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The Affinity for Carbon Monoxide, Electrochemical and Spectral Properties of Binuclear Copper(I) Complexes

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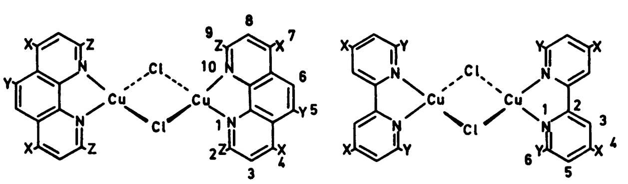
Binuclear copper(I) complexes $[CuXL]_2$($X=Cl^-$ and I^-; L=2,2′-bipyridine, 1,10-phenanthroline, and their derivatives) have been synthesized in acetone, which react with CO reversibly to give crystalline carbonyl adducts $[Cu_2X_2L_2(CO)]$. The cyclic voltammograms of $[CuXL]_2$ and $[Cu_2X_2L_2(CO)]$ show two couples of copper-centered oxidation-reduction waves, indicative of binuclear structure. One couple of waves in $[Cu_2X_2L_2(CO)]$ alone shifts to the anodic region, exhibiting the formation of monocarbonylated complexes. All the half-wave potentials are primarily governed by the basicity of a ligand L, and the contribution of a coordinated CO to the stabilization of Cu^I state by π back-bonding is found. The equilibrium constants of the reaction, $[CuXL]_2+CO\overset{K_{CO}}{\rightleftharpoons}[Cu_2X_2L_2(CO)]$, are lowered with the decrease in the transition energy of the ligand←metal charge transfer of $[CuXL]_2$. On this basis, it is concluded that CO competes with L concerning π back-bonding with copper(I). The ν_{CO} values of the coordinated CO exhibit apparent L-dependence, which is accounted for by the competition between Cu–L and Cu–CO π-bonding, and hence, ν_{CO} values are useful probe to inquire into the nature of Cu–CO bonding among these copper(I) complexes.

A greater knowledge of coordination chemistry of copper(I) particularly of binuclear structure, is important in view of current interest in understanding the structure-function relationship of the "type 3" copper proteins. We have recently reported novel binuclear copper(I) complexes,[1] which have two bridging halogen atoms. It has been demonstrated that the binuclear complexes reversibly react with carbon monoxide (CO) to form a monocarbonylated complex which have the stoichiometry of 1CO/2Cu, corresponding to that of hemocyanin,[2,3] and their affinity for CO is remarkably influenced by the bridging halogens and solvent.

To gain further insight into the nature of copper(I)-ligand binding, we present here a systematic electrochemical properties of binuclear copper(I) complexes containing several 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) derivatives (Figs. 1; **1a**—**f**, **2a**, and **2b**), and their carbonyl adducts. Furthermore, the relationship between the affinity for CO and the bonding nature of Cu^I–L or Cu^I–CO is examined on the basis of visible absorption and infrared spectra.



1a X=Z=H; Y=Cl
1b X=Z=H; Y=Br
1c X=Y=Z=H
1d X=Z=H, Y=CH_3
1e X=CH_3; Y=Z=H
1f X=ph; Y=Z=H
2a X=Y=H
2b X=CH_3; Y=H

Fig. 1. $[CuClL]_2$.

Experimental

Materials. The reagent grade copper(I) chloride was purified according to literature.[4] Reagent grade copper(I) iodide was used without further purification. They were all dried *in vacuo* (75—100 °C). 2,2′-Bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (4,4′-dmbp), 1,10-phenanthroline (phen), 5-chloro-1,10-phenanthroline (5-Cl-phen), 5-bromo-1,10-phenanthroline (5-Br-phen), 5-methyl-1,10-phenanthroline (5-mp), 4,7-dimethyl-1,10-phenanthroline (4,7-dmp), 4,7-diphenyl-1,10-phenanthroline (4,7-dpp), and 2,9-dimethyl-1,10-phenthroline (2,9-dmp) were commercially available (Wako Pure Chemical Ltd). 6,6′-Dimethyl-2,2′-bipyridine (6,6′-dmbp) was prepared according to literature.[5] They were recrystallized several times from acetone, and dried *in vacuo* before use.

