

## Effect of Substituents on the Charge Transfer Band of Copper(I) Complexes with 4-Monosubstituted Pyridines

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*Copper(I) complexes with 4-substituted pyridine (L) (L = 4-CH<sub>3</sub>-py, 4-Cl-py, 4-CH<sub>3</sub>CO-py, 4-CN-py, and py) have been prepared and their electronic absorption spectra have been measured in the region of 20–30 kK. All the complexes give the broad metal-to-ligand charge transfer (MLCT) band assigned to Cu d $\pi$ -Ligand  $\pi^*$ . The position of the MLCT band is mainly governed by the electron-withdrawing effect of the substituents, which is significantly associated with the stabilization of the pyridine ring  $\pi^*$  orbitals. With the aid of the MLCT band, it is demonstrated that the monomer [CuL<sub>4</sub>]ClO<sub>4</sub> is obtained from [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> and the binuclear [CuCl-L<sub>2</sub>]<sub>2</sub> forms from CuCl. The latter complex can reversibly react with carbon monoxide (CO) to give a carbonyl adduct ( $\nu_{\text{CO}} = 2060\text{--}2070\text{ cm}^{-1}$ ), while the former does not react with CO.*

### Introduction

Copper(I) ions naturally occur in the active site of copper-proteins such as hemocyanin [1]. To elucidate the protein structure/function relationship, some fundamental copper(I) complexes have been synthesized and characterized [2]. Recently, attention has also been paid to the usefulness of copper(I) complexes [3, 4] in organic syntheses. However, there are still few studies on copper(I) complexes in solution because (a) copper(I) complexes are air-sensitive and readily disproportionate to Cu(II) and Cu(0) in solution, and (b) they afford no EPR signals and optical absorption bands (d–d transition) due to d<sup>10</sup> electronic configuration.

The charge transfer (CT) band of the copper(I) complex having conjugated organic ligands, usually assigned to Cu(d $\pi$ )  $\rightarrow$  Ligand( $\pi^*$ ), provides insights into the nature of the metal–ligand binding. This band frequently appears in the visible region, advantageous for investigation of Cu(I) complexes in solution. The paucity of theoretical and experimental

information for the CT band of Cu(I) complex is paralleled by an equally sparse literature on the structures of Cu(I) complexes in solution. It is of importance to establish the practical use of the CT bands as a probe which reflects both electronic and geometrical structures of copper(I) complexes. Copper(I) complexes with pyridines presented here encounter the CT transition in the region of 20–30 kK. The purpose of this work is to explore the relationship between positions of CT bands and geometrical and electronic structures of the Cu(I) complexes with pyridines. Furthermore, it is also concerned with the reversible reaction with carbon monoxide, demonstrated by the variation of the CT bands.

### Experimental

#### Materials

Reagent grade copper(I) chloride was purified according to the literature [5]. Both copper(I) bromide and iodide were used without further purification; all materials were dried *in vacuo* (75–100 °C). [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> was prepared in the usual way [6] and recrystallized from ether under nitrogen. Pyridine (py), 4-methylpyridine (4-CH<sub>3</sub>-py), 4-chloropyridine (4-Cl-py), 4-acetylpyridine (4-Ac-py), and 4-cyanopyridine (4-CN-py) were commercially available. They were dried over potassium hydroxide and distilled under reduced pressure. 4-CN-py was utilized without further purification. Ethanol was dried and distilled before use. Sample preparation was accomplished under a nitrogen atmosphere. Nitrogen gas with a high purity (99.9995%) was used. The Cu(I) complex with pyridine was prepared as follows: 0.1–0.2 mmol of CuCl was added to 50 ml of pyridine as a solvent and the mixture was stirred under nitrogen at 25 °C. CuCl completely dissolved within 2 h, exhibiting the complete formation of the pyridine complex. The other Cu(I) complexes were prepared in a similar manner. In the case of 4-CN-py, 4000-fold excess of 4-CN-py (400 mmol) was added to 0.1 mmol CuCl in ethanol. CO gas was passed

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TABLE I. Absorption Maxima of Metal-to-Ligand Charge Transfer Bands of Copper(I) Complexes with 4-Substituted Pyridines and Highest Occupied  $\pi$  Orbital Ionization Potentials and  $\pi-\pi^*$  Transition Bands of 4-Substituted Pyridines.

