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Autoreduction of Copper(II) Complexes of 6,6′-Dialkyl-2,2′-bipyridine and Characterization of their Copper(I) Complexes

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Copper(I) complexes of 6,6′-dialkyl-2,2′-bipyridine (biL: alkyl = methyl, ethyl, and i-propyl) have been synthesized in acetone and ethanol. The resultant complexes are four-coordinate $Cu(biL)_2^+$, having pseudo-tetrahedral geometry. These give an intense metal-to-ligand charge transfer (MLCT) band at the visible region. The wavelength of the MLCT band decreases with the increase in bulkiness of an alkyl group. This is accounted for by the repulsive interaction between the copper atom and an alkyl group. The autoreduction of Cu(II)-6,6′-dialkyl-2,2′-bipyridine complexes in acetone and ethanol has been found. This is proved to be a thermal reaction due to its temperature-dependence. The reaction rate is strongly dependent on the alkyl substituents, a counter anion, and solvent. This reaction prefers ClO_4^- to Cl^- as a counter ion of copper(II): moderately strong Cu–Cl bond inhibits the formation of $Cu(biL)_2^{2+}$. The substituents influence remarkably on the rate, which increases in the following order, methyl ⩾ ethyl > i-propyl. This is significantly associated with the precursor copper(II) complex.

Introduction

Copper(I) complexes are usually air-sensitive and are readily oxidized by dioxygen. Hence, they are synthesized under inert atmosphere. Several copper(I) complexes [1], including phosphines, arsines, thiocarbamates and the cyanide ion, are very stable, indicative of high redox potentials. These ligands often reduce copper(II) halides to form their copper(I) complexes [1]. 2,9-Dimethyl-1,10-phenanthroline (dmp) and 6,6′-dimethyl-2,2′-bipyridine (dmbp) complex copper(I) ions to form very stable copper(I) complexes in non-aqueous solvents. The X-ray structure [2] of the dmbp copper(I) complex displays the pseudotetrahedral structure, which is due to the repulsive interaction between methyl groups of coordinated neighbouring ligands. It is well-known that the tetrahedral geometry prefers Cu^I to Cu^{II}, this leading to a high redox potential of a copper(II) complex. Thus copper(II) complexes of dmbp and, similarly dmp, may act as strong oxidizing agents. The reduction of Cu^{II}–dmp complexes has so far been investigated by use of reducing agents such as thiocyanate [3] and hydrogen peroxide [4], and with the aid of UV light [5, 6].

The question then arises: is the Cu^{II} of the dmp and dmbp complex reduced without any reducing agents and UV light? We found here the autoreduction of the Cu^{II}–dmbp (or dmp) complex in non-aqueous solvent with no aid of UV light. Hence, this manuscript concerns the synthesis and characterization of Cu^I and Cu^{II} complexes with bpy- and phen-containing sterically-hindered alkyl groups. The reduction of their Cu^{II} complexes is presented and the relationship between the reduction rate and bulky substituents is examined. Furthermore, we elucidate the factors governing this reduction reaction.

Experimental

Materials

Reagent grade copper(I) chloride was purified according to the literature [7]. $[Cu(CH_3CN)_4]ClO_4$ was prepared in the usual way [8], and recrystallized from ether under nitrogen. Reagent grade copper(II) perchlorate and chloride were also recrystallized from water. Acetone and ethanol were dried and distilled before use. Preparation of Cu(I) complexes was accomplished under a nitrogen atmo-

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TABLE I. Absorption Maxima and Extinction Coefficients[a] of Copper(I) Complexes of 2,2′-Bipyridine Derivatives.

Metal Source	Ligand	Solvent	λ_{max} (nm)	ϵ_{max} ($mol\ l^{-1}\ cm^{-1}$)
CuCl	bpy	acetone	440	2400[b]
	dmbp		455	3700
	debp		450	2000
	dpbp		445	2000
$[Cu(CH_3CN)_4]ClO_4$	bpy	acetone	440	4800[b]
	dmbp		455	6000
	debp		450	5000
	dpbp		445	5400
CuCl	bpy	ethanol	440	4800[b]
	dmbp		455	5900
	debp		450	5200
	dpbp		445	5600
$[Cu(CH_3CN)_4]ClO_4$	bpy	ethanol	440	5400[b]
	dmbp		455	5400
	debp		450	5600
	dpbp		445	5700

[a] Error limit, ±300. [b] Ref. [10].

sphere. Nitrogen gas with a high purity (99.9995%) was used.