Acetone was dried over anhydrous potassium carbonate, and distilled from 4 Å molecular sieves before use. Tetrabutylammonium perchlorate (TBAP) was prepared by the usual method.

Cyclic Voltammograms. Cyclic voltammetric (CV) measurement were made with a Hokuto model HA104 potentiostat/galvanostat driven by a Hokuto model HB107A function generator. Scans were recorded with a Rika Denki X-Y recorder. A conventional three-electrode system was utilized. A Pt wire served as the working electrode, and a Pt coil was used as the counter electrode. A commercial saturated calomel electrode (SCE) was utilized as the reference electrode. Current-voltage curves were measured at 0.05—0.5 V/s. The SCE was separated from the bulk of the solution with a fritted-glass bridge filled with solvent and supporting electrolyte. All potentials are reported in volts *vs.* SCE.

A solution of phen (1.0×10^{-4} mol) and anhydrous CuCl (1.0×10^{-4} mol) in 50 cm^3 of acetone was stirred under argon at 25 °C for 4 h. Complete complex formation was checked by monitoring the band at 440 nm (peak maxima). This solution was transferred anerobically into the electrolytic cell containing TBAP (5.0×10^{-3} mol), and maintained at constant temperature. Temperature was set at 5 and 25 °C. During measurments, argon atmosphere was kept over the solution in the electrolytic cell. The carbonyl adduct was prepared by directly passing CO gas into the stock solution prepared in a similar way. It was then transferred into the electrolytic cell in which CO atmosphere (1 atm) was maintained during measurements. The partial pressure of CO in the gas bubbled through the stock solution and the electrolytic cell was adjusted by mixing pure argon with pure CO, using two Kusano KG-1 rotameters and two precission needle valves. Partial pressure effect was examined only for $[CuCl(bpy)]_2$. The cyclic voltammograms of the copper(I) complexes containing the other phen or bpy derivatives were measured in similar ways.

Solution Equilibria. Visible spectra were recorded on Hitachi 200-10 spectrophotometer. The cell used for the determination of CO equilibria consisted of 1.0-cm quartz cuvette with gas inlet and outlet tubes, by means of which N_2 gas containing varying partial pressure of CO can be bubbled through the copper(I) complex solution. The change in absorbance maxima was measured as a function of the partial pressure of CO. The equilibrium constants given by Eqs. 1 and 2 were obtained.

$$[\mathrm{CuClL}]_2 + \mathrm{CO} \overset{K_{\mathrm{co}}}{\rightleftharpoons} [\mathrm{Cu_2Cl_2L_2(CO)}] \qquad (1)$$

$$K_{\mathrm{co}} = [\mathrm{Cu_2Cl_2L_2(CO)}]/[[\mathrm{CuClL}]_2](P_{\mathrm{co}}) \qquad (2)$$

The detailed procedure to obtain the equilibrium constants has been described elsewhere.1)

Measurements of Infrared Spectra. Infrared spectra were recorded on Hitachi 260-10 spectrophotometer. The spectra of saturated solutions of $[\mathrm{Cu_2Cl_2L_2(CO)}]$ were measured in 0.05-cm cavity KCl cells, with polystyrene film as calibration standard. KBr disk pellet was prepared as follows. A solution of L(1.0×10^{-3} mol) and CuCl(1.0×10^{3} mol) in 50 cm^3 acetone was stirred under argon for 4 h. A suspended brown solution was obtained. Carbon monoxide was then added to this solution; the initially brown color turned pale yellow and the precipitate dissolved into acetone. When the solution was cooled at −70 °C, a pale yellow crystals were obtained. This was stable at low temperature. The quick preparation of KBr disk pellets provided IR spectra of $[\mathrm{Cu_2Cl_2L_2(CO)}]$. The carbonyl adduct in KBr disk was stable for many hours.