Ligand R	4-R-pyridine				Copper(I) Source	
	pK <sub>a</sub> <sup>a</sup>	IP <sup>b</sup> (kK)	$\nu_{\pi-\pi^*}$ (kK)	$E\pi^*$ (kK) <sup>c</sup>	[Cu(CH <sub>3</sub> CN) <sub>4</sub> ]ClO <sub>4</sub> $\nu_{MLCT}$ (kK)	CuCl $\nu_{MLCT}$ (kK)
4-CH <sub>3</sub> -py	6.0	62.4	39.1	23.3	31.3	29.0
py	5.3	63.4	38.9	24.5	30.3	28.6
4-Cl-py	3.8	67.7	38.8	28.9	28.6	27.4
4-CH <sub>3</sub> CO-py	3.5	—	35.8	—	22.2	22.7
4-CN-py <sup>d</sup>	1.9	69.6	37.0	32.6	28.6	26.7

<sup>a</sup>Ref. 19. <sup>b</sup>Ref. 12. <sup>c</sup>The difference between IP and  $\nu_{\pi-\pi^*}$ , exhibiting the apparent energy of LV  $\pi^*$  orbital for 4-R-py.

<sup>d</sup>Ethanol was utilized as solvent; [Cu<sup>+</sup>] = 0.1 mM and [4-CN-py] = 400 mM.

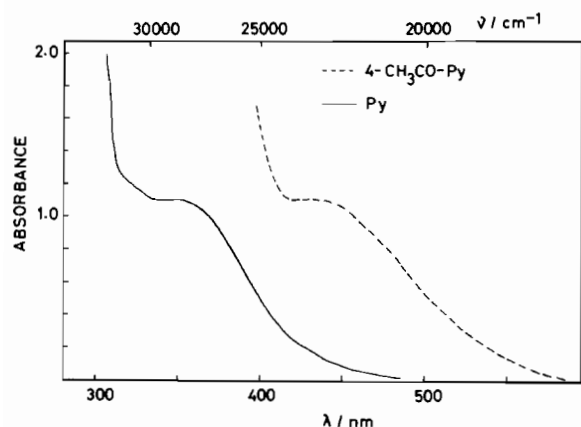


Fig. 1. Absorption spectra of 0.2 mM [Cu(pyridine)<sub>4</sub>]ClO<sub>4</sub> in pyridine (full line) and [Cu(4-acetylpyridine)<sub>4</sub>]ClO<sub>4</sub> in 4-acetylpyridine (broken line).

through the solution of copper(I) complex for 0.5 h, which was transferred into the cuvette under CO atmosphere and visible spectra were recorded. Decarbonylation was performed by use of nitrogen. The degree of reversibility was checked by repeating carbonyl-decarbonyl cycle for many times.

#### Physical Measurements

Visible spectra were recorded on a Hitachi 200-10 Spectrometer. Samples were transferred anaerobically into a cuvette with a tight stop cock (10 mm path length). Infrared spectra were recorded on Hitachi 260-10 spectrometer. Solution samples were measured as 20 mM of 4-R-py solution in 0.05 mm potassium chloride cavity cells by using polystyrene films as a calibration standard. Conductances were measured with a Kyoto elec. Co. Model CM-05 and a cell with two platinum electrodes.

#### Results and Discussion

The affinity of py for Cu(I) ion is small, and thus a large excess of the ligand is required to attain the complete complex formation: py is utilized as solvent. The visible spectrum of the pyridine solution of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> is presented in Fig. 1. The new absorption band at 30.3 kK appears as a shoulder of the  $\pi-\pi^*$  transition band of py, indicative of the formation of a Cu(I)-py complex. The X-ray crystallographic investigation [7] has demonstrated that pyridine-copper(I) complex synthesized from Cu<sup>II</sup>-(ClO<sub>4</sub>)<sub>2</sub> encounters a typical four-coordinate [Cu<sup>I</sup>-(py)<sub>4</sub>]ClO<sub>4</sub> with a tetrahedral symmetry. The above complex prepared by the reduction of Cu<sup>II</sup>-(ClO<sub>4</sub>)<sub>2</sub> in py by copper(0) metal [8] shows the same spectrum as in Fig. 1. Hence, [Cu(py)<sub>4</sub>]ClO<sub>4</sub> can be also formed from [Cu<sup>I</sup>(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub>, indicating the substitution of py for CH<sub>3</sub>CN. It has been demonstrated that the Cu(I) ion is bound to the pyridine nitrogen [9] of 4-CN-py although the nitrile group is also capable of coordinating with this ion. Hence, the Cu(I) ion is bound to the ring nitrogen.

