Structural Effect on the Stability of (Pyridine)$_2$Cu$^+$ Complexes in the Gas Phase: Nature of the Bond between Copper(I) Ion and Neutral Molecules

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Free energy changes ($\Delta G°$, copper cation basicity) for the reaction $L_2Cu^+ = Cu^+ + 2L$ were obtained in the gas phase for substituted pyridines based on the measurement of ligand-exchange equilibria in a Fourier transform ion cyclotron resonance (FT-ICR) spectrometer. For 3- and 4-substituted pyridines, the relative copper cation basicities (ΔCCB[L_2Cu^+]) were linearly correlated with the corresponding gas-phase proton basicities (ΔGB) with a slope of 1.01. On the basis of a linear relationship between the calculated copper cation basicities of dimeric and monomeric complexes at MP2/6-311+G(2p,2d)//B3LYP/6-311G*, ΔCCB[L_2Cu^+]$_{calcd}$ = 1.54ΔCCB[LCu^+]$_{calcd}$, the substituent effect on the ΔCCB for the first ligand was estimated to be 0.66 times smaller than the corresponding ΔGB. A comparison with the corresponding results for other Lewis cation basicity of the pyridine system showed that the magnitude of the substituent effect decreases in the order H^+ (1.00) > Me_3Si^+ (0.95) > Cl^+ (0.83) > Cu^+ (0.66) > Li^+ (0.47). This change was associated with the natural charges at the Lewis cation moiety and the natural atomic orbital (NAO) bond order of the M^+-N bond of the complex ion, indicating the decrease in covalent character of the M^+-N bond in this order. Furthermore, when a variety of neutral bases such as amines, carbonyl compounds, and ethers were included in a comparison between CCB[L_2Cu^+] and GB, it was found that there is a good linear relationship with significant deviations of small molecules and bulky tributylamine, which is attributed to their different steric environment at the binding sites from others, while there is no simple linear relationship with the lithium cation basicities (LCB). The similarity of the substituent effect between CCB[L_2Cu^+] and GB reflects the covalent character in the Cu^+ interaction. In conclusion, although the ionic (ion−dipole interaction) nature of the Cu^+ interaction results in a smaller substituent effect than that for the protonation, the covalent nature also plays an important role in the Cu^+ interaction with neutral molecules.

Introduction

The interaction of metal ion and neutral bases in the gas phase have been intensively studied in the past decades because under these conditions the intrinsic bonding characteristics are most directly revealed.[1−6] From these results it seems well-established that metal ion interactions are essentially electrostatic for the complexes involving alkali metal ions.[7−9] On the other hand, when the complexes involve transition metal ions, the situation may be somewhat different. Although it has been generally assumed that the Cu^+ interactions are also mostly electrostatic, the interactions seem to have a nonnegligible covalent character because Cu^+ presents in its ground state a d^{10} closed-shell structure with an empty 4s orbital. This may be consistent with theoretical results that the structures of the complexes involving Cu^+ resemble closely those of the corresponding protonated species in which the covalent bond is formed between a base and a proton.[10−12] The nonnegligible covalent nature in the Cu^+ interactions would be reflected in the energetic aspects (bond strengths), and this may result in different situations for the structural effects of ligands on the Cu^+ interaction. Although a comparison of the Cu^+ binding energies with proton affinities and with lithium cation affinities provides useful information on the nature of the interaction between the metal ion and neutral molecules, such experimental studies were limited. In earlier studies, Jones and Staley[13] found a fair linear relationship between $\Delta H°(L_2Cu^+)$ and $\Delta H°(LMn^+)$ for the oxygen bases with large deviations for R_2S, NH_3, and HCN. More recently, Deng and Kebarle[14] also observed similar deviations in plots of binding energies for L_2Cu^+ versus LLi^+ and L_2Ag^+. These deviations from the limited linear correlation based on the oxygen bases were in part interpreted by the hard and soft acids and bases principle. However, the actual bond energies are affected also by other important interactions such as electrostatic contributions and the formation of nonclassical structures in which the metal ion interacts simultaneously with two or more basic sites of the neutral molecule.[15−21] Furthermore, it was frequently found that there are family-dependent linear relationships among Lewis cation affinities (basicities) with a different slope for each family.[18,19,22] The choice of a reference ligand series is obviously crucial to discuss the linear relationship between two systems and/or the deviations from their correlations because the deviations from the linear relationship result from the differences in many factors that contribute to the binding interaction of Lewis cations with neutral molecules. Therefore, in order to understand the nature of the bond formed by Cu^+, it is necessary to separate quantitatively the overall

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binding energy into respective interaction terms. First of all, it is important to elucidate the electronic effect of ligands having a single binding site under constant geometrical environment at the binding site. For this purpose, aromatic compounds with a single basic site of which the electronic properties can be varied by a remote ring substituent are a particularly interesting set of ligands. Recently, we applied this approach to the study of the binding interaction of the trimethylsilyl cation, trimethylgermyl cation, lithium cation, and copper cation with a series of acetophenones.[21−25] It was found that the magnitude of the substituent effect (ρ value given by Hammett-type correlation analysis) was found to be smaller in the copper cation basicity (CCB) than the gas-phase proton basicity (GB) and larger than that for the lithium cation basicity (LCB) and that the substituent effect on the CCB was further characterized by the somewhat reduced resonance effects of para π-donor substituents compared with that of the corresponding GBs. These results suggest that the nature of the Cu$^+$ interaction is different from that found for the protonation processes and from that observed with the lithium cation where the interactions are essentially electrostatic. In the present study, we extended this approach to the CCB for the pyridine system with a nitrogen atom as the binding site.

