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Spectroscopic Studies of Copper(I) Complexes of 1,8-Di(2-pyridyl)-3,6-dithiaoctane in a Nonaqueous Solvent. The Halide-ion Effect on Their Structure

Susumu KITAGAWA,* Megumu MUNAKATA, and Shoji OKADA
Department of Chemistry, Faculty of Science and Technology, Kinki University,
Kowakae, Higashi-Osaka 577

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The complexes of 1,8-di(2-pyridyl)-3,6-dithiaoctane(pdto) with CuX(X=Cl and Br) and $[Cu(CH_3CN)_4]ClO_4$ have been synthesized in chloroform, methanol, ethanol, and acetone. Their absorption spectra show an intense metal-to-ligand charge-transfer band at 307 nm: This band is assigned to pyridyl nitrogen←Cu. $[Cu(pdto)]^+$ (**1**) has been prepared from $[Cu(CH_3CN)_4]ClO_4$, its pdto acting as a four-coordinate ligand. CuX reacts with pdto to yield two complexes: One is **1**, and the other is [CuX(pdto)] (**2**). Both complexes are four-coordinate, but in the **2** one of the two pyridyl groups is dissociated. The complex **2** is unstable and is oxidized by oxygen. Neither complex reacts with CO, indicating the tight binding of pdto with Cu(I). The **1** and **2** are equilibrated in solution. The ^{1}H NMR spectra well demonstrate that **2** is dominant in chloroform and that **1** is the principal form in alcohol, while the **1**/**2** ratio is 3/7. This solvent-dependence is ascribed to the coordination ability and/or polarity of the solvent.

Recent interest in copper proteins has been focused on the copper(I) complexes containing several types of donor atoms. In addition to ligands having N and O donor atoms, copper(I) complexes with ligands containing sulfur have been synthesized and characterized.[1–7] 1,8-Di(2-pyridyl)-3,6-dithiaoctane (pdto), which is a quadridentate N_2S_2-type ligand, gives both copper(I) and copper(II) complexes. The crystal structure of their perchlorate and hexafluorophosphate have been determined by X-ray crystallography.[7] The geometry of this copper(I) complex is tetrahedral, characteristic of usual four-coordinate copper(I) complexes. This suggests that the Cu(I) complex of pdto is four-coordinate, the set of donor atoms being of the N_2S_2-type. However, in the presence of a halide ion(X^-), all the donor atoms of pdto do not necessarily bind the Cu(I) ion in a nonaqueous solvent. We have previously pointed out[8,9] that copper(I) complexes prepared from CuX in a nonaqueous solvent are accompanied by halide ion-bindings, and sometimes their bridging, leading to a binuclear structure. In this sense, both the copper(I) starting material and the solvent used play an important role in the formation of the copper(I) complexes. It is of significance to substantiate the coordination chemistry of CuX–pdto systems in various solvents. The purpose of this work is to elucidate the structure of copper(I) complexes prepared from CuX and pdto, and their equilibria in solution, with the aid of absorption and ^{1}H NMR spectroscopy.

Experimental

Materials. Reagent-grade copper(I) chloride and bromide were purified according to the literature.[11] All the materials were dried *in vacuo* (75—100 °C). The $[Cu(CH_3CN)_4]ClO_4$ was prepared in the usual way,[12] and recrystallized from ether under nitrogen. The $AgClO_4$ was purchased from Wako LTD., and was used without further purification. 1,8-Di(2-pyridyl)-3,6-dithiaoctane(pdto) was prepared by the methods of Goodwin and Lions.[13]

The acetone, chloroform, methanol, and ethanol were all dried and distilled before use.

Preparation of $[Cu(pdto)]ClO_4$. A 50-cm^3 portion of a 2.5×10^{-5} mol pdto chloroform solution was added to 7.6 mg (2.5×10^{-5} mol) of $[Cu(CH_3CN)_4]ClO_4$ under nitrogen, and this mixture was stirred for 1 h. A colorless solution of $[Cu(pdto)]ClO_4$ was thus formed. This solution was transferred anaerobically into a cuvette (1 cm path length) with a stop cock, and the absorption spectrum was measured by means of a Hitachi 200-10 spectrometer. The complex in the other solvent was prepared in a similar way.