The ligand py itself exhibits no absorption band at lower than 33.3 kK, even if it is coordinated to a metal ion, and hence the band at 30.3 kK is exclusively assigned to the CT band of [Cu(py)<sub>4</sub>]. Bidentate 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen), which are well known as a chelating ligand against the lower valence metal ion, also form stable complexes with Cu(I) ion. The intense CT bands of both [Cu(bpy)<sub>2</sub>] and [Cu(phen)<sub>2</sub>] appear at 22.7 kK, assigned to the metal-to-ligand CT(MLCT) such as Cu( $d\pi$ ) → ligand( $\pi^*$ ) [10, 11]. The value of  $\nu_{max}$  = 30.3 kK is much larger than that ( $\nu_{max}$  = 22.7 kK) in the case of bpy and phen. This is because bpy and phen have highly delocalized electronic structure and their  $\pi$ -orbitals are considerably stabilized, especially their  $\pi^*$ -orbitals which significantly contribute to  $\pi$  back-bonding inter-

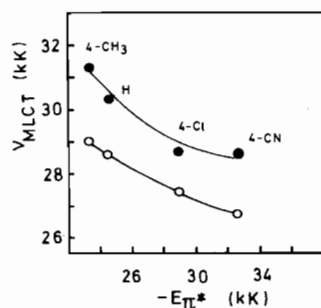


Fig. 2. Plots of  $\nu_{\max}$  value of the MLCT band vs. the energy of lowest vacant  $\pi^*$  orbital ( $E\pi^*$ ) of 4-substituted pyridines: ● [CuCl(4-R-py)<sub>2</sub>]<sub>2</sub>; ○ [Cu(4-R-py)<sub>4</sub>]ClO<sub>4</sub>.

action. The Cu(I) complexes with other py derivatives have the MLCT band at 22–31 kK. These MLCT bands are listed in Table I.

#### Substituent Effects on the MLCT Band

In a tetrahedral molecular environment, the metal valence d orbitals split into two sublevels. The more energetic sublevel is called  $t_2$  ( $d\pi$ ) including three d orbitals ( $d_{xz}$ ,  $d_{yz}$  and  $d_{xy}$ ), which can participate in  $\pi$  interaction with the ligands. The other is the e sublevel including  $d_{x^2-y^2}$  and  $d_{z^2}$ , which can interact in  $\sigma$ -bonding. The splitting of e and  $t_2$  is called the tetrahedral ligand field splitting, designated  $\Delta$ . The  $t_2$  orbitals which are associated with the MLCT band are most important here. On the other hand, there are two lowest vacant (LV)  $\pi^*$  orbitals [13] of py, which are  $a_2$  and  $b_1$  orbitals in the case of  $C_{2v}$  symmetry. The  $b_1$  orbital may be available for the interaction with Cu(I) ion because it has large electron densities on the 1-position (N) atom as well as the 4-position (C) atom. On the other hand, the  $a_2$  orbital has very small electron densities on the N atom. This  $b_1$  orbital will also be greatly affected by the substituents at the 4-position. In the first approximation, the position of the MLCT band depends on the energy difference between  $t_2$  and LV  $\pi^*$  orbitals. In a series of Cu(I) complexes containing py derivatives, the relative order of energy ( $E\pi^*$ ) for LV  $\pi^*$  orbitals of pyridine moiety is most important. The value of  $E\pi^*$  is estimated from the IP value [12] of the HO  $\pi$  orbital and  $\pi-\pi^*$  transition energy of 4-R-py, which are listed in Table I. Inspection of Table I shows that  $\pi^*$  orbital is well stabilized by the electron-withdrawing substituents (Cl and CN) as well as the HO  $\pi$  orbitals [14]. In Fig. 2, the frequencies of the MLCT band of Cu(I)-pyridine complexes are plotted against  $E\pi^*$ . There is a fairly good correlation between  $\nu_{\max}$  and  $E\pi^*$ , except for the case of 4-Ac-py. This shows the MLCT band appears in the lower energy region when 4-R-py has the more stabilized LV $\pi^*$  orbital (Fig. 3), which