Results and Discussion

Electrode Reactions. Figure 2 illustrates a typical cyclic voltammogram of $[\mathrm{CuCl(phen)}]_2$ (**1c**) in acetone/0.1 M TBAP (1 M=1 mol dm^{-3}). The oxidation-reduction reactions noted here correspond to the metal-centered reactions, $\mathrm{Cu^I/Cu^{II}}$ at 0.3—0.7 V *vs.* SCE, because the ligand phen encounters no reaction in this region. The cyclic voltammogram of **1c** (Fig. 2) shows two oxidation processes. The ^{1}H NMR spectrum of **1c** in acetone showed the signals attributed to only a single species indicative of no dissociation of **1c**. The first two peaks(1) in cyclic voltammogram at 0.22 and 0.44 V in Fig. 2 are coupled to the initial oxidation-reduction process of the other copper of **1c**. These are chemically reversible and non-Nernstian at a platinum electrode ($E_{\mathrm{p,a}}-E_{\mathrm{p,c}}$=0.1—0.2 V). These electrode reactions are represented by Eqs. 3 and 4.

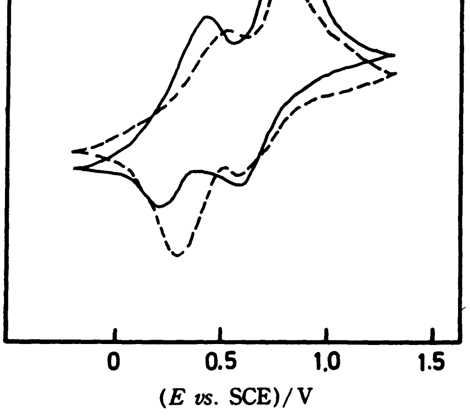


Fig. 2. Cyclic voltammograms of $[\mathrm{CuCl(phen)}]_2$(solid line) and $[\mathrm{Cu_2Cl_2(phen)_2(CO)}]$(dotted line) in acetone.

$$\mathrm{(phen)Cu^ICl_2Cu^I(phen)} \overset{-e}{\rightleftharpoons} \mathrm{(phen)Cu^{II}Cl_2Cu^I(phen)} \qquad (3)$$

$$\mathrm{(phen)Cu^{II}Cl_2Cu^I(phen)} \overset{-e}{\rightleftharpoons} \mathrm{(phen)Cu^{II}Cl_2Cu^{II}(phen)} \qquad (4)$$

On the other hand, copper(I) complex containing 2,9-dmp or 6,6′-dmbp showed a single oxidation process; this indicates that the dominant species is a mononuclear form. Appearance of the two oxidation peaks6) at this region is a good measure of the binuclear structure of the copper(I) complex in question. The other binuclear copper(I) complexes, **1a**, **1b**—**f**, **2a**, and **2b**, also have similar anodic properties. If differences in diffusion coefficients between the oxidation and reduction halves of redox couples are ignored, value of $E_{1/2}$ obtained in the above electrochemical experiments can be used. These formal half-wave potentials ($E_{1/2}$s) are listed in Table 1. Knowledge of these formal potentials enables one to quantify some interesting properties of the system.

Electrode Reactions under CO Atmosphere. In this electrode reaction, both two sets of coupled peaks should shift anodically if a dicarbonyl adduct is formed. The ^{1}H NMR and visible spectra have demonstrated that $[\mathrm{CuCl(phen)}]_2$ binds to CO at room temperature to give a monocarbonyl adduct $[\mathrm{(phen)CuCl_2Cu(CO)(phen)}]$.1) It is worth noting in Fig. 2 that the couple(1) alone moves anodically and the other couple(2) remains. This also support the formation of monocarbonyl adduct. In order to firmly assign this cyclic voltammogram, the partial pressure of CO is varied. When the partial pressure increases, the peak current of the couple(1) of $[\mathrm{CuCl(phen)}]_2$ decreases and a new couple(1) (a dashed curve in Fig. 2) appears.7) The high pressure of CO causes the increase in the peak current of the new couple(1) but it does not influence the redox potential. This fact exhibits that the monocarbonylated complex

