Nuclear Magnetic Resonance Studies of Copper(I) Complexes of Imidazoles. I. Their Preparation, Characterization, Equilibria, and Reaction with Carbon Monoxide

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Various copper(I) complexes with monodentate imidazole(im) have been prepared from $[Cu(CH_3CN)_4]X$ ($X=ClO_4^-$ and PF_6^-) in acetone. Their characterization has principally been made by ^1H NMR spectroscopy. Binary copper(I) complexes are $[Cu(im)_2]^+$ (**2**) and $[Cu(im)_3]^+$ (**3**), while the monoimidazole complex is a ternary two- or four-coordinate complex (**1**). In contrast with **2** and **3**, quantitative formation of $[Cu(im)_4]^+$ (**4**) does not occur in acetone. Even at $[im]/[Cu]<2$, **2** forms more preferentially than **1**. This is due to the linear structure of **2**. **2** and **3** provide stable CO adducts, both of which display complete reversibility. The affinity for CO of **3** is much stronger than that of **2**. Pyrazole copper(I) complexes were also prepared and examined as a comparison with imidazole complexes. Monodentate pyrazole hardly gives two- and three-coordinate complexes. This is attributable to its low basicity in contrast with that of imidazole.

The presence of copper(I)–imidazole binding[1–3] in copper proteins has been demonstrated physicochemically. Keen interest in the relationship between their functions and the structure of a copper(I)–imidazole moiety has prompted the syntheses and characterizations of low-molecular weight copper(I) compounds including ligation from histidine, histamine, imidazole,[4–5] and their derivatives.[6–17] Binary copper(I) compounds having only imidazole are significant in connection with the environment of "type 3" copper moiety[1–3] in copper proteins. Two-coordinate copper(I) compounds of chelating benzimidazole-containing ligands have been isolated, where the copper atom is linearly coordinated by two nitrogen atoms.[9,14] Tetrakis(imidazole)copper(I)[4] has been isolated and the structure has been demonstrated to be tetrahedral. This geometric feature is not necessarily rare in copper(I) compounds[18–23] as well as in silver(I) and mercury(II) compounds.[24] On the other hand, no binary three-coordinate complex of imidazole has ben found. Regarding a structural model of deoxyhemocyanin,[3] the synthesis and characterization of three-coordinate imidazole complexes are of great importance; furthermore, a detailed knowledge of their behavior in solution, such as equilibria and reactivity, is valuable.

In this work, we try to challenge the preparation of various coordination copper(I) compounds of imidazole. Another purpose of this work is to explore the coordination chemistry of an imidazole–copper(I) system by inquiring into the chemical reactivity in a solution together with equilibrium. Finally, we aimed at the establishment of a methodology to investigate a copper(I)–imidazole system since ESR and the visible absorption spectroscopy are of very little use in these complexes. NMR spectroscopy is a very important tool for copper(I) complexes in solution, and helps to answer such questions as to what and how many donors are coordinated to copper(I).[25,26] Consequently, the characterizations of the imidazole–copper(I) compounds studied here are due to NMR spectroscopy.

Experimental

Materials. $[Cu(CH_3CN)_4]ClO_4$ and $[Cu(RCN)_4]ClO_4$ ($R=C_2H_5$ and C_6H_5) were synthesized from copper(I) oxide[27] and copper wire,[28] respectively. $[Cu(CH_3CN)_4]PF_6$ was also prepared by a method described in the literature.[29] The obtained compounds were all checked by elementary analysis and optical absorption method with the aid of the absorbance at 440 nm of a derived bis(2,2′-bipyridine)copper(I) in acetone ($\varepsilon_{max}=4800\ M^{-1}\ cm^{-1}(1\ M=1\ mol\ dm^{-3})$).[30] Copper(I) oxide and copper wire were commercially available, refreshed with dilute HCl, washed with water and dried before use. Imidazole(im), pyrazole(pz), and 1-methylimidazole(1-meim) were commercially available. The first two were recrystallized several times from benzene and dried in vacuo, while the latter was dried over KOH and distilled at a reduced pressure.

Acetone-d_6 (Merck, 99.8%) was used as a solvent for ^1H and ^{31}P NMR measurements after drying with molecular sieves. High-purity nitrogen (99.9998%) and carbon monoxide (>99.95%) were utilized.

Preparation of Copper(I)-Imidazole Compounds. A solution of imidazole (2.0 mg, 2.9×10^{-5} mmol) and $[Cu(CH_3CN)_4]ClO_4$ (5.1 mg, 1.5×10^{-5} mmol) in 5 mL of acetone-d_6 was stirred under nitrogen for 5 min. In order to vary the ratio of [im] to [Cu], a stock solution of imidazole was added to a constant amount of copper(I). While maintaining a nitrogen atmosphere, the resultant solutions were transferred into an NMR sample tube and the NMR spectra were recorded.