2,9-Dimethyl-1,10-phenanthroline(2,9-dmp) and 6,6′-dialkyl-2,2′-bipyridine (6,6′-R_2-bpy) were obtained as follows. 2,2′-Bipyridine(bpy) and 1,10-phenanthroline(phen) were commercially available. 6,6′-Dimethyl-2,2′-bipyridine (dmbp), 6,6′-diethyl-2,2′-bipyridine(debp), and 6,6′-di(i-propyl)-2,2′-bipyridine (dpbp) were synthesized [9] from 2-methylpyridine, 2-ethylpyridine, and 2-(i-propyl)pyridine, respectively. 2-Methylpyridine and 2-ethylpyridine were commercially available. 2-(i-propyl)pyridine was prepared from 2-ethylpyridine. The purity of these compounds were checked optically and by ^1H NMR. 2,9-Dimethyl-1,10-phenanthroline was purchased from DOJIN LTD.

The Cu(I) complex of dmbp was prepared as follows: 3.0×10^{-5} mol of $[Cu(CH_3CN)_4]ClO_4$ (or CuCl) was added to 100 ml of ethanol (or acetone) solution containing 6.0×10^{-5}–1.2×10^{-4} mol of dmbp, and the mixture was stirred under nitrogen at 25 °C. The progress of the formation reaction was monitored by visible spectra. The other Cu(I) complexes were prepared in a similar way. The pKa values were determined spectrophotometrically. pH was adjusted by use of 0.1 *M* CH_3COOH/0.1 *M* CH_3COONa.

The Cu(II) complex of dmbp was prepared by the addition of 100 ml ethanol (acetone) solution containing 4.0×10^{-5}–4.0×10^{-4} mol of dmbp to 1.0×10^{-5}–1.0×10^{-4} mol of $Cu(ClO_4)_2 6H_2O$ (or $CuCl_2$-$2H_2O$). The solution was degassed by bubbling with nitrogen. The quantitative determination of $Cu(dmbp)_2^+$ was made by visible spectrophotometry with the aid of the MLCT band of 455 nm. The solution was stored in the dark during the progress of the reduction reaction. The same solution was also made under exposure to air and in the dark: air proved to have no effect on the reaction. The other samples containing the complexes of dmp, debp, and dpbp were examined in a similar way.

Visible spectra were recorded on a Hitachi 200-10 spectrometer. Samples were transferred anaerobically into a cuvette with a tight stopcock (10 mm path length for measurements of 300–500 nm region, and 100 mm path length for 600–800 nm region).

Results and Discussion

Metal-to-Ligand Charge Transfer (MLCT) Bands

The Cu(I) complexes of bpy and its derivatives, $Cu(biL)_2$, give an intense MLCT band at 440–455 nm, which is a good indicator of the formation of Cu(I) complexes. The λ_{max} does not show the solvent-dependence. The absorbance of the MLCT band of $Cu(biL)_2^+$ is saturated when small excess of biL is added to the ethanol solution, as well as in the case of non-substituted bpy [10]. This reveals that biL has large stability constants for copper(I) ion in ethanol. The observed wavelength (λ_{max}) and extinction coefficient (ϵ_{max}) of the MLCT bands are listed in Table I.

Table I reveals that the ϵ_{max} value of copper(I) complexes in solution is small in comparison with those in ethanol. This leads us to expect that Cu(biL)$_2$ is not completely formed in acetone. Further addition of excess biL, however, causes no appreciable increase in absorbance. It has been demonstrated [10] that bpy and phen react with CuCl to form a dimer copper(I) complex such as [(biL)CuCl$_2$Cu(biL)], in acetone, which has relatively low ϵ value. In the case of CuCl/(6,6'-R$_2$-bpy in acetone, a similar dimer complex may form to some extent, and the equilibrium of monomer–dimer exists.

According to ϵ_{max} value in Table I, Et and i-Pr derivatives, which show relatively low ϵ_{max} value, favor dimer. The structural difference between monomer and dimer is well reflected by the ϵ_{max} value, while λ_{max} is non-sensitive. It has been elucidated that the cleavage of the Cu–Cl bond, and thus the formation of monomer, is promoted by polar or donor solvents such as alcohols [10]. This study also uses ethanol as a solvent. In this case, the observed ϵ_{max} displays similar values between two cases of CuCl and [Cu(CH$_3$CN)$_4$]ClO$_4$. Consequently, from both metal sources the monomer complex of 6,6'-R$_2$-bpy studied here also forms in ethanol.