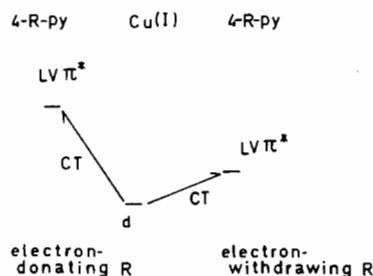


Fig. 3. d-Orbital and the lowest vacant  $\pi^*$  orbital energy ordering and their correlation with the MLCT band.

implies the intensification of  $\pi$  back-bonding interaction between Cu(I) and py.

The experimental HO  $\pi$  IP value varies almost in parallel with the lone pair IP value which is an apparent linear function of pKa value [12]. On this basis, we can also find a good relationship between  $\nu_{\max}$  and pKa values (Table I). In this sense, pKa is a simple way of predicting the behaviour of the MLCT band of Cu(I)-pyridine complexes containing CH<sub>3</sub>, Cl, and CN substituents.

The Ac group possesses the electron-withdrawing nature which lowers the basicity of py nitrogen and gives almost the same pKa value as that of 4-Cl-py. We would thus expect that the  $\nu_{\max}$  of 4-Ac-py derivative is also close to that of the 4-Cl-py derivative. However, [Cu(4-Ac-py)<sub>4</sub>] has an anomalously small MLCT energy, which cannot be simply accounted for by the electron-withdrawing effect of substituents. The Ac group has a conjugated electronic structure which can interact with both HO and LV  $\pi$  orbitals of py. This type of interaction is excluded in the case of 4-CH<sub>3</sub>-py and 4-Cl-py. It is noteworthy in Table I that  $\pi-\pi^*$  transition energy of 4-Ac-py is the smallest in all the py derivatives studied here, which implies the considerable stabilization of the LV  $\pi^*$  orbital. Such a stabilization of LV  $\pi^*$  orbital leads to the small MLCT energy. This is also found in the case of bpy, which is a kind of py derivatives. This specific intramolecular interaction of  $\pi$  orbital is also expected to occur in 4-CN-py. However, the MLCT energy for 4-CN-py is much larger than in 4-Ac-py (Table I). As shown in Fig. 2, the CN group mainly influences the LV  $\pi^*$  orbital in a similar manner as Cl group.

#### Halide Ion Effects on the MLCT Band

When CuX (X = Cl, Br, and I) was utilized as a starting material, the MLCT band of Cu(I) complex experienced the red shift in comparison with that of the corresponding [Cu<sup>I</sup>(4-R-py)<sub>4</sub>]ClO<sub>4</sub>. Table II shows the halide ion dependence on the MLCT bands, indicating the coordination of the halide ion to Cu(I) atom. The  $\nu_{\max}$  value decreases in the order, I > Br > Cl. If the order of the crystal

TABLE II. Halide Ion Effects on Metal-to-Ligand Charge Transfer Bands of 4-Substituted pyridine Complexes with CuX.

	pyridine $\nu_{\max}$ (kK)	4-CH <sub>3</sub> CO-pyridine $\nu_{\max}$ (kK)
CuCl	28.6	22.7
CuBr	29.0	23.3
CuI	29.9	23.5