Carbonylated compounds were prepared by passing carbon monoxide through a solution of imidazole copper(I) compounds. Low-pressure carbon monoxide was obtained[33] by mixing nitrogen with carbon monoxide and making adjustments with three Kusano KG-1 rotameters and three precise needle valves. The rotameters were individually calibrated throughout their ranges with nitrogen and carbon monoxide.

Physical Measurements. 200 MHz ^1H NMR spectra were obtained with a JEOL FX200 spectrometer. Between 200 and 1000 transients were accumulated using a 14-μs (90°) pulse;

8 K data points were collected over a band width of 2500 Hz. A probe temperature was set at −90 °C, being calibrated to an accuracy of ±1 °C using the temperature-dependent difference between the CH_3 and OH shifts of pure methanol. ^{31}P NMR spectra operating at 80.79 MHz were recorded: 500 transients were accumulated using an 18-μs (80°) pulse and 8 K data points were collected over a band width of 4000 Hz. The solution of copper(I) imidazole containing 50 mM copper(I) with a ratio [im]/[Cu]=2 and 3 was transferred under a nitrogen atmosphere into a sealed IR cell constructed with KBr plates having a 0.05 mm path length. The IR spectrum was recorded at 25 °C. The remaining solution was then exposed to carbon monoxide for 5 min; that solution was transferred to a sealed IR cell and the spectrum was again recorded. All the spectra were calibrated with the aid of polystyrene film.

Results and Discussion

^{1}H NMR Spectra of Imidazole Complexes of Copper(I). $[\mathrm{Cu(CH_3CN)_4}]\mathrm{ClO_4}$ reacts with imidazole under anaerobic conditions to give various copper(I) complexes whose formation depends upon the concentration of imidazole. All of the complexes are colorless and show no optical spectra. Thus, their formation and structural characterization were investigated by ^{1}H NMR spectroscopy.

Three metal-free imidazole signals with integrated intensities of 1:1:2 were assigned[31,32] from the downfield region to 1-H, 2-H, and 4,5-H, respectively. The coordinated imidazole generally gave four resolved signals,[6,32] with the downfield shift assigned from downfield to 1-H, 2-H, 5-H, and 4-H. Those imidazole copper(I) species in solution encounter a chemical-exchange effect at ambient temperature and exhibit four averaged broad ^{1}H NMR signals. This averaging of the signals is released when a solution is cooled to −90 °C.[30]

Formation of Binary Copper(I) Complexes. By ^{1}H NMR spectroscopy, we can distinguish the species in a solution. Figure 1 illustrates these features as a function of [im]. The metal-binding imdazole gives well resolved signals which are reproducible within, at most, ±0.02 ppm on repeated runs. Especially, imidazole C–H proton signals are good markers for a species in solution. Now we will focuss on imidazole C–H protons in the 6—9 ppm region. When a small amount of imidazole (r=[im]/[Cu]≤1) was added to $[\mathrm{Cu(CH_3CN)_4}]\mathrm{ClO_4}$, three signals ($A_{2,4,5}$) appeared. As [im] further increased, the new signals ($B_{2,4,5}$) increased with a decrease in the intensity of signals $A_{2,4,5}$ (Fig. 1(2)). Signals $A_{2,4,5}$ were located at the upfield region more than signals $B_{2,4,5}$. Signals $A_{2,4,5}$ are assigned to mono(imidazole)complex(**1**), while signals $B_{2,4,5}$ are attributable to bis(imidazole)complex(**2**). Complex **2** was predominantly formed by the addition of ca. two equivalent of imidazole. When more than two equivalent of imidazole was added to $[\mathrm{Cu(CH_3CN)_4}]\mathrm{ClO_4}$, a set of new signals($C_{2,4,5}$) appeared, located at higher field than signals for **1** and **2**. We successfully detected signals $C_{2,4,5}$ concurrently with those of **2** at [im]/[Cu]=2.5 (Fig. 1(4)). These signals $C_{2,4,5}$ were ascribed to tris(imidazole)copper(I) (**3**). Nearly equal intensities of signals B and C (Fig. 1(4)) support the quantitative formation of **2** and **3**. As [im] further increased [im]/[Cu]=3—4), signals $C_{2,4,5}$ apparently broadened, even at low temperatures, accompanying a slight upfield shift. Under these concentrations, the principal species was **3**. At an imidazole concentration greater than four equivalent, signals were further broadened, indicating a signal-averaging between the coordinated and metal-free imidazole. This broadening makes it difficult to detect tetrakis(imidazole)copper(I) (**4**). At r=4, **4** is a likely minor species. Interestingly, excess imidazole ([im]/[Cu]>4) turned a colorless solution blue at the ambient temperature. This reveals the occurrence of the oxidation of copper(I).[33] The observed ^{1}H NMR chemical shifts obtained here are listed in Table 1.

