Table 3. Electronic[a], infrared[b] and magnetic data for $[Cu(phen)_2L]PF_6$.

L	$\pi \rightarrow \pi^*$	LMCT	d–d transition	$\nu(NCN)_{complex}$	$\nu(NCN)_{neutral}$	μ_{eff}
4-Me(pcyd)	207(4.38), 228(4.12), 280(3.98)	522(4.33)	731(3.8)	2085	2227	2.06
pcyd	211(4.51), 234(4.33), 270(4.29)	518(4.11)	729(3.64)	2161	2227	2.01
2-Cl(pcyd)	204(4.68), 229(4.62), 270(4.51)	513(4.13)	727(3.71)	2106	2243	1.95
$2,5Cl_2(pcyd)$	202(4.45), 241(4.29), 291(4.08)	497(4.29)	711(3.74)	2148	2250	1.88

[a] λ in nm ($\log \varepsilon$); [b] IR data (KBr) in cm^{-1}; [c] magnetic data in BM.

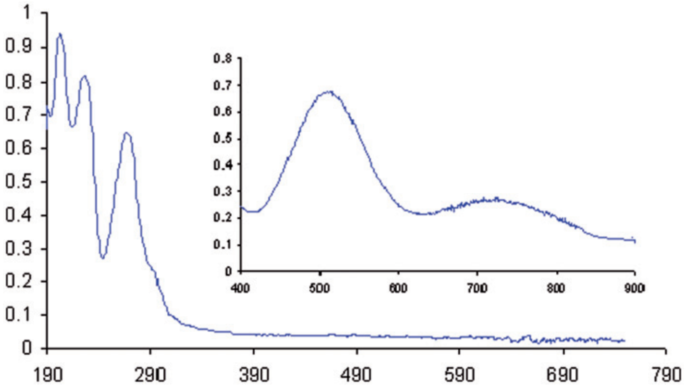

Figure 4. Absorption spectra of $[Cu(phen)_2(2\text{-}Cl_2pcyd)]PF_6$ in acetonitrile.

to higher energy as the electron-withdrawing ability of the substituents on the phenyl ring of the phenylcyanamide or donor number of the solvent is increased, consistent with LMCT assigned to cyanamide anion $p_\pi \rightarrow d_{x^2-y^2}$. Solvent dependence of charge-transfer energy on solvent polarity is a well-known phenomenon [37]. Pentaamineruthenium(III) complexes of phenylcyanamide showed two LMCT transitions from the Ru(III)-cyanamide chromophore, arising from two non-degenerate pairs of nonbonding electrons (π_nb) that are delocalized in the cyanamide [1, 6].

The effective magnetic moment (μ_{eff}) of the complexes was measured by the Evans method [38] (table 3). The magnitude of μ_{eff} is consistent with the magnetic moment for Cu(II) complexes (1.7–2.2 BM) [39].

Electrochemical data for the complexes are collected in table 4 and a representative voltammogarm of $[Cu(phen)_2(2,5\text{-}Cl_2pcyd)]PF_6$ is in figure 5. The electrochemical measurements were made in acetonitrile solutions of the complexes with 0.1 M TBAH as supporting electrolyte and 2×10^{-3} M complex. The cyclic voltammograms at Pt disk electrode for these complexes display only one reversible Cu(II)/Cu(I) redox couple. The phenylcyanamide derivative reduction L(0/−) couples show

Table 4. Electrochemical data[a] for $[Cu(phen)_2L]PF_6$.

L	Cu(II)/Cu(I)	L(*I*/0)
4-Me(pcyd)	−217	623
pcyd	−221	671
2-Cl(pcyd)	−224	708
2,5-Cl_2(pcyd)	−238	785

[a] Data in mV *vs.* NHE (0.1 M TBAH, acetonitrile solution) at a scan rate of 100 mV s^{-1}.

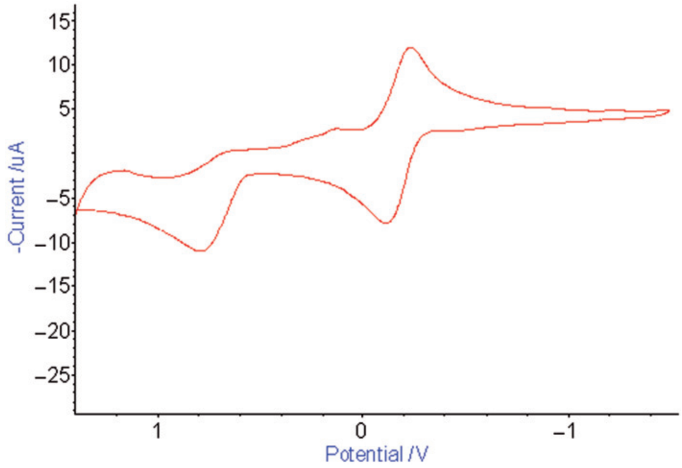

Figure 5. Cyclic voltammogram of $[Cu(phen)_2(2,5\text{-}Cl_2pcyd)]PF_6$ in acetonitrile, 0.1 M TBAH, at 100 mV s^{-1}.

quasi-reversible to irreversible behavior [1, 8]. The Cu(II/I) reduction couple has some reversible behavior, indicated by equivalent current intensity of cathodic and anodic peaks and largely insensitive to the nature of the phenylcyanamide ligand (table 4), even though the σ and π donor properties of this ligand vary significantly with the nature of the substituent on the phenyl ring. The anodic sweep showed only an irreversible wave which is assigned to the cyanamide ligand L(0/−) couple. The range of L(0/−) couples (table 4) of $[(phen)_2Cu(L)]PF_6$ complexes is a consequence of the coupling of the cyanamide moiety with the phenyl ring and the perturbation introduced by the nature of the phenyl ring substituents. The (L(0/−) couple also shifts to more positive potentials as the electron-withdrawing ability of the substituents on the phenyl ring increase from CH_3 to Cl.

Supplementary data

Supplementary data are available from CCDC, 12 Union Road, Cambridge CB2 IEZ, UK, on request, quoting deposition number 682539 (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk; http://wwww.ccdc.cam.ac.uk).

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