Gas-phase copper cation basicity (CCB) is defined as the Gibbs free energy associated with the thermodynamic equilibrium (eq 1), analogously to gas-phase basicity toward a proton (GB):

$$\text{L-Cu}^+ = \text{L} + \text{Cu}^+ \tag{1}$$

where $\Delta G_1° = -RT \ln K_1$ and CCB $= \Delta G_1°$. In a similar manner, the gas-phase copper cation affinity (CCA) is defined as the enthalpy change of the reaction (eq 1), CCA $= \Delta H_1°$. Earlier data reported by Jones and Staley[13] and Deng and Kebarle[14] were based on the determination of ligand exchange equilibria:

$$\text{L}^1\text{Cu}^+\text{L}^1 + \text{L}^2 = \text{L}^1\text{Cu}^+\text{L}^2 + \text{L}^1 \tag{2}$$

$$\text{L}^1\text{Cu}^+\text{L}^2 + \text{L}^2 = \text{L}^2\text{Cu}^+\text{L}^2 + \text{L}^1 \tag{3}$$

$$\text{L}^1\text{Cu}^+\text{L}^1 + 2\text{L}^2 = \text{L}^2\text{Cu}^+\text{L}^2 + 2\text{L}^1 \tag{4}$$

where L^1 and L^2 are two different ligands. In these studies and the present study, the choice of the L$_2$Cu$^+$ complexes rather than LCu$^+$ was based on experimental convenience, because the first two bond energies Cu$^+$−L and CuL$^+$−L are approximately equal and much higher than those observed with additional ligands[26−32] and because it is difficult to stop the formation of the dimeric complexes. The special stability of L$_2$Cu$^+$ enables the measurements of the exchange equilibria. Since these results are for the two strongest bonding interactions, they are very valuable even though they provide somewhat restricted information.

Experimental Section

ICR Measurements. Equilibrium-constant measurements were performed on an Extrel FTMS 2001 spectrometer. An IonSpec Data Station was also used for several measurements. Details of the experimental techniques used for measuring the equilibrium constants (K) for the ligand transfer reaction (eqs 3 and 4) were described previously.[21] Only significant changes and/or additional procedures are given here. All measurements were performed in the temperature range of 50−70 °C at a constant magnetic field strength of 3.0 T. The pressures of the neutral reactants were measured by means of a Bayard−Alpert-type ionization gauge with appropriate correction factors being applied to correct the gauge readings for the different ionization cross sections of various compounds.[33] The overall pressures of the neutrals were maintained at $(4-13) \times 10^{-5}$ Pa by controlled rates through leak valves (Anelva) from a parallel inlet manifold into the reaction cell in the vacuum chamber. Cu$^+$ was generated by laser irradiation with an Nd:YAG (Continuum, Minilite II) at 532 nm (10 mJ or less) of pure copper pieces mounted at the end-face of a solid probe rod. After an appropriate reaction period of 6−20 s, depending upon the reactant and pressures, equilibrium was attained and the relative abundances of L^{1}Cu$^+$L^1, L^{1}Cu$^+$L^2, and L^{2}Cu$^+$L^2 were measured on the basis of signal intensities in the ICR spectra. For cooling excited metal ions, helium or argon gas was added by using a pulsed valve; however, significant differences were not observed in the ligand-transfer equilibrium. Therefore, most measurements were carried out without buffer gas. Each experiment was performed at several ratios of partial pressures and at different overall pressures. The arithmetic-mean values of equilibrium constants were used to calculate $\Delta G°$ at 343 K with an average uncertainty of ± 1 kJ mol^{-1} in most of these cases. The occurrence of the ligand-transfer reaction was examined by an ion-eject experiment using the SWIFT technique.[34]

Pyridine derivatives used in this study were available from commercial sources. All the materials were degassed prior to use by several freeze−pump−thaw cycles on the sample-inlet system of the ICR. Their purities were checked by use of an FT-ICR mass spectrometer.

Calculations. Theoretical calculations were carried out with the Gaussian 03 program suite.[35] The geometries were fully optimized at the DFT-B3LYP level of theory using several basis sets. Vibrational normal-mode analyses were performed at the same level to ensure that each optimized structure was a true minimum on the potential energy surface. Single-point calculations were performed at the MP2/ 6-311+G(2d,2p) levels of theory using the B3LYP/6-311G and B3LYP/6-31+G* optimized geometries. Unscaled B3LYP/6-311G and B3LYP/6-31+G** frequencies were used to obtain thermochemical quantities, the enthalpy, and free energy corrections. No corrections for the basis-set superposition error (BSSE)[36] were made, because the magnitude of BSSE was found to be small. DFT calculations for iodine cation complexes DGDZVP and Lan2LDZ were used. Atomic charges and natural atomic orbital (NAO) bond orders were calculated by the natural population analysis (NPA) and natural bond orbital (NBO) methods implemented in the Gaussian 03 package.