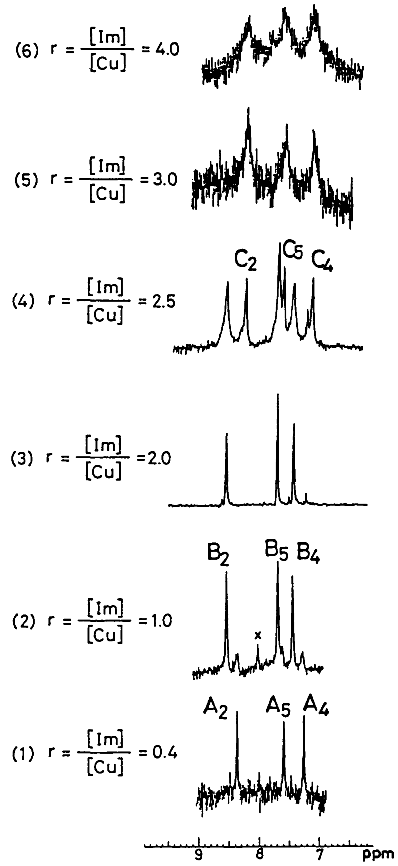


Fig. 1. ^{1}H NMR spectra at −90°C of acetone-d_6 solution of copper(I) complexes of imidazole. A, B, and C corresponds to signals of compound **1**, **2**, and **3**, respectively. Suffix denotes the assignement of proton signals of imidazole. x=impurity.

What structures have the solution species **1**—**4**? Among copper(I) complexes which have so far been

Table 1. Observed ^{1}H NMR Chemical Shifts[a] of Mononuclear Copper(I) Complexes,[b] $[CuL_nL'_m]ClO_4$

L(*n*)	L′(*m*)	1-H(Me)	2-H	4-H	5-H
Imidazole(metal-free)		13.06	7.97	7.25	7.25
(1)	CH_3CN[c]	12.49	8.38	7.28	7.61
(2)	—	12.61	8.53	7.42	7.68
(2)	CO (1)[d]	12.47	8.35	7.25	7.60
(3)	—	12.41	8.22	7.12	7.59
(3)	CO (1)	12.42	8.21	7.11	7.58
1-Methylimidazole (metal-free)		3.74	7.69	6.98	7.21
(2)	—	3.94	8.32	7.34	7.57

a) Shifts in ppm from $Si(CH_3)_4$. Error limit, ±0.02 ppm. Observed at −90 °C. b) $[Cu(CH_3CN)_4]ClO_4$ was used as a starting material. c) Number of coordinated molecules was not determined. d) The observed shifts at $P_{CO}=1$ atm. Under $P_{CO}=0.1$ atm, 12.48, 8.42, 7.32, and 7.63 ppm for 1-, 2-, 3-, and 5-H, respectively.

synthesized and characterized, four-coordinate tetrahedral species[23] are popular. Recently, various two-[7,9,14,18–22] and three-coordinate[13,34–46] copper(I) complexes have been synthesized; these types have become familiar. Two-coordinate complexes display a linear structure, while three-coordinate structures exhibit a triangular[34–43] or T-shape form,[15,44–46] the former being more preferable when the usual monodentate ligands coordinate. We have clarified the number of coordinating imidazole among **1**—**4**. Next, other ligands should be determined among solution species **1**—**3**. In our systems, potential donor ligands are ClO_4^-, CH_3CN, and acetone. The latter can be excluded from the donor groups due to its very poor coordinating ability against a soft metal ion.[47] Concerning (1) nitrile and (2) counter anion binding, we have used various starting materials of copper(I) such as $[Cu(RCN)_4]ClO_4$ (R=CH_3, C_2H_5, and C_6H_5). Also, we have demonstrated[25] that methyl proton signals of CH_3CN distinguish well between the coordinated and dissociated CH_3CN. Thus, signals of the nitriles for solutions of **2** and **3** have been examined. Table 2 shows the observed shifts of the nitriles. All of the ^{1}H signals locate at metal-free positions, indicating no coordination of acetonitrile. The imidazole signals of **2** and **3** have also been recorded as a function of R, and the obtained shifts are listed in Table 3. An inspection of Table 3 reveals that the imidazole signals of **2** and **3** show independence upon starting nitrile derivatives. Lastly, with the aid of ascorbic acid as a reducing agent, **2** was also synthesized from $Cu^{II}(ClO_4)_2$ and imidazole; such a system is free from nitrile. Both the ^{1}H NMR spectra with and without CH_3CN show that those imidazole signals[48] completely agree with each other.