Table 1. OXIDATION-REDUCTION POTENTIALS OF $[\mathrm{CuClL}]_2$ AND $[\mathrm{Cu_2Cl_2L_2(CO)}]$

L	($E_{1/2}$ *vs.* SCE)/V$^{\mathrm{a)}}$			
	$[\mathrm{CuClL}]_2$		$[\mathrm{Cu_2Cl_2L_2(CO)}]$	
	(1)	(2)	(1)	(2)
5-Cl-phen	0.37	0.72	0.43	0.70
phen	0.33	0.69	0.40	0.68
5-mp	0.31	0.67	0.40	0.69
4,7-dmp	0.26	0.66	0.38	0.67
4,7-dpp	0.32	0.67	0.41	0.68
bpy	0.31	0.74	0.41	0.68
4,4′-dmbp	0.26	0.70	0.39	0.70
2,9-dmp	0.66		0.69	
6,6′-dmbp	0.69		0.65	

a) [Complex]=2.0×10^{-3} M and [TBAP]=0.1 M in acetone at 25°C.

forms with the increase of the CO pressure. Hence, the new couple(1) is attributable to the copper coordinated with CO. The selective anodic shift of the copper coordinated by CO has also been found in $Cu^ICu^IL'(CO)$,[6] in which the stabilization of the copper(I)(Cu–CO) is attributable to the π back-bonding interaction between CO and Cu. It is interesting to compare the relative stability of two copper(I) ions in the binuclear monocarbonyl complex. In the case of $[Cu_2Cl_2L_2(CO)]$ studied here, the first oxidation occurs at $Cu^I(CO)$, while it occurs at the Cu^I without coordinated CO in the case of $[Cu^ICu^I(CO)L']$. It should be remembered that copper(I) prefers the tetrahedral geometry while copper(I) favors the square-planar one. $[Cu_2Cl_2L_2(CO)]$ has a flexible structure[1] and the geometry around each copper atom is different and may not be simply square-planar; one is distorted square-pyramidal (CO-coordinated) and the other is tetrahedral.[8] On this basis, the five-coordinate copper(I) is less stable than the tetrahedral one in spite of the coordination of CO. On the other hand, [CuCu(CO)-L'][6] has square-planar and square-pyramidal geometry around each copper atom. The square-planar copper is less stable than the square-pyramidal copper because the latter is stabilized by π back-bonding interaction with CO. Consequently, the contribution of geometry around the copper atom may predominate over the effect of stabilization of CO as the fifth ligand in the carbonyl copper(I) complexes studied here.

Relationship between $E_{1/2}$ and pK_a of Ligands. Figure 3 shows that the $E_{1/2}$ values for copper(I) complexes containing phen derivatives are plotted against the pK_a values of phens. The straight lines exhibit a good relationship between $E_{1/2}$ and pK_a: the negative slope reveals that the ligand having the higher pK_a destabilizes the copper(I) complexes. Similar results have been found in copper(I) complex in aqueous solution.[9] This is accounted for by the following two reasons. Firstly, when the coordinated ligand gives a more negative charges to the copper(I) ion, this ion will be more unstable. In fact, the aliphatic amines having the greater basicity (pK_a=10—11) form very unstable complexes with copper(I) ion, which are readily oxidized to copper(II) complexes. On the other hand, copper(II) ion favors the ligand having the greater basicity and forms the stable complex.[10] Hence, the ligand having the greater basicity contributes to the stabilization of its copper(II) complexes more effectively than that of copper(I) complex. Secondly, the π conjugated structure of the ligand can accept electronic