Results

Measurements of Gas-Phase Copper Cation Basicity. Gas-phase copper cation basicities (CCB) were determined by measuring the equilibrium constants of the reversible ligand-transfer reactions on an FT-ICR spectrometer. When two pyridine derivatives L^1 and L^2 were present in the ICR cell, initial reactions forming L^{1}Cu$^+$ and L^{2}Cu$^+$ were followed by further addition of ligands to produce the dimeric adducts L^1-Cu$^+$L^1, L^{1}Cu$^+$L^2, and L^{2}Cu$^+$L^2 within a second, as shown in Figure 1a. The reactions forming the dimer complexes stopped without further addition of ligands. These reactions were followed by ligand-exchange reaction (eqs 2 and 3). The free energy change ($\Delta G_4°$) for two ligands exchange reaction (eq 4) is given by

$$\Delta G_4° = \Delta G_2° + \Delta G_3° \tag{5}$$

Figure 1b shows a typical time profile for dimeric adduct ions of pyridines with Cu$^+$. On the basis of ligand-exchange equilibrium measurements involving 20 different pyridines, the free energy changes, $\Delta G_4°$, for the reaction (eq 4) were obtained.

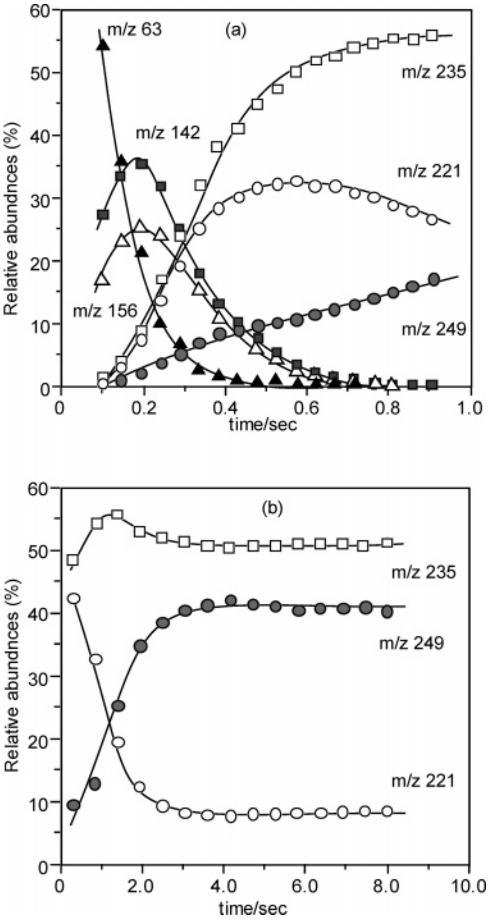


Figure 1. Time profile of copper complexes formed from a binary mixture of 3-methylpyridine and pyridine (3-MeC_5H_4N, 1.5 × 10^{-5} Pa C_5H_5N, 8.8 × 10^{-5} Pa). (▲) *m/z* 63, Cu^+; (■) *m/z* 142, $(C_5H_5N)Cu^+$; (△) *m/z* 156, $(3\text{-}MeC_5H_4N)Cu^+$; (○) *m/z* 221, $(C_5H_5N)_2Cu^+$; (□) *m/z* 235, $(C_5H_5N)Cu^+(3\text{-}MeC_5H_4N)$; (●) *m/z* 249, $(3\text{-}MeC_5H_4N)_2Cu^+$.

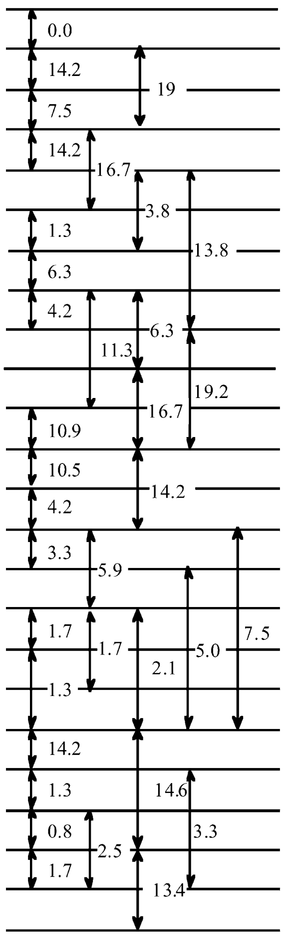
From these results a ladder of the CCB[L_2Cu^+] was constructed as shown in Table 1.

These relative scales were converted to absolute values for CCB by calibrating to the known value for MeCN that was recently revised on the basis of threshold collision-induced dissociation measurements.[31] The Δ*G*° values measured for respective ligand-transfer equilibria (eq 4) and the copper cation basicities (CCB[L_2Cu^+]) are summarized in Table 1 along with the corresponding GB values.[37]

Structures of (Pyridine)$_n$Cu$^+$ Complexes and the Calculated CCBs and CCAs. The geometries of the monomeric and dimeric complexes of pyridine with Cu^+ were optimized by use of B3LYP with several basis sets (numbering is shown in Scheme 1). The selected geometrical parameters, CCAs, and CCBs are summarized in Table S1. Although the π-complex structures were reported as local minima for the complexes between benzene and Cu^+,[38−40] such π-complexes were not found as a stable structure with the pyridine.