Table 2. Observed ^{1}H NMR Chemical Shifts[a] of Nitriles[b]

Solution[c]	CH_3CN	C_2H_5CN		C_6H_5CN		
		CH_3	CH_2	*o*-H	*m*-H	*p*-H
Metal-free	2.22	1.23	2.55	7.94	7.70	7.84
$[Cu(nitrile)_4]^+$	2.41	1.30	2.76	8.11	7.77	7.94
$[Cu(im)\text{-}(nitrile)_m]^+$	2.32	1.28	2.71	7.98	7.73	7.90
$[Cu(im)_2]^+$	2.20	1.23	2.55	7.96	7.72	7.86
$[Cu(im)_2(CO)]^+$	2.22	1.23	2.56	7.96	7.71	7.86
$[Cu(im)_3]^+$	2.19	1.23	2.55	7.96	7.71	7.85
$[Cu(im)_3(CO)]^+$	2.20	1.23	2.55	7.96	7.71	7.85

a) Shifts in ppm from $Si(CH_3)_4$. Error limit ±0.02 ppm. Observed at −90 °C. b) $[Cu(nitrile)_4]ClO_4$ as a starting material was used in order to prepare copper(I)-imidazole complexes. c) The solution in which a principal copper(I)-imidazole complex forms. The predominant species are denoted in this column.

Table 3. Effect of Nitriles[a] on the Observed ^{1}H NMR Chemical Shifts[b] of Imidazole in Copper(I) Complexes

RCN[a]	Complexes	1-H	2-H	4-H	5-H
C_2H_5CN	$[Cu(im)(C_2H_5CN)_m]^+$	12.61	8.54	7.43	7.69
	$[Cu(im)_2]^+$	12.66	8.53	7.42	7.68
	$[Cu(im)_2(CO)]^+$	12.47	8.35	7.25	7.60
	$[Cu(im)_3]^+$	12.41	8.22	7.12	7.59
	$[Cu(im)_3(CO)]^+$	12.47	8.21	7.11	7.58
C_6H_5CN	$[Cu(im)(C_6H_5CN)_m]^+$	12.47	8.41	7.30	7.62
	$[Cu(im)_2]^+$	12.64	8.53	7.42	7.68
	$[Cu(im)_2(CO)]^+$	12.51	8.34	7.24	7.59
	$[Cu(im)_3]^+$	12.41	8.21	7.12	7.59
	$[Cu(im)_3(CO)]^+$	12.42	8.21	7.11	7.58

a) $[Cu(RCN)_4]ClO_4$ was used as a starting material. Solvent was acetone-d_6. b) Shifts in ppm from $Si(CH_3)_4$. Error limit, ±0.02 and ±0.04 ppm for 2,4,5-H, and 1-H, respectively. Observed nitrile shifts were catalogued in Table 2.

Species **1** was checked, although it was the most difficult case to be characterized by NMR. **1** is formed only if $r<1$, wherein the principal species in solution are binary $[Cu(CH_3CN)_n]^+$ ($n=2$ or 3)[49,60] rather than **1**. Even at −90°, ^{1}H NMR spectroscopy failed to detect separated CH_3 signals of the CH_3CN ascribed to each species. This is because CH_3CN is chemically exchanged faster than the NMR time scale and its signal is averaged out. The chemical exchange is not depressed for nitrile. Table 2 reveals that only **1** gives nitrile signals different from a metal-free position. Imidazole proton signals of **1** show a nitrile-dependence as illustrated in Tables 1 and 3; these shift downfield by 0.08—0.16 ppm when a starting copper source $[Cu(CH_3CN)_4]$ is replaced by $[Cu(C_6H_5CN)_4]$. This nitrile-dependence is significantly associated with the coordination of CH_3CN in **1**. Consequently, it is concluded that the binding of nitrile occurs in **1** while not in **2** and **3**.