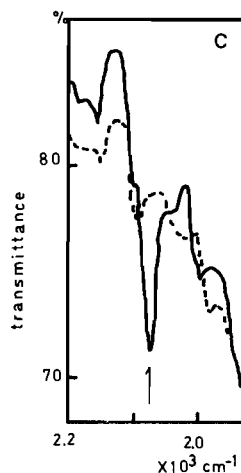
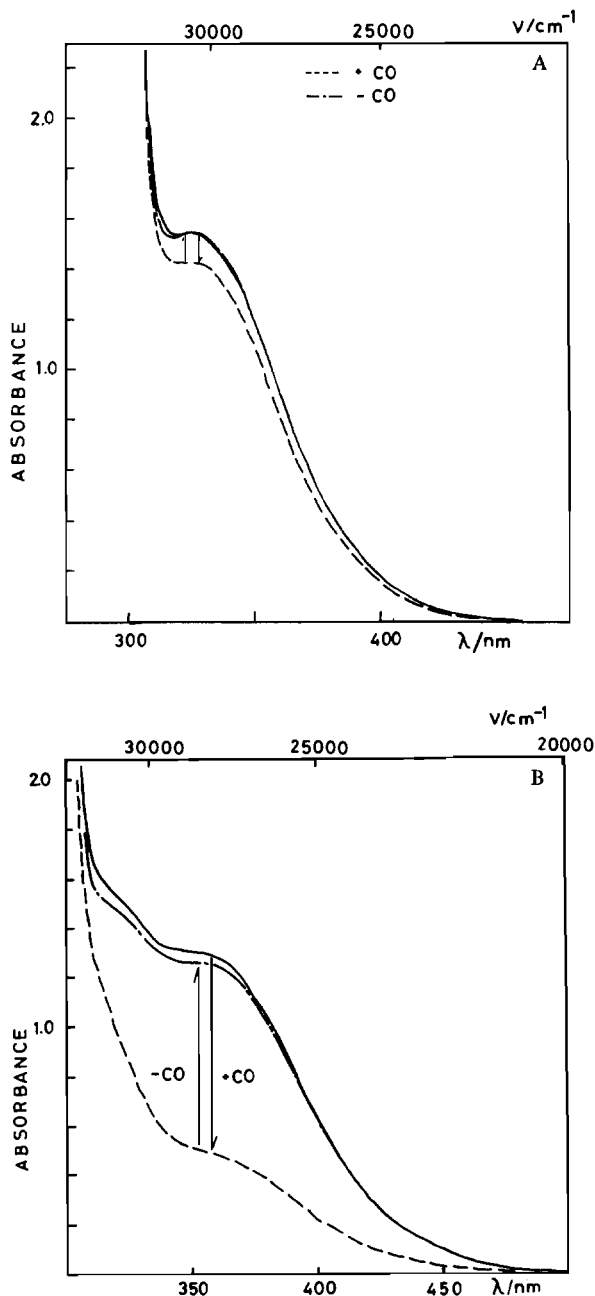
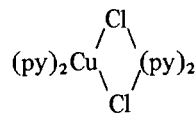


Fig. 4. Absorption spectra of (A) [Cu(pyridine)<sub>4</sub>]ClO<sub>4</sub> and (B) [CuCl(pyridine)<sub>2</sub>]<sub>2</sub> in pyridine. (a) Under nitrogen (full line); (b) under carbon monoxide (1 atm) (broken line); (c) CO-purged with nitrogen (dot-dash line). Infrared spectra (C) of the [CuCl(4-cyanopyridine)<sub>2</sub>]<sub>2</sub> (broken line) and its carbonyl adduct (full line) as ethanol solution in the region of 1940–2200 cm<sup>-1</sup>.

field splitting  $\Delta$  for these Cu(I) halide ion complexes is as follows,  $I < Br < Cl$ , the most destabilized is the  $t_2$  orbital in the case of Cl. The difference in energy,  $\Delta\epsilon$ , between the  $t_2$  and LV  $\pi^*$  orbital is minimum in the case of Cl and maximum in the case of I. This view explains the halide ion-dependence on the MLCT band (Table II).

This is also the case for bpy and phen complexes with Cu(I) [11]. It is worth noting that the order of  $\Delta$  corresponds with that of the well-known spectrochemical series [16]. This series may hold for the Cu(I) complexes presented here, although there are few instances in the case of lower valence metal complexes.

Inspection of Table I reveals that the MLCT energy of Cu(I) complex containing a coordinated halide ion is specifically smaller than that of [Cu(py)<sub>4</sub>]ClO<sub>4</sub>, exhibiting the formation of a novel form. In the presence of a halide ion, the Cu(I) complex tends to have a binuclear structure having bridging halogen atoms [11, 17]. If the present Cu(I) complex also undergoes the similar structure, it is considered as a four-coordinate binuclear structure,



CuCl and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub> in Py gave molar conductivities of 4.09 and 50.0 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>, respectively. The CuCl/py systems encounter anomalously low conductivities. On the basis of the fact

that the  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  in py forms  $[\text{Cu}(\text{py})_4]\text{ClO}_4$  which is a 1:1 electrolyte, this low conductivity strongly supports the presence of the binuclear structure.