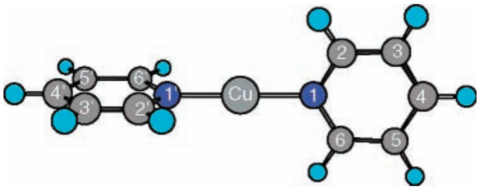
Two stable structures for the dimeric complex were found when a larger basis set was used; that is, the two pyridine groups lie in orthogonal or planar conformation. However, the energy difference (Δ*E*) between two conformers is quite small, less than 2 kJ mol^{-1}, and an energy barrier between two conformers is also less than 2 kJ mol^{-1} (Figure S1). In addition, a more stable conformer varies with the basis set and theory. These results indicate free rotation of the pyridine moiety within the adducts. The calculated bond distances vary slightly with the basis set used. In particular, the CuN1 distance in the dimeric complex increases from 1.875 Å (B3LYP/6-311G) to 1.916 Å (B3LYP/6-311+G**) while the change of other bond distances is relatively small. The same trend was observed for the monomeric complex. Although the geometrical features of the Cu^+ complexes depend on basis sets, the calculated binding energies at the MP2/6-311+G(2d,2p) level of theory are nearly identical. In addition, these calculated CCB[L_2Cu^+] values for pyridine are found to be in good agreement with the experimental value (446 kJ mol^{-1}) within so-called chemical accuracy (8 kJ mol^{-1}) for an absolute scale. We therefore used the B3LYP/6-311G and B3LYP/6-31+G* optimized geometries for the energy calculations of a series of (pyridine)$_n$Cu$^+$ (*n* = 1 and 2) complexes because of their convenient computing time.

TABLE 1: Measured Free Energy Changes for Ligand-Exchange Equilibria ($L^1{}_2Cu^+ + 2L^2 = L^2{}_2Cu^+ + 2L^1$), Copper Cation Basicities, and Corresponding Proton Basicities

Subsitutent in pyridines	Measured ΔG°	CCB[L_2Cu^+][a]	GB[b]
4-N(Me)$_2$		515.9	971.1
1,2-Me$_2$-imidazole		515.9	952.7
4-NH$_2$		501.7	947.7
1-Me-imidazole		494.1	927.6
3,4-Me$_2$		479.9	925.5
3,5-Me$_2$		477.4	923.4
4-OMe		476.1	929.7
2,6-Me$_2$		469.9	930.9
4-Me		465.7	915.5
3-Me		463.2	911.7
2-Me		457.3	917.1
H		446.4	898.3
butylamine		436.0	886.6
3-COMe		431.8	882.4
2-Cl		428.4	870.3
3-Cl		425.9	871.5
2-CN		424.7	841.0
3-F		424.3	870.3
2-F		423.4	852.7
3-CF$_3$		410.0	860.6
CH_3CN		408.8 [c]	753.5
4-CF$_3$		407.9	861.9
3-CN		406.3	845.2
4-CN		394.6	848.9

[a] Absolute scales of CCB[L_2Cu^+], copper cation basicities (values are given in kilojoules per mole). [b] Reference 37. Proton basicities (GB) are given in kilojoules per mole. [c] Reference 31.

SCHEME 1: Numbering of (Pyridine)$_2$Cu$^+$ Complex



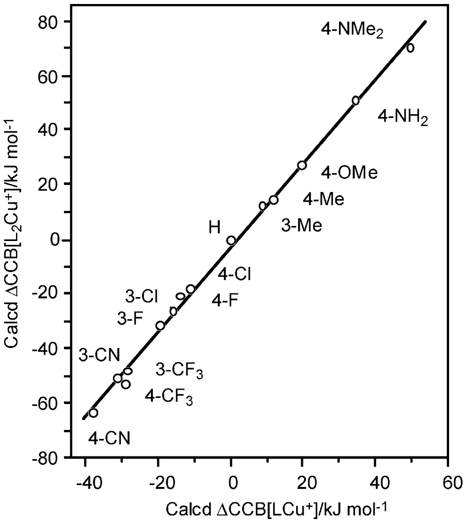


Figure 2. Plot of ΔCCB[L$_2$Cu$^+$]$_{calc}$ vs ΔCCB[LCu$^+$]$_{calc}$.

Comparison of Calculated Binding Energies of Cu$^+$ between the First and Second Ligands. It is well-known that Cu$^+$ forms very strongly bonded dicoordinated linear complexes and that the first two bond energies, Cu$^+$−L and LCu$^+$−L, are approximately equal and much higher than those with additional ligands as mentioned above.[26−32] Indeed, recent experimental results for H_2O,[30a] NH_3,[30g] Me_2O,[30h] MeCN,[31] and Me_2CO[32] indicate that the second binding energy is nearly identical to the first one. In addition, it is found that there is a good linear relationship between the first binding energy and the sum of the first and second binding energies of these ligands:

$$\mathrm{CCA}[\mathrm{L_2Cu^+}]_{\mathrm{exp}} = 6.5 + 1.91\mathrm{CCA}[\mathrm{LCu^+}]_{\mathrm{exp}} \quad (R^2 = 0.997) \quad (6)$$