In order to clarify the coordination of a perchlorate ion, PF_6^- is used instead of ClO_4^-: The former possesses much less coordinating ability[24] than ClO_4^-. ^1H NMR signals of perchlorate salts of **1**—**3** are the same as those from their hexafluorophosphate salts. ^{31}P NMR spectra of the resultant species were measured as to whether or not the ^{31}P NMR signal shifts to the position denoting a strong association with copper(I). Both imidazole-free and imidazole-containing (two-equivalents) solutions of $[Cu(CH_3CN)_4]PF_6$ gave a single ^{31}P signal, appearing at −143.9 ppm from H_3PO_4, that are characteristic of a metal-free PF_6^-. Accordingly, the counter anion proves to be dissociated for all the species, **1**—**3**.

Now, we conclude that **2** and **3** are two- and three-coordinate copper(I) complexes, respectively, wherein neither nitrile nor an anion is bound to copper(I). The results regarding **2** are in good agreement with the accepted view that 1:2 complexes with monodentate ligands like NH_3[58] are truely two-coordinate in solution. **2** is possibly linear, as has been demonstrated by its X-ray structure,[7,9,14] while **3** is trigonal. This is reasonable since 1:3 complexes of copper(I) are easily formed with CN^-,[34,52] pyridine,[53,54,59] Cl^-, and CH_3CN.[55—57] **1** has at least one ligand other than imidazole. In referring to structures which have so far been demonstrated for copper(I) compounds, $[Cu(im)(CH_3CN)]^+$ or $[Cu(im)(CH_3CN)_3]^+$ is considered as a possible species. Mono-, bis-, and tris(imidazole)complexes are successfully prepared in an acetone solution; their formation and equilibria are summarized in Scheme 1. Throughout this investigation, $[Cu(CH_3CN)_4]ClO_4$ has been proven to be equivalent to $[Cu(CH_3CN)_4]PF_6$ concerning a reaction with imidazole.

It is noteworthy in Table 1 that the increase in the coordiation number from **2** to **3** causes imidazole signals to shift upfield. This is accounted for by the delocalization of a positive charge upon the imidazole ring.[6] The downfield shift upon coordination to copper(I) is attributable to a scattering of positive charge onto imidazole ring, and the increase in the number of coordinating imidazole dilutes the scattered positive charge on each imidazole ring. Chemical shifts for **1** are not directly compared with those for **2** and **3** because the former is a ternary compound.

Formation of Carbonylated Copper(I) Imidazole Complexes. When CO gas was passed into a solution of **1**—**3**, the resultant colorless solution gave new sharp ^1H NMR signals whose chemical shifts are different from those of the precursor (Fig. 2). The binding of CO causes an upfield shift of coordinating imidazole. The carbonylated complex (**3-a**) of **3** has been definitely determined to be $[Cu(im)_3(CO)]^+$ since dissociated imidazole signals were not observed.

We have determined the structure of a carbonylated species as well as the binary systems mentioned in the previous section. The coordinated imidazole signals of **2-a** and **3-a** showed no dependence upon the starting materials of $[Cu(RCN)_4]ClO_4$ (R=CH_3, C_2H_5, and C_6H_5), indicating no nitrile-binding in **2-a** and **3-a**. Also, no anion binding to copper(I) in **2-a** and **3-a** has demonstrated by ^1H and ^{31}P NMR for imidazole-$[Cu(CH_3CN)_4]PF_6$ systems. Consequently, these species are $[Cu(im)_2(CO)]^+$ and $[Cu(im)_3(CO)]^+$. Figure 2(3) reveals that the signal intensities of $[Cu(im)_2(CO)]^+$ and $[Cu(im)_3(CO)]^+$ are nearly equal, indicating the occurrence of only addition reaction of CO (Fig. 1(4)).

CO-bubbling into the solution of **1** gave imidazole ^1H shifts that just correspond to those of **2-a**. This is either because the carbonylated compound of **1** accidentally gives the same chemical shifts as **2-a**, or because carbon monoxide drives the equilibrium to the formation of **2-a** rather than the addition to **1**. To determine which is more probable is beyond the abilities of the present NMR method.

Decarbonylation was carried out by passing nitrogen into the solution. **3-a** is the most stable and, thus, prolonged nitrogen bubbling is required. This stability reminds us that $[Cu(dien)(CO)]^+$[61] and $[Cu(HB(pz)_3)(CO)]^+$[63] (dien=diethylenetriamine ;HB(pz)$_3$=hydrotris(pyrazol-1-yl)borate). Neither compounds lose CO, even at high temperatures or in