Preparation of [CuX(pdto)]. A 50-cm^3 portion of a 2.5×10^{-5} mol pdto chloroform solution was added to 2.5×10^{-5} mol of CuX under nitrogen, and this mixture was stirred for 3 h. In other solvents, the copper complexes were prepared in a similar way. A 10.4 mg (5.0×10^{-5} mol) of $AgClO_4$ was added to the resultant solution. The solution was stirred for 0.5 h and filtered off under nitrogen, and the filtrate was transferred anaerobically into a cuvette for the measurement of the absorption spectra.

Physical Measurements. The ^{1}H NMR spectra were measured on a JEOL FX200 FT NMR spectrometer. Between 256 and 320 transients were accumulated with the use of a 13-μs pulse (90°). 4 K data points were collected over the band-width of 2500 kHz. The temperature was set at -90 ± 2 °C (acetone-d_6 and methanol-d_4) and -59 ± 1 °C (chloroform-d).

The conductances were measured at 25 °C with a Kyoto Elec. Co. Model CM-05, and a cell with two platinum electrodes.

Cyclic voltammetric measurements were made with a Hokuto Model HA104 potentiostat/galvanostat driven by a model HB107A function generator. A Pt wire served as the working electrode, while a Pt coil was used as the counter electrode. A commercial saturated calomel electrode (SCE) was utilized as the reference electrode. Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte.

Results and Discussion

$[Cu(pdto)]ClO_4$. Figure 1(1) shows the absorption spectrum of $[Cu(pdto)]ClO_4$ in the region of 300—500 nm. Only a single band appears at 307 nm when 1 equivalent of pdto is added to $[Cu(CH_3CN)_4]ClO_4$ in $CHCl_3$. The intensities of this band did not increase further upon the addition of an excess of pdto, indicating that pdto has a high

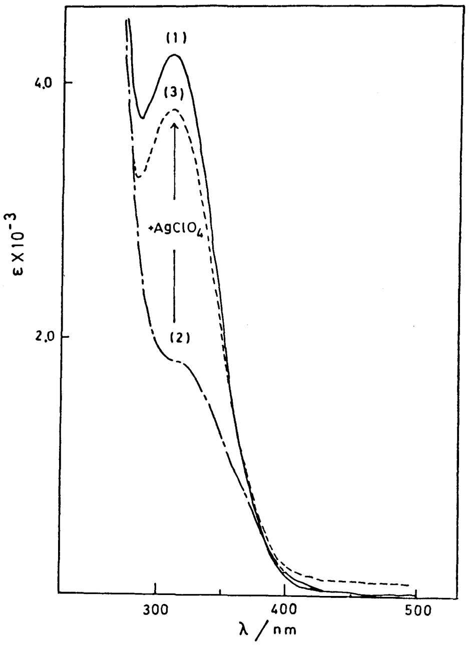

Fig. 1. Absorption spectra of a $CHCl_3$ solution. (1): 5.0×10^{-4} M† of [Cu(pdto)]ClO_4, (2): 5.0×10^{-4} M of [CuCl(pdto)], (3): the addition of 1.0×10^{-3} M of $AgClO_4$ to a solution of (2).

affinity for the Cu(I) ion and yields a [Cu(pdto)]ClO_4 quantitatively. The pdto itself has no absorption band in this region. The dithioether–Cu(I) complexes, such as [Cu(2,5-dithiahexane)$_2$]BF_4 and [Cu(3,6-dithiaoctane)$_2$]BF_4, have no absorption bands in this region.[2] This leads to the conclusion that there is no charge-transfer band between thioether S and Cu(I) in the region of 300—800 nm.[14] We have elsewhere demonstrated that [Cu(py)$_4$]ClO_4 reveals, at 330 nm an intense band, which is assigned to the metal-to-ligand charge transfer(MLCT) band as py←Cu(I).[9] Consequently, the band at 307 nm of [Cu(pdto)]ClO_4 is also ascribed to the MLCT band of py(pdto)←Cu(I).