If this relationship (eq 6) holds for the present pyridine system, it is possible to assume the CCB[LCu$^+$] for the first ligand from the CCB[L$_2$Cu$^+$] values obtained in the present study. Since the ligands that have their first and second binding energies determined experimentally are limited and considerably smaller in size compared to the pyridine derivatives, it is necessary to examine whether the correlation given by eq 6 holds for the present system. This is another aim for the theoretical calculations because the CCB[LCu$^+$] values for monomeric complex, (pyridine)Cu$^+$, could not be determined in the present measurements by the ligand-exchange equilibrium method. The calculated CCBs and CCAs for pyridine given in Table S1 indicate that the binding energy with the first ligand is nearly identical to the second one regardless of the levels of theory used for the calculations. However, closer examination of the calculated binding energies for a series of pyridines given in Tables S2 and S3 shows that the second binding energies tend to be somewhat smaller than the first ones as the substituent in the pyridine ring is more electron-donating. The *f*(CCA) and *f*(CCB) values, which are the ratios of CCB[L$_2$Cu$^+$] to CCB[LCu$^+$] and CCA[L$_2$Cu$^+$] to CCA[LCu$^+$], respectively, decrease consistently with increasing basicity of a ligand: from 2.04 and 1.99 for 4-CN to 1.91 and 1.84 for 4-NMe$_2$, respectively, indicating that the stronger base has appreciably weaker second binding energy compared to the first one. This result suggests that in the dicoordinated complex of pyridine the repulsive interaction between two ligands reduces the second binding energy.

In addition, the plot of the calculated ΔCCB[L$_2$Cu$^+$] for two ligands against the corresponding ΔCCB[LCu$^+$] for the first ligand (Figure 2) shows that there is an excellent linear relationship with a slope of 1.54 (eq 7). A linear relationship with a similar slope is also obtained for CCAs (eq 8):

$$\Delta\mathrm{CCB}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.54\Delta\mathrm{CCB}[\mathrm{LCu^+}]_{\mathrm{calc}} - 2.7 \quad (R^2 = 0.996) \quad (7)$$

$$\Delta\mathrm{CCA}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.59\Delta\mathrm{CCA}[\mathrm{LCu^+}]_{\mathrm{calc}} - 2.5 \quad (R^2 = 0.999) \quad (8)$$

For the calculated ΔCCBs and ΔCCAs with the B3LYP/6-31+G* optimized geometries (Table S3), the corresponding plot gave an excellent linear relationship having an identical coefficient:

$$\Delta\mathrm{CCB}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.55\Delta\mathrm{CCB}[\mathrm{LCu^+}]_{\mathrm{calc}} - 1.0 \quad (R^2 = 0.990) \quad (9)$$

$$\Delta\mathrm{CCA}[\mathrm{L_2Cu^+}]_{\mathrm{calc}} = 1.60\Delta\mathrm{CCA}[\mathrm{LCu^+}]_{\mathrm{calc}} - 0.4 \quad (R^2 = 0.998) \quad (10)$$

A similar coefficient of 1.55−1.60 was obtained for the acetophenone−copper cation complexes.[25] These correlations reveal that the subsituent effect on the binding energy for the second ligand is significantly smaller than that for the first ligand, indicating that the magnitude of the substituent effect for the monomeric complex cannot simply be predicted from one determined for the dimeric complex by a statistical correction, that is, dividing by a statistical factor of 2.

Discussion

Binding Site of Pyridines with Copper Ion. The most basic site in the pyridine derivatives is considered to be the nitrogen atom of the pyridine ring according to their proton basicities. Table 1 shows that the CCBs of 3-cyanopyridine and 4-cyanopyridine are close to acetonitrile, in which the binding occurs to the lone pair electrons on the cyano nitrogen atom.[31] This result contrasts to the proton basicity scale, that is, the GB value of acetonitrile is smaller than those of 3- and 4-cyanopyridine by 84 kJ mol^{-1} or more. This forces us to examine the binding site of these pyridine derivatives with copper ion. Theoretical calculations would provide useful information for the binding site. The calculation results for the substituent-binding Cu$^+$ complexes are also summarized in Tables S2 and S3. The calculated CCAs and CCBs indicate that in 2- and 3-cyanopyridine the binding with a copper ion must occur at the cyano group, while in the 4-cyanopyridine the binding occurs probably at the nitrogen atom of the pyridine ring. For 4-NMe$_2$ and 4-NH$_2$ derivatives the binding site is undoubtedly the nitrogen atom of the pyridine ring, and this is consistent with the results from the protonation reactions.

Correlation of ΔCCB[L$_2$Cu$^+$] with ΔGB. Figure 3 shows a plot of ΔCCB[L$_2$Cu$^+$] of substituted pyridines against the corresponding GBs. There is a good linear relationship with a slope of 1.01 for 3-and 4-substituted derivatives, indicating that the polar effect of the substituent contributes to the stability of the L$_2$Cu$^+$ complex in a similar manner to the protonated species. Since the substituent effect of the ΔCCB[L$_2$Cu$^+$] values reflects the effect of two pyridine molecules on the stability of the Cu$^+$ complexes, the slope of 1.01 reveals that the substituent effect on the ΔCCB for the monomeric complex must be much smaller than that for the dimeric complex.

As was previously mentioned, we may assume the substituent effect on the ΔCCB[LCu$^+$] for the monomeric complex based

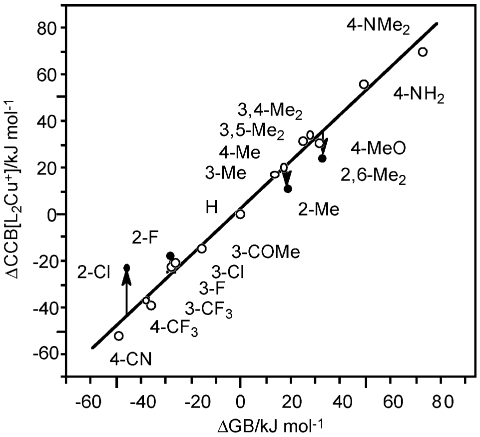


Figure 3. Correlation between experimental CCB[L_2Cu^+] and GB.