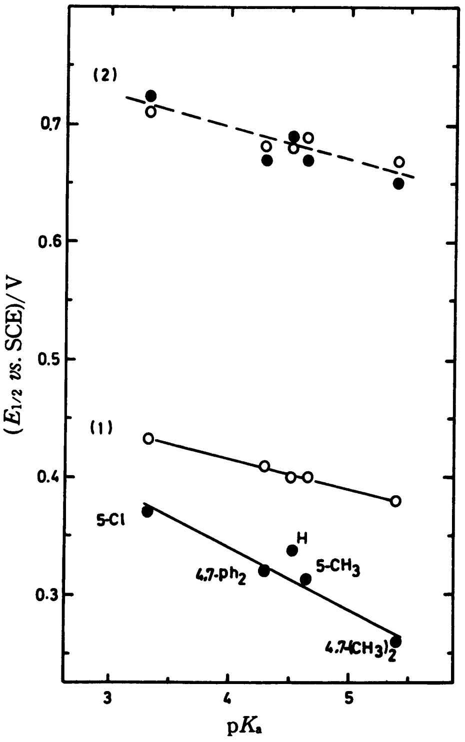


Fig. 3. Plots of half-wave potentials ($E_1/_2$) of $[CuClL]_2$ (●) and $[Cu_2Cl_2L_2(CO)]$ (○) vs. pK_a of the ligand (L; phen derivatives).

TABLE 2. METAL-TO-LIGAND CHARGE TRANSFER BANDS OF $[CuClL]_2$ AND FORMATION CONSTANTS OF THEIR CARBONYL ADDUCTS

Complex	pK_a a)	λ_{MLCT}/nm b)	K_{CO}/atm^{-1} c)
1a	3.43	445	0.9
1c	4.53	440	1.2
1d	4.65	443	1.1
1e	5.40	437	1.6
1f	4.30	463	—
2a	3.62	440	1.3 d)
2b	4.40	433	—
$[Cu(2,9\text{-}dmp)_2]$	—	455	— e)
$[Cu(6,6'\text{-}dmbp)_2]$	4.23	455	— e)

a) The pK_a values of the coordinated ligands; 50% v/v dioxane–water. Ref. 9. b) Error limit, ±1 nm. c) Error limit, ±0.1 atm^{-1}. d) Ref. 1. e) No reaction with CO.

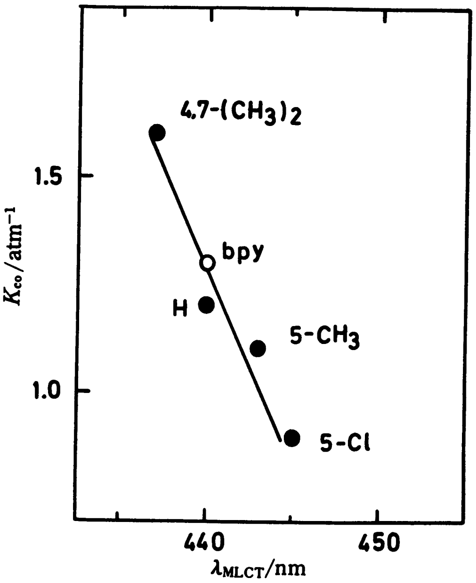


Fig. 4. Plots of equilibrium constants (K_{co}) of the reaction (1) vs. the wavelengths of metal-to-ligand charge transfer (MLCT) band of $[CuClL]_2$ (L; phen derivatives (●) and bpy (○)).

charge from copper(I) ion through π back-bonding. The substituent which enhances the donor ability of the nitrogen of the ligand tends to destabilize the lowest vacant (LV) π^* orbital[11,12] of the ligand which is significantly associated with the π back-bonding. This effect has been demonstrated in the case of 4-substituted pyridines.[13] On this basis, the ligand with the greater basicity is disadvantageous for π back-bonding interaction with copper(I) ion, and it lowers the redox potential of the resultant copper(I) complex. Consequently, in a series of bidentate ligands possessing donor atoms which have both σ and π bonding natures, their copper(I) complexes are destabilized with an increase in their pK_a values.