[Cu(pdto)]ClO_4 was also prepared in several solvents, such as methanol, ethanol, and acetone. The values of λ_{max} and ε_{max} are listed in Table 1, together with the molar conductivities (Λ_M) of the solution of [Cu(pdto)]ClO_4. In the case of acetone, the MLCT band is covered with the absorption peak of acetone itself. As is shown in Table 1, the λ_{max} value of the MLCT band is unaffected by the solvent used, while the ε_{max} value shows a solvent-dependence which falls within 4.0—4.5×10^3 M^{-1} cm^{-1}. A solution of [Cu(pdto)]ClO_4 gives molar conductivities of 1.1, 104, 46, and 160 for $CHCl_3$, CH_3OH, C_2H_5OH, and $(CH_3)_2CO$ respectively, which are characteristic of a typical 1:1 electrolyte.[10] This strongly supports the dissociation of the ClO_4^- ion and the coordination of the four donor atoms(N_2S_2) of pdto. Hence, [Cu(pdto)]ClO_4 prepared from [Cu(CH_3CN)$_4$]ClO_4 and pdto in the above solvents is a four-coordinate monomer, just as in the solid state.[7]

TABLE 1. ABSORPTION MAXIMA, EXTINCTION COEFFICIENTS OF THE MLCT BAND, AND MOLAR CONDUCTIVITIES OF [Cu(PDTO)]X AND [CuX(PDTO)]

Solvent	X	λ_{max} / nm[a]	ε_{max} / M^{-1} cm^{-1} [b]	Λ_M / Ω^{-1} cm^2 mol^{-1}
$CHCl_3$	Cl	314[d]	1.9×10^3	—[e]
	Br	314[d]	1.9×10^3	—[e]
	ClO_4	309	4.1×10^3	1.1
CH_3OH	Cl	307	4.5×10^3	85
	ClO_4	307	4.5×10^3	104
C_2H_5OH	Cl	307	4.0×10^3	33
	Br	307	4.0×10^3	34
	ClO_4	307	4.0×10^3	46
$(CH_3)_2CO$	Cl	—[f]	—[f]	71
	Br	—[f]	—[f]	61
	ClO_4	—[f]	—[f]	160

a) Error limit, ±2 nm. b) Error limit, $\pm0.1\times10^3$ M^{-1} cm^{-1}. c) The standard Λ_M values of a typical 1:1 electrolyte are 95(CH_3OH), 41(C_2H_5OH), and 120((CH_3)$_2$CO) Ω^{-1} cm^2 mol^{-1}. Ref. 10. d) The absorption peak appears as a shoulder. e) The Λ_M value is very small (<1 Ω^{-1} cm^2 mol^{-1}). f) The absorption peak is covered by that of acetone.

The ^1H NMR spectra were measured for [Cu(pdto)]ClO_4 in several solvents. All the ^1H NMR spectra at room temperature are influenced by the chemical-exchange effect to give unresolved broad signals for each proton of pdto. At a low temperature, the chamical exchange is depressed and the ^1H NMR spectra exhibit well-resolved signals of 2-pyridyl group of pdto, but the methylene protons still show unresolved signals because of collapsing to each other. Figures 2(1) and (4) show the aromatic region of the ^1H NMR spectra in the acetone solution, indicating the unbound and bound 2-pyridyl groups of pdto respectively. The unbound 2-pyridyl group gives four signals which can be readily assigned to 6,4,3,5-H(from downfield to upfield) with the aid of the double-resonance technique. When pdto is coordinated to Cu(I), the 2-pyridyl group signals shift downfield. The protons in the 3 and 5 positions are almost collapsing, but the 3-H signal has a slight bias toward downfield. The assignments of these signals were done with the aid of the double-resonance technique; the signals of 8.73, 8.14, 7.69, and 7.67 ppm are 6, 4, 3, and 5-H respectively. Four similar signals with the same intensity are also observed in the cases of methanol (Fig. 4) and chloroform.