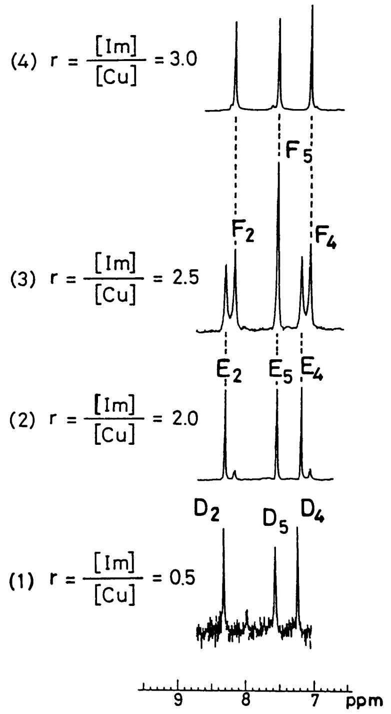


Fig. 2. ^1H NMR spectra at −90 °C of acetone-d_6 solution of copper(I) complexes of imidazole. All samples were prepared under CO atmosphere. D, E, and F correspond to signals of complexes **1-a**, **2-a**, and **3-a**, respectively. Suffix denotes the assignment of proton signals of imidazole.

vacuo in the solid state. These copper(I) complexes and **3-a** commonly have a tetrahedral structure with an N_3C donor set. The greater is the basicity of the N donor ligand, the more the electron density on copper increases.[62] Therefore, the rich electron density on copper enhance the π back-bonding and stabilize the Cu–CO bond. The basicity of dien is greater in five pK_a units[59] than that of imidazole. This gap in basicity is significantly associated with a reversible binding of CO. The carbonyl–decarbonyl cycle can be repeated many times for all a solutions of copper(I) imidazole compounds in this work, while dien system can not. The obtained reversible reactions are summarized in Scheme 1.

Sorrell et al.[7] have reported by use of IR spectra that bis(imidazole)copper(I) does not react with CO unless other bases are present in solution. On the basis of the inertness of bis(imidazole)copper(I) species, they suggest that the coordination sphere of each copper in hemocyanin is a two-coordinate; however, near one of the copper centers is an additional donor that can coordinate and promote CO binding to that copper. Indeed, three-coordinate copper(I) tends to readily provide a monocarbonyl complex, as has also been demonstrated here. However, the reactivity of bis(imidazole)copper(I) against CO appears opposite to our results. They have also illustrated that bis(pyrazole)copper(I) readily reacts with CO to produce its monocarbonyl adduct. Then, two questions arise: (1) Whether or not bis(imidazole)copper(I) reacts with CO? and (2) why there are marked difference in reactivity toward CO between copper(I) complexes of pyrazole and imidazole? In response to question (2), we point out that the difference in the ligand basicity, which contributes to the stability[7] of a precursor, is of significance. The answer to question (1) is that **2** does react with CO, contrary to Sorrell's conclusion. It should be noted that the NMR spectra were measured at different conditions from the IR spectra. The clearest difference is the temperature: −90 °C was established for the NMR measurement, while the ambient temperature was set for IR. Does this low temperature render an equilibrium shift to the formation of a carbonylated complex? For example, [CuCl(bpy)]$_2$ in acetone under a $P_{co}=1$ atm at 25 °C gives a monocarbonyl adduct[30] with ca. 57% yield to the precursor. This adduct was completely formed at −90 °C. Figure 2 ((2) and (3)) reveals the quantitative formation of **2-a** and **3-a**, amounts that clearly correspond to those of precursors, **2** and **3** (Fig. 1(4)), respectively. This fact was obtained at low temperature and does not exhibit any marked difference in the reactivity[7] of **2** and **3**.

In comparison with a low-temperature species, the species formed at ambient temperature were checked by the IR spectra. The stretching frequencies (ν_{co}) of the coordinated CO was measured for carbonyl complexes in an acetone solution. Fortunately, acetone gives no significant absorption bands at 2000—2200 cm^{-1}. Solutions prepared with a ratio of [im]/[Cu]=2 provided a single band at 2076 cm^{-1}, while a degassed solution gave no band in this region (Fig. 3). This band is attributable to ν_{co} of the coordinating CO. A band at 2069 cm^{-1} having the stronger intensity appeared at r=3. The band at r=2 is broader than that at r=3. The gap (7 cm^{-1}) between two bands is not large enough to be seen as two different bands, since the linewidth of those IR bands are broad. The ν_{co} band of [CuL$_3$(CO)]$^+$ appeared in the region lower than 2100 cm^{-1}, while that of