#### The Reversible Reaction with CO

The yellow solution of  $[\text{Cu}^{\text{I}}(4\text{-R-py})_4]\text{ClO}_4$  has no affinity for CO, as is well illustrated in Fig. 4(A) which reveals little change on the intensity of the MLCT band in the presence of CO (1 atm). This fact shows that the substitution of CO for py or the conformational change into a square-pyramidal structure upon the addition of CO is unlikely in the tetrahedral  $[\text{Cu}(4\text{-R-py})_4]\text{ClO}_4$ . Such a rigidity of the structure has been also found in four-coordinate  $[\text{Cu}^{\text{I}}\text{L}_2]\text{ClO}_4$  (L = bpy and phen) complexes [11] which show no affinity for CO. On the other hand, the complexes prepared from CuX have remarkably high affinity for CO even at room temperature (Fig. 4(B)). When CO gas was passed through the solution of the complex, the intensity of the MLCT band showed a pronounced decrease, indicative of the formation of a carbonyl complex. To obtain the direct evidence, the infrared spectra of the complex in solution were observed in the region of CO stretching frequencies. Figure 4(C) demonstrates the appearance of  $\nu_{\text{CO}}$  signal of CO coordinated to Cu(I) atom. This type of signal in this region was not observed in the absence of CO, nor when CO gas was passed through the solution of  $[\text{Cu}(\text{py})_4]\text{ClO}_4$ . The  $\nu_{\text{CO}}$  value of  $2070\text{ cm}^{-1}$  is characteristic of the terminal coordination of CO (Cu–CO) because the bridging CO encounters the lower  $\nu_{\text{CO}}$  frequencies such as  $1926\text{ cm}^{-1}$  of  $[\text{Cu}_2(\text{tmen})_2(\mu\text{-CO})(\mu\text{-phCO})_2](\text{Bph}_4)$  [15]. Molar conductivity of this carbonyl complex in py was  $2.0\text{ ohm}^{-1}\text{ cm}^2\text{ mole}^{-1}$ , similar to that of the precursor, indicating no dissociation of chloride ion. It has been reported [18] that dichlorocuprate(I) ion in aqueous solution reacts with CO to give a stable crystalline carbonyl complex,  $[\text{Cu}(\text{CO})\text{Cl}]_2$ , which has a binuclear structure having two bridging chloride atoms. On the other hand, the carbonyl complex studied here is unstable at room temperature and CO molecule coordinated to Cu(I) atom is readily removed by degassing with nitrogen. The carbonyldecarbonyl cycles can be repeated for many times at room temperature. Hence,  $[\text{CuCl}(\text{py})_2]_2$  may not encounter the substitution of CO for py. We have demonstrated the five-coordinate CO adduct [11] of the binuclear  $[\text{Cu}^{\text{I}}\text{XL}]_2$  (X = Cl, Br, and I; L = bpy and phen), which also shows high degree of reversibility at room temperature. This carbonyl complex containing py is presumably mono or bis adduct of CO upon the precursor complex, such as  $\text{Cu}_2\text{py}_4\text{Cl}_2(\text{CO})_n$  ( $n = 1$  or  $2$ ).

The  $\nu_{\text{CO}}$  values were observed for carbonyl adducts with 4-CN-py and py. The value of  $2060\text{ cm}^{-1}$  in the case of py is smaller than that in the case of 4-

CN-py ( $\nu_{\text{CO}} = 2070\text{ cm}^{-1}$ ). The  $\pi$  back-donation interaction between Cu(I) and CO is significantly associated with Cu–CO bonding. The smaller  $\nu_{\text{CO}}$  value than the free  $\nu_{\text{CO}}$  well illustrates the important role of such interaction in Cu(I) carbonyl complexes. If the py competes with CO concerning the  $\pi$  back-donation interaction with Cu(I) atom, the  $\nu_{\text{CO}}$  frequencies will sensitively vary depending upon the py derivatives. In fact,  $\nu_{\text{CO}}$  signal appears in the higher frequency region in 4-CN-py than in py, indicating that  $\pi$  back-bonding interaction is stronger in 4-CN-py. This feature obtained from CO frequencies concerning  $\pi$  back-bonding interaction of pyridines with Cu(I) ion is in excellent agreement with that obtained from the MLCT band in the previous section. Consequently, the MLCT band measurements are an useful probe into the nature of the metal–ligand binding, and on the basis, the structure of Cu(I) complexes in solution.

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