Halide Ion-binding. *Absorption Spectra*: The pdto also reacts with CuX(X=Cl and Br) in $CHCl_3$, CH_3OH, C_2H_5OH, and $(CH_3)_2CO$ to yield clear solutions. Both methanol and ethanol solutions give the MLCT band at 307 nm with an ε_{max} value of *ca.* 4×10^3 M^{-1} cm^{-1}, which is in good agreement with that of [Cu(pdto)]ClO_4. It is worth noting that the MLCT band of the $CHCl_3$ solution has a λ_{max} value of 314 nm and an ε_{max} value of 1.9×10^3 M^{-1} cm^{-1}, both different from those of [Cu(pdto)]ClO_4 in $CHCl_3$. The ε_{max} is anomalously small. The large excess of pdto did not increase the absorbance, indicating that the ε_{max} of 1.9×10^3 M^{-1} cm^{-1} is characteristic of [CuCl(pdto)]. The difference in both ε_{max} and λ_{max}

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† 1 M = 1 mol dm^{-3}.

is associated with the halide ion-binding to Cu(I).

In order to demonstrate the halide ion-binding, we use a comparable amount of $AgClO_4$,[8] which will break down the Cu–Cl bond if it exists. The white precipitate of AgCl appeared rapidly upon the addition of $AgClO_4$ to the solution of CuX and pdto, resulting in a spectrum similar to that of [Cu(pdto)]ClO_4 (Fig. 1). This drastic change in the MLCT band would not occur without halide ion-binding to Cu(I). This reaction, thus, follows Eq. 1;

$$[CuX(pdto)] + AgClO_4 \longrightarrow [Cu(pdto)]ClO_4 + AgClO_4 \qquad (1)$$

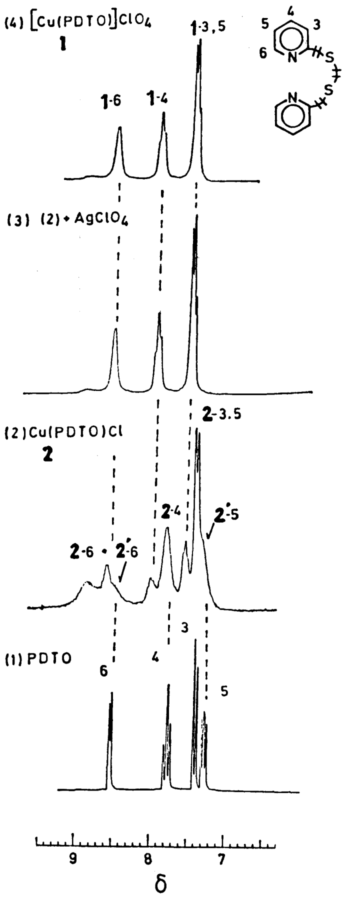


Fig. 2. ^1H NMR spectra at −90 °C of an acetone-d_6 solution.
(1): 5.0×10^{-3} M of pdto, (2): equimolar quantities (5.0×10^{-3} M) of CuCl and pdto, (3): the addition of 1.0×10^{-2} M $AgClO_4$ to a solution of (2), (4): 5.0×10^{-3} M of [Cu(pdto)]ClO_4.

If the precursor complex, [CuX(pdto)], is a four-coordinate, one of the donor atoms(N_2S_2) of pdto should be dissociated; in this sense, a N_2S or NS_2 donor set may be considered. The coordination of two N and one S atoms is unfavorable, because the complex contains a very unstable chelate ring of eight members. The NS_2 is most feasible for explaining the spectral change; the rupture of the Cu–X bond by Ag^+ is followed by the formation of the bonding of Cu–py, and, consequently, the absorbance of the MLCT band increases. The alcohol solution undergoes a minor change in absorbance upon the addition of $AgClO_4$.

Molar Conductivities: The molar conductivities, Λ_M(X) (or $\Lambda_M(ClO_4)$), of a solution containing equimolar amounts of CuX and pdto(or $[Cu(CH_3CN)_4]ClO_4$ and pdto) have been measured (Table 1). Table 1 shows that the Λ_M(X) of the acetone solution is much smaller than the $\Lambda_M(ClO_4)$, indicative of the presence of halide ion-binding. On the other hand, the alcohol solution also gives a Λ_M(X) smaller than the $\Lambda_M(ClO_4)$. This difference is possibly attributable to the difference in the mobilities of ClO_4^- and Cl^- in alcohol. This trend has been found in the systems containing *n*-Bu_4NClO_4 or *n*-Bu_4NCl in *n*-propanol.[15] Otherwise, the difference in Λ_M might arise from the presence of species having a coordinated halide ion, of which minute quantities are demonstrated by the ^1H NMR spectra to be considered below. The $\Lambda_M(ClO_4)$ of the $CHCl_3$ solution is quite small (1.1 Ω^{-1} cm^2 mol^{-1}). Unfortunately, the value Λ_M(X) is less than 1 Ω^{-1} cm^2 mol^{-1}, undetectable with our instrument, also implying the presence of a coordinated halide ion.