It is worth noting in Fig. 3 that the gradient of the straight line(1) of the CO adducts is smaller than that of the precursor complex, indicative of the contribution of a coordinated CO to the stabilization of copper(I) ion: even if phen derivatives with the higher basicity destabilizes $\mathrm{Cu^I}$ state in a moiety ($\mathrm{LCu(CO)}{<}^{\mathrm{X}}_{\mathrm{X}}$) of a CO adduct, coordinated CO stabilizes $\mathrm{Cu^I}$ state through π back-bonding. On the other hand, the copper(I) ion in the residual moiety (${}^{\mathrm{X}}_{\mathrm{X}}{>}\mathrm{CuL}$) shows a p$K_a$-dependence of $E_{1/2}$ similar to that of the precursor one. In this sense, CO is a good π acceptor. This nature of CO leads to the expectation that CO competes with L for π back-bonding. In fact, the intense MLCT band between L and copper(I) ion in the visible region disappears[1] when CO binds $[\mathrm{LCuCl_2CuL}]$. This indicates that CO is significantly associated with π back-bonding and subsequently, it enhances the stabilization of copper(I) state, competing with a bidentate ligand L.

Relationship between K_{CO} and λ_{MLCT}. The stability of the CO adduct is examined with the aid of the equilibrium constants. The K_{CO} values obtained for the binuclear complexes (Eqs. 1 and 2) are listed in Table 2, together with the peak maxima of the metal-to-ligand charge transfer (MLCT) band of $[\mathrm{CuClL}]_2$, λ_{MLCT}. This K_{CO} exhibits the affinity for CO of copper(I) ion. K_{CO} reflects the competition of L with CO concerning the metal-ligand binding. A good measure to depict the Cu–L π back-bonding is λ_{MLCT}, whose greater value indicates the significant association of π back-bonding in Cu–L bond. In order to examine the relationship between stability of CO adducts and their π back-bonding nature of Cu–CO bonding, K_{CO} is plotted against λ_{MLCT} (Fig. 4). Figure 4 shows the good correlation between K_{CO} and λ_{MLCT}, indicative of considerable contribution of π back-bonding to the stabilization of CO adducts. The stronger Cu–L π back-bonding (the greater λ_{max}) results in the weaker CO-affinity (the smaller K_{CO}). It is concluded that L controls the affinity for CO of copper(I) through π-bonding although overall stability of the CO adduct, of course, results from the delicate balance between bondings of Cu–CO and Cu–L and the resultant geometry.

Coordinated Carbonyl Stretching Frequencies. To gain further insight into the nature of the Cu–CO bonding, CO-stretching frequencies of the copper(I) complexes have been measured. These ν_{CO} values are presented in Table 3. Inspection of Table 3 reveals that they fall within the range 2063—2088 cm^{-1}. It is well known that π back-bonding plays an important role in the metal–CO bond. This π back-bonding brings about a shift of ν_{CO} toward the lower frequency region.[14] On this basis, the smaller value of ν_{CO} indicates the stronger π back-bonding in the Cu–CO bond. Floriani *et al.*[15—18] have synthesized several four-coordinate carbonyl copper(I) complexes containing aliphatic amines such as ethylenediamine and their derivatives. These ν_{CO} values fall within 2055—2080 cm^{-1}, and the bond distances of Cu–CO($r_{\mathrm{Cu-CO}}$) and C–O($r_{\mathrm{C-O}}$) are 1.73—1.80 Å, and 1.11—1.17 Å, respectively. They, however, could not find the evident relationship between the ν_{CO} and $r_{\mathrm{Cu-CO}}$ or $r_{\mathrm{C-O}}$ in their four-coordinate copper(I) complexes containing the terminal CO. A five-coordinate carbonyl, copper(I) complex has been synthesized by Gagne *et al.*[19,20] This gave $\nu_{\mathrm{CO}}=2068$ cm^{-1}. Five coordinate $[\mathrm{Cu_2X_2L_2(CO)}]$ studied here also encounters ν_{CO} values of 2063—2088 cm^{-1}. These terminal CO provides no ν_{CO} values characteristic of the five-coordinate form. The stretching frequencies of CO coordinated to $\mathrm{Cu^I}$ seem to have no evident correlation with a coordination number and geometry around copper, such as tetrahedral or square-pyramidal. Then, a question arises. What does the ν_{CO} inform us about carbonyl copper(I) complexes? It is worth noting that most of carbonyl copper(I) complexes are ternary ones containing Cu, CO, and L. On the basis of the discussion in the previous section, we are now in a position to focus on the ν_{CO} in relation to the Cu–CO bonding influenced by L through the Cu–L bonding. This effect of the coordinated ligand should be examined by use of a series of structural analogs of carbonyl copper(I) complexes in order to exclude the contribution of other structural factors. We have explored the Cu–CO bonding of $[\mathrm{Cu_2X_2L_2(CO)}]$ with the aid of the formation constants of carbonyl copper(I) complexes,[1] which depend on the coordinated ligands and halide ions. We now refer to monocarbonyl copper(I) complexes studied here. These are relevant to inquire into the nature of Cu–CO bonding as a function of L and X$^-$. Table 3 shows that the ligand L influences the ν_{CO} values appreciably: the CO adduct of **1a** (or **1b**) has a greater ν_{CO} value than that of **1c** while the affinity for CO of these complexes is cataloged with the increasing order **1a**<**1c** (Table 2). This is accounted for by the π-acceptor capability of phen derivatives. As is discussed in the previous section, 5-Cl-phen π encounters stronger π back-bonding from copper(I) ion than non-substituted phen,