TABLE 2: *s* Values, Lewis Cation Basicity, and Calculated Properties of (Pyridine)M^+ Complexes

Lewis cation	s[a]	$\Delta G°$,[b] kJ mol^{-1}	q_{M^+}[c]	bond order[d]	bond length (M^+−N), Å
H^+	1.00 (1.00)	898.3 (888.9)	0.441	0.669	1.013
Me_3Si^+	0.95[e] (0.81)	197.0 (224.2)	0.710	0.512	1.940
Cl^+	0.83[f] (1.00)	(796.5)	0.272	0.657	1.814
Cu^+	0.66 (0.71)	231.4[g] (232.1)	0.862	0.359	1.855
Li^+	0.47[h] (0.58)	146.9 (150.3)	0.977	0.106	1.907
I^+	0.44[i] (0.99[j], 0.94[k])	(525.9)[j]	0.502[j]	0.551[j]	2.122[j]

[a] Based on eq 11. Values in parentheses are for the calculated basicities at MP2//6-311+G(2d,2p)//B3LYP/6-311G. [b] Lewis cation basicity of pyridine. Values in parentheses are the calculated basicities at MP2//6-311+G(2d,2p)//B3LYP/6-311G. [c] Natural charge of M^+ given by the natural population analysis at B3LYP/6-311+G(2d,2p)//B3LYP/6-311G. [d] NAO bond order given by the natural bond orbital (NBO) analysis at B3LYP/6-311+G(2d,2p)//B3LYP/6-311G. [e] Reference 21. [f] Reference 31, *s* value for chlorine cation affinities against proton affinities. [g] Estimated value from 446.4 kJ mol^{-1} for L_2Cu^+ by use of *f*[CCB] given in Table S2. [h] Calculated from data in ref 19. [i] Reference 42. [j] Calculated at B3LYP/DGDZVP//B3LYP/DGDZVP. [k] Calculated at B3LYP/Lan2LDZ//B3LYP/Lan2LDZ.

on a good linear relationship between ΔCCB[L_2Cu^+]$_{calc}$ and ΔCCB[LCu^+]$_{calc}$. By use of a coefficient of 1.54, a slope of 0.66 (=1.01/1.54) has been evaluated for the linear relationship between the ΔCCB for the monomeric complex and GB. The magnitude of 0.66 indicates that the substituent effect on the binding energy is significantly reduced in the Cu^+ complex compared to that in the protonated system.

It is interesting to compare the corresponding correlation given by eq 11 for the relevant Lewis cation (M^+) basicities of pyridines, because the magnitude of the substituent effect must be associated with the nature of the bond between a Lewis cation and a ligand.[18]

$$\Delta \mathrm{CCB}[\mathrm{LM}^+] = s\Delta \mathrm{GB}[\mathrm{LH}^+] \qquad (11)$$

Although the lithium cation basicities, LCB[LLi^+], of pyridine derivatives are limited, the available data cover a wide range of substituents from 4-NMe_2 to 4-CF_3.[19] More limited data for chlorine cation[41] and iodine cation[42] are available in the literature. The results of these systems are summarized in Table 2 along with the natural charges of the M^+ moiety, the NAO bond orders of the M^+−N bond, and their bond distances of the M^+−N bond. It is found that the *s* value decreases in the order for H^+ > Me_3Si^+ > Cl^+ > Cu^+ > Li^+ > I^+. The decreasing order of *s* does not relate to the Lewis cation basicity of pyridine and the bond distance of the M^+−N bond. Instead, it seems to be qualitatively related to the magnitude of the positive charge in M^+ and the NAO bond order of the M^+−N bond except for I^+. A similar trend of the *s* value was observed for the Lewis cation basicities of the acetophenone series as follows, H^+ (1.00) > Me_3Si^+ (0.95) > Cu^+ (0.80) > Li^+ (0.72),[25] although the *s* value for the acetophenone system is less sensitive to the change of Lewis cation compared with the pyridine system. In addition, the calculated charge of M^+ was found to increase in this order. Thus, the smaller *s* value suggests the more positive charge is localized at the Lewis acid moiety in the adduct ions compared with that for the protonation. The *s* value of 0.66 for the Cu^+−pyridine complex would result from the increased ionic nature of the bond formed with Cu^+ compared with the protonation. An *s* value of 0.44 reported for the iodine cation basicities[42] is, however, inconsistent with this interpretation because these bonds are likely to have substantial covalent character, as indicated by the small charge of I^+ and a large bond order of the N−I^+ bond compared with the Li^+ complex. The reason for this discrepancy is not clear at present. However, it should be noted that the *s* values of 0.99 and 0.94 were obtained for the calculated iodine cation basicities of pyridines at B3LYP/DGDZVP and B3LYP/Lan2LDZ, respectively (Table S5). Similarly, the *s* value of 0.83 for Cl^+ is smaller than the calculated value of 1.00 that is consistent with a large covalent bond character of N−Cl^+ bond, as indicated by a small charge of Cl^+ and a large bond order of the N−Cl^+ bond. These results suggest that the serious disagreement between experimental and calculated *s* values for I^+ may be due to inadequate calculations because the levels of theory used here do not describe properly heavy atom effects such as relativistic effects. Another possibility is the accuracy problem of experimental data resulting from the experimental difficulties in the determination of the equilibrium constants of ligand-exchange reactions because the formation of the dimeric complexes, L_2I^+, during the ligand-exchange process obstructs efforts to obtain the precise equilibrium constant values between monomeric complexes in a similar manner to the case of the Cu^+ complex as seen in Figure 1a. Further studies would be needed, obviously.