It is worth noting that the λ_{max} values of the MLCT band depend on the ligand used, indicating the significant contribution of the alkylsubstituents. The λ_{max} values increase in the order H < i-Pr < Et < Me. The substituents have three effects on the copper(I) complexes: the geometry around the copper atom, the Cu–N bond length, and the electronic properties of the donor atom through the bonds. The pKa values of bpy, dmp, debp and dpbp are 4.26, 4.90, 4.95, and 4.98, respectively. These values indicate a gap between bpy and alkyl substituted bpy, while there is little difference among substituted bpy.

It is worth noting that although there are large differences in pKa of bpy and dpbp, the λ_{max} values of their copper(I) complexes are close to each other. This suggests that the electronic effect of substituents is not principal, leading to the conclusion that the alkyl group used here exerts a minor electronic effect on λ_{max} values among copper(I) complexes. Hence, it is necessary to take into account the difference in λ_{max} among Me, Et, and i-Pr by the alternative factor.

The X-ray structure displays the tetrahedral geometry of Cu^{I}(dmbp)$_2$ having the bond length (Cu–N) of 2.02–2.05 Å [2], a usual bond length among copper(I) complexes even in the presence of the methyl substituent. This indicates that the bulkiness of methyl group causes little elongation of the Cu–N bond length. We have demonstrated [11] that the MLCT band shifts to the low energy region when the overlapping of metal d and ligand π^* orbitals increases and/or their energy gap decreases.

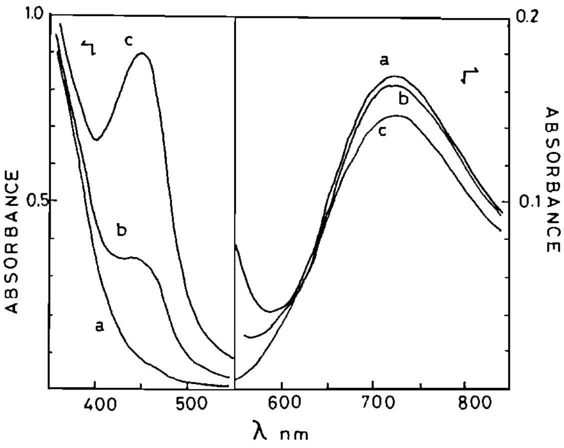

Fig. 1. Visible spectral change due to the autoreduction of Cu(II)–dmbp complex in ethanol. [CuCl$_2$] = 1 m*M*; [dmbp] = 4 mM; (a) after 6 minutes; (b) 5 hours; (c) 35 hours.

The geometry of Cu(dmbp)$_2$ is forced to be of tetrahedral form to avoid the repulsive interaction between substituents of the neighbouring ligands. In Cu(dmbp)$_2$, the extent of overlapping is thus significantly associated with the symmetry of the orbitals, this causing the MLCT band to shift to a lower energy region than that of Cu(bpy)$_2$.

The other alkyl groups, such as Et and i-Pr, allow the MLCT band to shift to the high energy region in comparison with the Me group. In any event, the tetrahedral geometry is not so sensitive to alkyl groups because the repulsive interaction of alkyl groups between coordinated neighbouring bpy is large enough, even for methyl groups. The bulkiness of the group increases remarkably from Me to i-Pr. The group occupying large space may cause R–Cu repulsion, which results in the elongation of Cu–N bond length. The elongation of Cu–N bond leads to the unstabilization of metal complexes, which may be accompanied by a poor π back-bonding. The increasing order in λ_{max} of i-Pr < Et < Me explains well the effect of these alkyl groups. Hence the four-coordinate Cu(biL)$_2$, having sterically-hindered groups, plays an important role of Cu–biL bonding rather than the geometry about copper atom. If the MLCT band concerning π-back bonding is associated with stabilization of copper(I) complex [11], the copper(I)–dmbp complex may be the most stable.

Autoreduction of Cu(II) Complexes of biL

Autoreduction

The Cu(II)–dmbp complex in ethanol gives the d–d transition band at 735 nm. The Cu(II)–bpy complex also has the d–d transition band in the similar region. The remarkable difference between

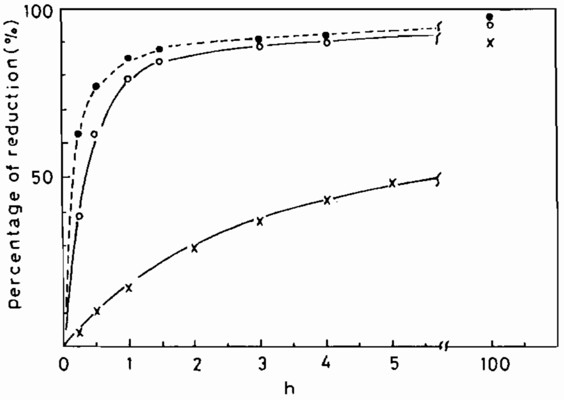

Fig. 2. The effect of substituents on the reduction rate of Cu(II)–6,6′-dialkyl-2,2′-bipyridine complexes in ethanol. (●) dmbp; (○) debp; (×) dpbp.