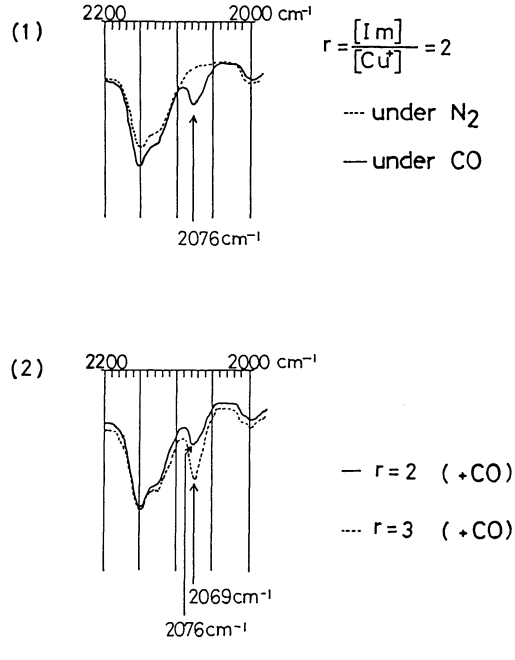
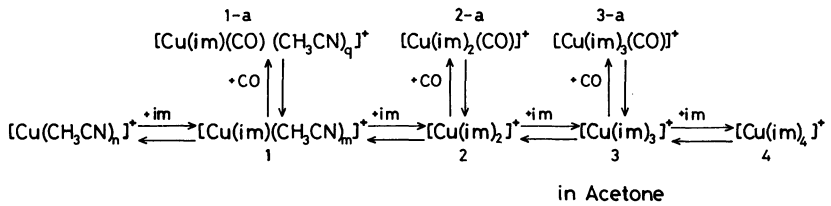


Fig. 3. Infrared spectra at 25 °C of carbonylated copper(I) complexes in acetone. The band ascribed to carbonyl stretching is indicated by an arrow together with its wave number.



Scheme 1.

[CuL$_2$(CO)]$^+$ appeared in the region greater than 2100 cm^{-1} (L=pyrazole and its derivatives).[7] Accordingly to these facts, these bands were assigned to ν_{co} of [Cu(im)$_3$(CO)]$^+$. Even at r=2, the detection of **3-a** indicates that **3-a**[64] forms more readily than **2-a**. The IR spectra of solution samples require a very high concentration of the coordinating CO. The concentration of 50—100 mM is 25—50 fold larger than in the case of ^{1}H NMR measurements. Therefore, the IR spectrum fails to detect its ν_{co} signal when **2-a** is present as a minor species. The detection is dependent on the degree in the stability constants of the resultant CO adduct. In conclusion, **2** does react with CO, giving 100% **2-a** at −90 °C, and less **2-a** at ambient temperature.

Copper(I) Pyrazole Complexes. Similarly, copper(I) pyrazole (pz) compounds were also examined by ^{1}H NMR spectroscopy at −90 °C.[65] From the ^{1}H NMR spectra obtained at r=[pz]/[Cu]=0.5—4, various chemical exchange phenomena were found. At r=1—2, the 3-H signal was broadened accompanying with a slight shift, while 5-H and 4-H signals remain sharp. This broadening is not due to the paramagnetic copper(II) species generated by the oxidation of copper(I) species because of its selective broadening. This selective broadening is attributable to a chemical exchange[66] among [Cu(pz)L$_x$]$^+$ (L= another ligand, possibly CH$_3$CN), [Cu(pz)$_2$]$^+$, and L. Such a chemical exchange phenomena is in good contrast with the case of imidazole. At r=2—3, all the signals of pyrazole became broadened, indicating a chemical exchange[67] between a metal-free and coordinating ([Cu(pz)$_n$]$^+$; n=2 and 3) pyrazoles; thus, the presence of a considerable amount of metal-free pyrazole in solution. On the other hand, the chemical exchange rate in [Cu(im)$_n$]$^+$ (n=2 and 3) at r=2.5 was so slow that the ^{1}H NMR spectra were simultaneously observed (Fig. 1). Accordingly, the formation of [Cu(pz)$_3$]$^+$ is harder than that of [Cu(im)$_3$]$^+$. The difference between copper(I) complexes of pyrazole and imidazole is ascribed to the basicity of the ligand,[48,53] A chelating ligand of pyrazole is required if a stable and less labile copper(I)–pyrazole complexes is to be synthesized. Carbonylated copper(I) complexes of pyrazole are quantitatively formed and all their signals are sharp, revealing a slow chemical exchange.[69] Of course, the carbonyl–decarbonyl cycle is readily repeated. In summarizing these results, there was the remarkable difference in forming two-coordinate copper(I) complexes between pyrazole and imidazole. Also, no distinguishable difference between their carbonylated copper(I) complexes were detected by low temperature ^{1}H NMR spectroscopy.