It should be noted that 2,6-Me_2-, 2-Me-, 2-F-, and 2-Cl-substituted pyridines in the plot of ΔCCB[L_2Cu^+] against ΔGB (Figure 3) show appreciable deviations from the line obtained for 3- and 4-substituted pyridines. The reduced stabilization of 2-methyl and 2,6-dimethyl groups in the Cu^+ complex may be due to steric hindrance at the binding site. Similar deviations were observed for a plot of Cl^+ against proton affinities.[41] The calculated bond distance between Cu and N is indeed longer than that of the 3- and 4-methylpyridine complexes. Contrary to that, the increased stabilization by 2-fluorine and 2-chlorine may result from the through-space attractive interaction between Cu^+ and lone-pair electrons of Cl and F. In fact, the calculated bond angle of N1−C2−X is somewhat smaller than 120°; N1−C2−Cl, 116.6°, and N1−C2−F, 115.0°, respectively.

General Trends in Comparison between CCB[L_2Cu^+] and GB. A scale of CCBs now covers a range of 243 kJ mol^{-1}, from water to 4-*N*,*N*-dimethylpyridine, when the CCBs of acetophenone derivatives determined previously in our laboratory[25] and several values determined from the CID experiments[30] are included. Deng and Kebarle[14] reported a similar range of CCBs, including several bases determined by Jones and Staley.[13] Their scale of absolute values was considered to be inappropriate because they used an inadequate value of NH_3 as an anchor,[31] but their relative values may be used for construction of a scale of CCBs. Indeed, there is an excellent linear relationship between their values and the currently accepted values, though

TABLE 3: Copper Cation Basicities and Gas-Phase Proton Basicities

bases	CCB[L_2Cu^+], kJ/mol	GB,[a] kJ/mol
substituted acetophenones		
X = 3′,5′-Me$_2$	405.0[b]	845.6
X = *m*-Me	393.6[b]	836.4
X = H	385.5[b]	829.3
X = *p*-COMe	376.2[b]	822.2
X = *m*-F	366.2[b]	813.8
X = *m*-Cl	369.3[b]	815.5
X = *m*-CF$_3$	357.0[b]	807.1
X = *p*-CF$_3$	354.2[b]	805.0
Bu_3N	455.6[c]	967.8
$PrNH_2$	429.4[c]	884.1
$BuNH_2$	436.0[c]	886.6
NH_3	424.3[d]	818.4
Me_2CO	347.9[e]	786.2
Et_2CO	364.2[c]	807.5
Pr_2CO	384.4[b]	815.5
$MeCONMe_2$	431.7[c]	877.0
$MeCO_2Me$	347.8[c]	790.8
Me_2SO	418.4[c]	853.5
Me_2O	313.0[f]	764.4
Et_2O	347.0[c]	799.1
MeOH	304.5[c]	724.7
EtOH	318.9[c]	744.8
Me_2S	378.2[c]	802.9
MeSH	341.2[c]	740.9
H_2O	274.9[g]	666.9

[a] Reference 37. [b] Reference 25. [c] Revised values based on eq 12 with values reported by Kebarle et al.[14] [d] Reference 30g. [e] Reference 30f. [f] Reference 30h. [g] Reference 30a.

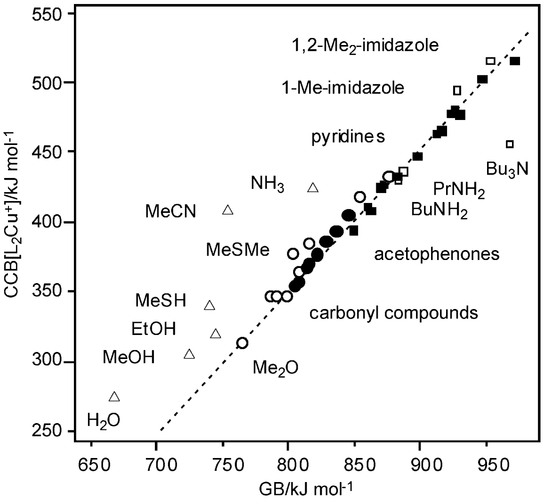


Figure 4. Comparison between CCB[L_2Cu^+] and GB: (●) acetophenones; (■) pyridines; (○) carbonyl compounds.

the number of compounds common to both data sets is limited to pyridine, acetonitrile, 1-methylimidazole, acetone, and water:

$$CCB[L_2Cu^+]_{Kebarle} = 1.06CCB[L_2Cu^+] - 10.7 \qquad (R^2 = 0.994) \quad (12)$$

This relationship allows us to revise the CCBs compiled by Deng and Kebarle. The revised values and several acetophenones determined previously in our laboratory[25] are summarized in Table 3 along with their GBs.