the Cu(II) complexes of bpy and dmbp is found in the reduction reaction of their Cu(II) ion: the dmbp complex is automatically reduced in ethanol while the bpy complex requires a reducing agent whenever the reduction reaction occurs. Figure 1 shows the time-course of spectral changes, and illustrates the reduction reaction of the Cu(II)–dmbp system. The absorbance of the typical d–d transition band at 735 nm decreases when small excess of dmbp is added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$, and concurrently, the MLCT band at 455 nm which is ascribed to $Cu^I(dmbp)_2$, appears. The maximum absorbance of 455 nm band can be obtained from the absorbance of the corresponding copper(I) complex (Table I). This maximum value must correspond to the final absorbance in this reaction.

On the basis of this value, the percentage of the reduced Cu(I) complex to the initial concentration of copper can be derived. The reduction is accelerated as the concentration of the ligand increases. This is significantly associated with the formation of the Cu(II)–dmbp complex. The reduction of a Cu(II) ion without a reducing agent is quite interesting in relation to the action of ligands having sterically hindered substituents.

The reduction of the Cu(II)–dmp complex by reducing agents such as thiocyanate [3] and hydrogen peroxide [4] have been reported. Ultraviolet light [5, 6] also reduces the Cu(II)–dmp complex in methanol. These reductions, however, require the assistance of reducing agents or UV light. The characteristics of the reduction which we have found is that the reduction of Cu(II)–dmp in ethanol proceeds without reducing agents and light source. This type of autoreduction of Cu(II) complexes has been found in Cu(II) complex of 8-dimethylarsinoquinoline [1, 13].

Substituent Effect

In order to obtain the relationship between the reaction rate and the size of alkyl substituent, we have used bpy derivatives substituted by methyl, ethyl, and i-propyl at 6 and 6′ position. The progress of this reaction is monitored by both decreases in absorbances of their d–d bands, and increases in absorbances of their MLCT bands, as mentioned previously. The synchrony of the changes in the absorbances of these two bands was obtained. This exhibits that in this reaction the precursor Cu(II) complex is utilized for the formation of $Cu^I(dmbp)_2$. The influence of substituents upon the reaction rate is well demonstrated in Fig. 2. Inspection of Fig. 2 exhibits that the order in the reduction rate is dmbp ⩾ debp > dpbp. As discussed in the previous section, their Cu(I) complexes have a tetrahedral geometry, characteristic of typical Cu(I) complexes. Alkyl substituents in 6 (or 6′) position forces the structure of the complex to be tetrahedral geometry because the repulsion between alkyl substituents in neighbouring ligands exists. In addition, the bond distance of Cu–N may be responsible for the size of an alkyl group because the large group causes the repulsive interaction between the metal and the group. This interaction significantly influences the stability of both Cu(I) and Cu(II) complexes. The bulky i-propyl group may considerably effect the Cu–N bond distance, leading to the de-stabilization of the complex. The degree of the de-stabilization is greater in Cu(II) complexes than in Cu(I) complexes, because Cu(II) requires a shorter bond length than Cu(I). Hence, the formation of Cu(II)–dpbp complex is less than in the case of dmbp. It is worth noting that the rate in the case of debp is close to that in the case of dmbp (Fig. 2).

Concerning the reduction, debp is almost equivalent to dmbp. On the other hand, the reduction rate in the case of dpbp is considerably slow. Even dpbp, having the larger substituent, quantitatively complexes Cu(I) ion in non-aqueous solvents. On this basis, the slow rate is significantly associated with the formation of the corresponding copper(II) complexes because it is expected that dpbp does not form $Cu(dpbp)_2$ without any barrier. Because bpy derivatives, having sterically-hindered groups, hardly bind metal ions except for copper(I) and iron(II) ions, very hindered dpbp is a good, selective reagent for copper(I).

Solvent Effect

When ethanol was used as solvent, the autoreduction reaction of both $CuCl_2$–dmbp and $Cu(ClO_4)_2$–dmbp complexes proceeded. The former complex, however, encounters slower reaction rates than the latter complex, indicating that the Cl^- anion inhibits the reaction. This is accounted for by the coordination of Cl^- to Cu(II), due to which the

TABLE II. Visible Absorption Bands[a] of Cu^{II}–biL Complexes.