Table 3. CO-stretching frequencies of carbonyl adducts

Precursor complex	ν_{CO}/cm^{-1}	
	In the solid state[a]	In solution[b]
1a	2088	2085
1b	2082	—
1c	2063	2076
1d	2068	—
2a	2066	2075
$[\mathrm{CuI(bpy)}]_2$	2064	—

a) KBr disk. Error limit, ±1 cm^{-1}. b) In acetone. Error limit, ±2 cm^{-1}.

and it should weaken the π back-bonding between copper(I) and CO, leading to the decrease in CO-affinity of the precursor complex. The similar trend in ν_{CO} is also obtained from $[Cu_2X_2L_2(CO)]$ in solution, as shown in Table 3. As is expected from the affinity for CO in Table 2, ν_{CO} obtained for **1d** is similar to that for **1c**. Hence, the effect of the methyl group at 5-position of phen is smaller than that of the halogeno groups.

The ν_{CO} of **2a** containing bpy is close to that of **1c**, both in solution and in solid states. Substitution of I^- for Cl^- in **2a** causes ν_{CO} signal to shift slightly to the lower frequency region. Similar phenomena are also found in $[Cu_2(tmen)_2(CO)_2X]$ ($X=Cl^-$, Br^-, and I^-).[17] This trend in ν_{CO} is reasonable in the light of the fact that $[CuI(bpy)]_2$ has stronger affinity for CO than $[CuCl(bpy)]_2$ (Table 3 in the Ref. 1). This slight change in ν_{CO} upon substitution of halide ion indicates that L is more effective for carbonyl stretching frequencies than halide ions, and this is in good contrast to the fact that a halide ion exerts its drastic effect upon the affinity for CO of the precursor complex. In conclusion, ν_{CO} values are available to investigate the bonding nature of Cu-CO among the structural analogs of carbonyl copper(I) complexes. The ν_{CO} values as well as K_{CO} reflect the competition of CO with L concerning the π-bonding.

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7) In addition to this, a single anodic peak at 0.20 V appears, when the sweep range was set between −1.5 and +1.0 V. This may be ascribed to the two electron redox reaction($Cu^0 \rightleftharpoons Cu^{II}$) of another species which forms under CO atmosphere. This is excluded from the present consideration.

8) In $[Cu_2Cl_2L_2(CO)]$, one is four-coordinate copper(I) and another is five-coordinate copper(I). This type of complex is more flexible than a complex containing a macrocyclic ligand because there are no restraints between two moieties of bpy and bridging halogen atoms. Hence, the most possible structure is tetrahedral and square-pyramidal geometry around copper(I) atoms.

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