Figure 4 shows a plot of the CCB[L_2Cu^+] values against the corresponding GB values. On the whole, there is a fair linear relationship. When several ligands such as H_2O, MeCN, NH_3, MeOH, EtOH, MeSH, and Bu_3N are excluded, a good linear relationship between CCBs and GBs is obtained:

$$CCB[L_2Cu^+] = 0.99GB - 104.5 \qquad (R^2 = 0.987, n = 40) \quad (13)$$

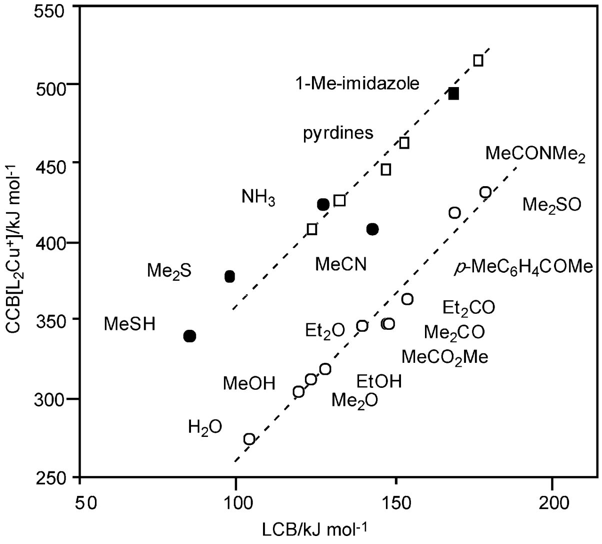


Figure 5. Plot of CCB[L_2Cu^+] against LCB[LLi^+].[37]

This linear correlation includes pyridines, acetophenones, amines, carbonyl compounds, and ethers. Strictly speaking, there seem to be family-dependent correlations; however, their differences are not so crucial. This contrasts with the correlations observed between LCBs and GBs.[19] Figure 5 shows that there are family-dependent correlations between CCB[L_2Cu^+] and LCB[LLi^+], indicating clearly different structural effects between Cu^+ and Li^+ complexes, although the Cu^+−ligand interactions as well as the Li^+ interaction are described as mostly electrostatic. These results reveal that the nature of the binding interaction between a copper ion and a base is similar to that for protonation and indicate the importance of covalent character in the Cu^+ interaction. This may be reasonable because it is considered that the covalent character of Cu^+ interactions is associated with electron donations from bonding orbitals or lone pairs of the ligand molecule toward the 4s empty orbital of the metal and with back-donations from the occupied d orbitals of the metal toward antibonding empty orbitals of the ligand. On the other hand, the ionic character of the Cu^+ interaction results in the reduced substituent effect compared with the protonation because of a localized positive charge at the metal ion moiety.

Finally, it should be noted that several compounds which deviate upward in Figure 5 have stronger binding energies with Cu^+ than the expected ones from their GBs on the basis of the linear relationship for pyridines, acetophenones, and other carbonyl compounds. All these compounds are relatively small in size, suggesting that their larger CCBs result in part from the lesser steric hindrance in the formation of the dimeric complexes; that is, the CCB is more sensitive to the geometrical environment at the binding site than GB because of the larger size of a copper ion than a proton. This is consistent with the downward deviation of Bu_3N since there may be steric hindrance to form this dimeric complex compared to primary amines. The downward deviations observed for 2-methyl and 2,6-dimethylpyridine in Figure 3 also show this trend.

Conclusions

The relative copper cation basicities (ΔCCB[L_2Cu^+]) of substituted pyridines determined in the gas phase were linearly correlated with the ΔGBs (proton basicities) with a slope of 1.01. Based on a linear relationship between the calculated copper cation basicities of dimeric and monomeric complexes, $\Delta CCB[L_2Cu^+]_{calcd} = 1.54\Delta CCB[LCu^+]_{calcd}$, the substituent effect on the ΔCCB for the monomeric complex has been estimated to be 0.66 times smaller than the corresponding ΔGB.

In addition, a comparison with the corresponding results for other Lewis cation basicity of the pyridine system, ΔCCB[LM^+] = $s\Delta$GB[LH^+], showed that the magnitude of the substituent effect decreases in the order H^+ (1.00) > Me_3Si^+ (0.95) > Cl^+ (0.83) > Cu^+ (0.66) > Li^+ (0.47). This decrease was associated with the increasing positive charge of M^+ of the complexes and with the decreasing NAO bond order of the M^+−N bond; that is, the increase of ionic character of the bond between a Lewis cation and a neutral molecule. Furthermore, when a variety of neutral bases such as amines, carbonyl compounds, and ethers were included, it was found that there is a good linear relationship between CCB[L_2Cu^+] and GB but not with LCB. This similarity between CCB[L_2Cu^+] and GB reflects the covalent character in the Cu^+ interaction. In conclusion, although the ionic (ion−dipole interaction) nature of the Cu^+ interaction results in a smaller substituent effect than that for protonation, the covalent nature also plays an important role in the characterization of the Cu^+ interaction with neutral molecules. In addition, it has been shown that the CCB is more sensitive to the geometrical environment at the binding site than GB because of the larger size of Cu^+ than a proton.

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Supporting Information Available: Calculated Lewis cation (Cu^+, H^+, Li^+, Cl^+, Me_3Si^+, I^+) affinities and basicities of pyridines, and conformation dependence of the energy of Py_2Cu^+ complex (Tables S1−S5 and Figure S1). This material is available free of charge on the Web at http://pubs.acs.org.

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