^1H NMR Spectra: The ^1H NMR spectra were measured in order to elucidate the species in solution. Figure 2(2) shows the ^1H NMR spectra at −90 °C of [CuCl(pdto)] in acetone. This spectrum is quite different from that of [Cu(pdto)]ClO_4 (Fig. 2(4)); three types of 2-pyridyl signals were observed. Type-1 signals have the same chemical shifts as those of Fig. 2(4), indicating the formation of [Cu(pdto)]Cl. Type-2 signals are ascribed to coordinated 2-pyridyl of [CuCl(pdto)]. The last Type-2′ corresponds to

TABLE 2. OBSERVED ^1H NMR SHIFTS[a] OF [Cu(PDTO)]ClO_4 AND [CuCl(PDTO)]

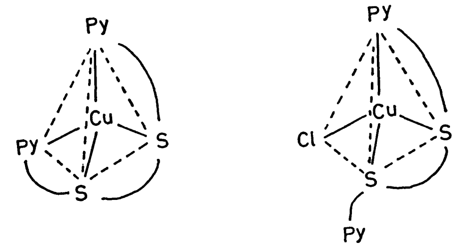
Complex	Solvent	6-H	5-H	4-H	3-H
pdto	$CDCl_3$[b]	8.58	7.23	7.76	7.25
	CD_3OD[c]	8.46	7.34	7.85	7.47
	$(CD_3)_2CO$[c]	8.57	7.35	7.85	7.47
[Cu(pdto)]ClO_4	$CDCl_3$[b]	8.51	7.47	7.92	7.49
	CD_3OD[c]	8.57	7.51	7.97	7.53
	$(CD_3)_2CO$[c]	8.73	7.67	8.14	7.69
[CuCl(pdto)]	$CDCl_3$[b]	8.83[d]	7·39[d]	7.83[d]	7.44[d]
	$(CD_3)_2CO$[c]	8.98[d]	7.51[d]	7.92[d]	7.53[d]
[CuBr(pdto)]	$(CD_3)_2CO$[c]	9.02[d]	7.56[d]	7.94[d]	7.46[d]

a) In ppm from TMS. b) Measured at −59 °C. c) Measured at −90 °C. b) The shifts of a bound py are presented; the shifts of an unbound py are similar to those of metal-free py.

Table 3. Concentration ratio[a)]

	Solvent	I	II
CuCl[b)]	$CDCl_3$	0	100
	CD_3OD	100	0
	$(CD_3)_2CO$	30	70
CuBr[c)]	$(CD_3)_2CO$	6	94

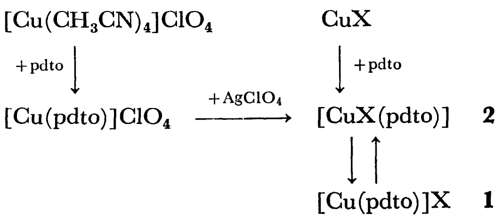
a) Obtained from the ^1H NMR spectra, in percentages. b) [CuCl]/[pdto] = 1. c) [CuBr]/[pdto] = 1.



1 **2**

Fig. 3. Proposed structure of $[Cu(pdto)]^+$ (**1**) and $[CuX(pdto)]$ (**2**).