A knowledge of the equilibria and reactivity and the accumulated ^{1}H NMR data on imidazole in various copper(I) complexes would contribute to an advancement in the copper(I) chemistry involving imidazole and its derivatives and an application to copper proteins.

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48) The reduction was made by refluxing the solution. These copper(I) compounds reduced by ascorbic acid definitely gave the same ^{1}H NMR signals of coordinating imidazole as those obtained from copper(I) sources. Additional signals were also observed which are easily assigned to oxidized ascorbic acid.

49) ^{63}Cu NMR spectra are available for an investigation of tetrahedrally coordinated copper(I) compounds.[26] Due to the great quadrupolar interaction, other copper(I) compounds having the lower symmetry give hardly detected ^{63}Cu NMR signal as a consequence of the broadening. By use of ^{63}Cu NMR spectroscopy, it has been demonstrated that acetone solution of $[\mathrm{Cu(CH_3CN)_4}]\mathrm{ClO_4}$ provides no ^{63}Cu signal, indicative of significant decomposition[50,51] of $[\mathrm{Cu(CH_3CN)_4}]^+$ into the lower coordination form. On the other hand, its acetonitrile solution clearly gave single signal ascribed to $[\mathrm{Cu(CH_3CN)_4}]^+$.

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64) Exact addition of two equivalent of imidazole at the concentration is very difficult problem. If a slight excess of imidazole is present in solution, **3-a** may readily form under CO atmosphere.

65) A metal-free pyrazole gave three ^{1}H NMR signals at 13.1 (1-H), 7.83 (3- and 5-H), and 6.42 ppm (4-H), with relative intensities of 1, 2, and 1, respectively. In copper(I)-pyrazole systems, well-separated four signals were obtained, and the coordination shift for all pyrazole protons was appreciated, ranging from 0.11—0.43 ppm. At $r<1$, except for 1-H (13.3 ppm) very sharp signals displaying multiplets were obtained, whose assignment is 5-H (8.26), 3-H (7.94), and 4-H (6.70). The chemical shift of 4-H and 5-H signals is insensitive to the structures such as $[\mathrm{Cu(pz)}_n]^+$ and $[\mathrm{Cu(pz)}_m\mathrm{(CO)}_p]^+$. On the other hand, 3-H signal is sensitive, indicative of a good probe to inquire into the structure in solution.

66) At $1\leq r\leq 2$, several exchange processes are considered from ^{1}H NMR spectra, which show characteristic broadening of 3-H signal. Possible processes are considered as follows:

$$\begin{aligned}&[\mathrm{Cu_A(pz)L}_n]^+ + [\mathrm{Cu_B(pz)(pz)^*}]^+ \\ &\quad \rightleftarrows [\mathrm{Cu_A(pz)(pz)^*}]^+ + [\mathrm{Cu_B(pz)L}_n]^+, \qquad \text{(i)}\end{aligned}$$

$$[\mathrm{Cu(pz)L}_x]^+ + \mathrm{L} \rightleftarrows [\mathrm{Cu(pz)L}_{x+1}]^+, \tag{ii}$$

wherein L is another ligand, possibly CH_3CN. This is characteristic of copper(I)–pyrazole system.

67) The linewidth of all the signals increases with increase in *r*. Hence, the line-broadening of signals is attributable to the following chemical exchange processes (iii) and/or (iv).

$$\mathrm{Cu(pz)_2} + \mathrm{pz}^* \rightleftarrows \mathrm{Cu(pz)(pz^*)} + \mathrm{pz} \tag{iii}$$

$$\mathrm{Cu(pz)_3} + \mathrm{pz}^* \rightleftarrows \mathrm{Cu(pz)_2(pz^*)} + \mathrm{pz} \tag{iv}$$

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69) At r=1—3, three different ^{1}H NMR spectra were obtained. They all displayed well-separated and sharp four signals. The tentative structure of these carbonylated complexes is determined in analogy with that of copper(I)–imidazole complexes. At r=1, $[\mathrm{Cu(pz)(CO)L}_x]^+$ (L=another ligand; x=1 or 2) forms, whose signals are assigned to 1-H (13.4 ppm), 5-H (8.27), 3-H (7.89), and 4-H (6.70). At r=2, four signals at 13.2 (1-H), 8.25 (5-H), 7.74 (3-H), and 6.68 (4-H) are ascribed to $[\mathrm{Cu(pz)_2(CO)}_y]^+$ (possibly y=2). Finally, at r=3, $[\mathrm{Cu(pz)_3(CO)}]^+$ gives signals at 8.25 (5-H), 7.67 (3-H), and 6.67 (4-H).