Solvent	biL[b]	Metal Source			
		$Cu(ClO_4)_2 6H_2O$		$CuCl_2 2H_2O$	
ethanol	free	810		900	
	dmp	740	1020	735	1010
	dmbp	735		720	
acetone	free	820		870	
	dmp	746	1065	880	1070
	dmbp	726	1080	910	1060

[a] nm in unit, error limit ±20 nm. [b] Concentration; [biL]/[Cu] = 4.

formation of tetrahedral $Cu(dmbp)_2^{2+}$ is depressed. This role of Cl^- anion is emphasized in the case of acetone solvent. The mixture of $CuCl_2$ and dmbp ([dmbp]/[Cu] = 4) in acetone exhibited no reduction reaction of copper(II). In order to shed light on the factor governing the reduction reaction, d–d absorption bands of the precursor copper(II) complex were measured. Table II lists the d–d absorption bands of $CuCl_2$ and $Cu(ClO_4)_2$–biL systems in two solvents. Inspection of Table II indicates that $CuCl_2$–dmbp (or dmp) in acetone has the d–d absorption band greater than 800 nm. $Cu^{II}(dmp)_2Cl_2$ and $Cu^{II}(dmp)Cl_2$ gives the d–d absorption band at 780 and 790 nm, respectively [14]. Hence, most of dmbp (or dmp) does not complex $Cu^{II}Cl_2$ in acetone. This leads to no reduction reaction.

We have previously demonstrated [10, 12] that acetone, which has low polarity and poor coordination ability, does not promote the cleavage of the Cu^I–Cl bond, and hence copper(I) complex of bpy or phen accompanies Cu–Cl bonding in acetone. This phenomenon is also analogous to that of the $CuCl_2$/dmbp/acetone system. On the other hand, in the case of $Cu(ClO_4)_2$–dmbp, the band at 746 nm appears even in acetone, and consequently the Cu–dmbp complex forms appreciably. This is well illustrated by the absorption maxima in Table II.

In addition to the criterion of whether the autoreduction of copper(II) proceeds or not, the dependence of the reduction rate on substituents is to be clarified. In $Cu(ClO_4)_2$dmbp system, the reduction occurs both in acetone and ethanol, but the rate is slower in the former solvent. The d–d absorption band in Table II gives no significant reasoning on the differences about the behavior of two reactions. Although physical properties of solvent should be mentioned, the role as a substrate of solvent can be considered. An interestingly suggestive case is found in the oxidation of methanol as a solvent in photoinduced reduction of $Cu^{II}(dmp)$ [5, 6]. In the present study, the increase in acetaldehyde was also detected as the reduction of copper(II) complexes in ethanol proceeded. On this tentative result, the difference between two solvents is associated with the oxidized substrate which is involved in the reduction of copper(II), and from which an electron is transferred into copper(II) in copper(II) complexes.

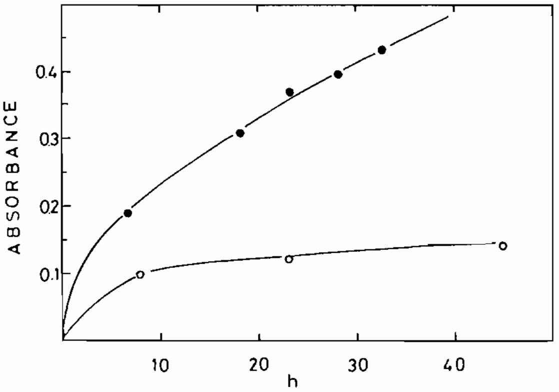

Fig. 3. Temperature effect on the reduction rate of Cu(II)–dmp complex in ethanol. [$CuCl_2$] = 0.1 mM; [dmp] = 0.4 mM; (○) 25 °C; (●) 40 °C.

Lastly, we have examined the reduction in order to elucidate the thermal reaction or photoreaction. When the $Cu(ClO_4)_2$–dmbp system is placed in the dark, the reduction reaction is unchanged. This indicates that the reduction is thermal reaction. Figure 3 shows the temperature effect on this reaction rate. High temperature apparently accelerates the rate, also indicative of a thermal reaction.

There are several reduction reactions of copper(II) complexes [1], whose coordinated ligands take an important role in the reduction of copper(II), *i.e.*, arsines, phosphines and the cyanide ion. Some reduction is significantly associated with electronic properties of the donor atoms of ligands. In this manuscript, the reduction of copper(II) is not attributed to the donor atoms of ligands (that is, the electronic properties) but to the geometry of a complex, which is exclusively defined by the sterically hindered group of a ligand. Hence, if we can control the geometry of a complex, which prefers Cu^I to Cu^{II}, the reduction of copper(II) complexes, and thus, synthesis of copper(I) complexes, is made with ease.

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