the signals of which shifts are similar to those of a metal-free 2-pyridyl. The computer simulation of the three types of signals gives the ratios of intensities of the Type 1, 2, and 2′ signals; thus, $r_{1/2}=3/7$ and $r_{2/2'}=1$ are obtained. The equal intensities of Type-2 and Type-2′ signals indicate the coordination of pdto as a NS_2 donor set; one 2-pyridyl of pdto is dissociated, as has been discussed in the previous section, and of course, a five-coordinate species is avoided. Upon the addition of $AgClO_4$ as well as in the case of absorption spectra, the Type-2 and Type-2′ signals disappear and the intensity of the Type-1 signals increases. The final spectrum well corresponds to that of $[Cu(pdto)]ClO_4$ (Figs. 2(3) and (4)). These ^1H NMR spectra excellently illustrate the halide ion-binding to Cu(I) and the formation of Cu-2-pyridyl bonding after the removal of the halide ion by Ag^+. We are now in a position to present a structure which best explains the spectral properties obtained here: The proposed structure of [CuX(pdto)] is Structure **2** in Fig. 3, where one 2-pyridyl group of pdto is coordinated to Cu(I), while the other is dissociated. $[Cu(pdto)]^+$ is also presented as Structure **1** in Fig. 3. The ^1H NMR spectrum of a $CDCl_3$ solution exhibits the signals of [CuCl(pdto)], but no signals of [Cu(pdto)]Cl, indicating the formation of [CuCl(pdto)] to a great extent. In this case, $AgClO_4$ also influences this spectrum and provides a spectrum similar to that of $[Cu(pdto)]ClO_4$ in $CDCl_3$. The observed ^1H NMR shifts are listed in Table 2. On the other hand, the ^1H NMR spectrum of CD_3OD solution with CuCl and pdto is just the same as that of $[Cu(pdto)]ClO_4$ (Fig. 4). Hence, CuCl reacts with pdto in alcohols, mostly yielding [Cu(pdto)]Cl. This is also suggested by the same values of λ_{max} and ε_{max} between CuCl and $[Cu(CH_3CN)_4]ClO_4$.



Scheme 1.

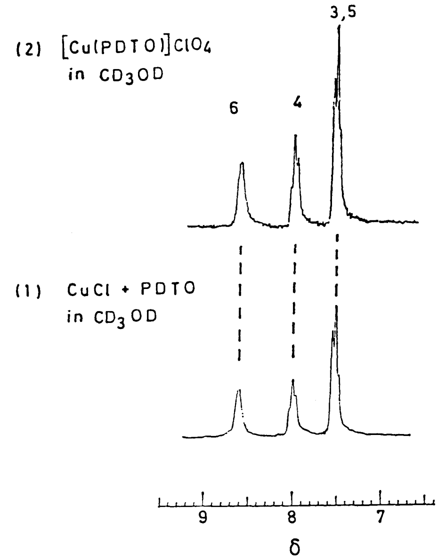


Fig. 4. ^1H NMR spectra at −90 °C of a methanol-d_4 solution.
(1): Equimolar quantities (5.0×10^{-3} M) of CuCl and pdto, (2): 5.0×10^{-3} M of $[Cu(pdto)]ClO_4$.

Solution Equilibria: The absorption, ^1H NMR spectra, and molar conductivities characterize the reaction of CuX with pdto, comprising a part of Scheme 1. The equilibrium between Complex **1** and **2** is dependent on the solvent used. Complex **2** dominantly forms in $CHCl_3$, while Complex **1** selectively forms in alcohol. In acetone, Complex **2** is in equilibrium with Complex **1**. The ^1H NMR spectra (Fig. 2) provides a **1**/**2** ratio of 3/7. Chloroform has a lower polarity than acetone, as has been characterized by the dielectric constant, ε. Methanol has the greatest ε value among the four solvents used. The order is 32.7 (methanol) > 24.6(ethanol) > 20.7(acetone) > 4.8(chloroform).[15)] This order is also considered to be that of the coordination ability of the solvents. On this basis, the step of Cu–X bond fission is likely to be significant in the complex formation. In alcohol, its bulk properties and/or its coordination ability allow the Cu–X bond fission to occur readily and promote the coordination of the four donor atoms (N_2S_2) of pdto. On the other hand, in a non-polar solvent such as chloroform, halide ion-binding to Cu(I) appears to be tight: Hence, it is not broken even by the 2-pyridyl of pdto. The similar halide ion-binding has also been found in the acetone solution of CuX and 2,2′-bipyridine(bpy);[8)] a binuclear $[CuX(bpy)]_2$ preferably forms in acetone, while a monomer $[Cu(bpy)_2]^+$ principally forms in alcohol. Consequently, alcohol is available for the breakdown of the Cu–X bond.

It is to be noted in Table 3 that **1**/**2** ratio is smaller in the case of Br^- than in the case of Cl^-. This indicates that Complex **2** prefers Br^- to Cl^-, the Cu–Br bond being stronger than the Cu–Cl bond. This is reasonable, for CuCl itself is rather more unstable than CuBr upon exposure to air.

The oxidation-reduction potentials of the copper of [CuCl(pdto)] and [Cu(pdto)]ClO_4 in acetone at 25 °C have been measured by means of cyclic voltammetry(CV). [Cu(pdto)]ClO_4 gave a single pair of waves corresponding to the electrode reaction of Cu^I/Cu^{II}, the half-wave potential of which is 0.60 V *vs.* SCE. In the case of an acetone solution containing equimolar quantities of CuCl and pdto, two pairs of waves were observed. The first pair, in the cathodic region, has an $E_{1/2}$ value of 0.60 V *vs.* SCE, indicative of the Cu^I/Cu^{II} reaction of [Cu(pdto)]Cl, while the second, with an $E_{1/2}$ value of 0.49 V, is attributable to the Cu^I/Cu^{II} reaction of [CuCl(pdto)]. Hence, copper(I) states are more stable in [Cu(pdto)]Cl than in [CuCl(pdto)].

Neither [Cu(pdto)]ClO_4 nor [CuCl(pdto)] reacts with CO, as is demonstrated by monitoring the absorption and ^{1}H NMR spectra. This indicates that pdto in both complexes tightly binds the Cu(I) atom, which prevents the substitution reaction, and that they keep the structure, presumably a tetrahedral environment, around the Cu(I) atom, the rigidity of which inhibits the addition reaction and accompanying conformational change.

[Cu(pdto)]ClO_4 is quite stable against oxygen, while [CuCl(pdto)] is gradually oxidized upon exposure to air. This is accounted for by their redox properties obtained from CV. Hence, pdto stabilizes the copper (I) ion when all four donor atoms of pdto bind the Cu(I) ion.

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References

1) P. S. K. Chia, S. E. Livingstone, and T. N. Lockyer, *Aust. J. Chem.*, **19**, 1835 (1966).

2) E. W. Ainscough, A. M. Brodie, and K. C. Palmer, *J. Chem. Soc., Dalton Trans.*, **1979**, 2375.

3) E. N. Baker and G. E. Norris, *J. Chem. Soc., Dalton Trans.*, **1977**, 877.

4) E. N. Baker and P. M. Garrick, *J. Chem. Soc., Dalton Trans.*, **1978**, 416.

5) K. D. Karlin, P. L. Dahlstrom, J. R. Hyde, and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, **1980**, 906.

6) E. W. Ainscough, E. N. Baker, A. M. Brodie, N. G. Larsen, and K. L. Brown, *J. Chem. Soc., Dalton Trans.*, **1981**, 1746.

7) G. R. Brubaker, J. N. Brown, N. K. Yoo, R. A. Kinsey, T. M. Kutchan, and E. A. Mottel, *Inorg. Chem.*, **18**, 299 (1979).

8) S. Kitagawa and M. Munakata, *Inorg. Chem.*, **20**, 2261 (1981).

9) S. Kitagawa, M. Munakata, and A. Higashie, *Inorg. Chim. Acta*, **59**, 219 (1982).

10) W. J. Geary, *Coord. Chem. Rev.*, **7**, 181 (1971).

11) L. F. Andrieth, J. C. Bailar, W. C. Fernelius, W. C. Johonson, and R. E. Kirk, *Inorg. Synth.*, **2**, 1 (1946).

12) P. Hemmerich and C. Sigwart, *Experientia*, **19**, 488 (1963).

13) H. A. Goodwin and F. Lions, *J. Am. Chem. Soc.*, **82**, 5013 (1960).

14) V. M. Miskowski, J. A. Thich, R. Solomon, and H. J. Schugar, *J. Am. Chem. Soc.*, **98**, 8344 (1976).

15) D. F. Evans, J. Thomas, J. A. Nades, and S. M. A. Matesich, *J. Phys. Chem.*, **75**, 1714 (1971).

16) J. A. Riddick and W. B. Bunger, "Technique of Chemistry. II," Wiley-Interscience, New York (1970).